COMPILATION OF SITE VISIT-BASED TECHNICAL EVALUATIONS OF HYDROGEN PROJECTS
1996 – 2001

EDWARD G. SKOLNIK
ENERGETICS, INCORPORATED
901 D STREET, SW
SUITE 100
WASHINGTON, DC 20024

AUGUST 2002

Table of Contents

Hydrogen Storage Research Projects

Hydrogen Utilization Research Projects

Introduction

In 1996, Dr. Ed Skolnik of Energetics, Incorporated, began a series of visits to the locations of various projects that were part of the DOE Hydrogen Program. The site visits/evaluations were initiated to help the DOE Program Management, which had limited time and limited travel budgets, to get a detailed snapshot of each project. The evaluations were soon found to have other uses as well: they provided reviewers on the annual Hydrogen Program Peer Review Team with an in-depth look at a project – something that is lacking in a short presentation – and also provided a means for hydrogen stakeholders to learn about the R&D that the Hydrogen Program is sponsoring.

The visits were conducted under several different contract mechanisms, at project locations specified by DOE Headquarters Program Management, Golden Field Office Contract Managers, or Energetics, Inc., or through discussion by some or all of the above.

The methodology for these site-visit-evaluations changed slightly over the years, but was fundamentally as follows:

- Contact the Principal Investigator (PI) and arrange a time for the visit.

- Conduct a literature review. This would include a review of the last two or three years of Annual Operating Plan submittals, monthly reports, the paper submitted with the last two or three Annual Peer Review, published reviewers' consensus comments from the past few years, publications in journals, and journal publications on the same or similar topics by other researchers.

- Send the PI a list of questions/topics about a week ahead of time, which we would discuss during the visit. The types of questions vary depending on the project, but include some detailed technical questions that delve into some fundamental scientific and engineering issues, and also include some economic and goal-oriented topics.

- Conduct the site-visit itself including:

    - Presentations by the PI and/or his staff. This would be formal in some cases, informal in others, and merely a "sit around the table" discussion in others. The format was left to the discretion of the PI.

    - A tour of the facility featuring, whenever possible, a demonstration of the process in operation.

    - Detailed discussions of the questions sent to the PI and other topics.

- Writing a report on the visit

This compilation presents the reports for all the site-visits held between February 1996 and July 2001, each written shortly after the visit. While nothing has been changed in the actual content of any of the reports, reformatting for uniformity did occur.

In each report, where the questions and their respective answers are discussed, the questions are shown in **bold**. In several cases, the PI chose to answer these questions in writing. When this occurs, the PI's answers are produced "verbatim, in quotes, using a different font." Discussion of the questions, tour/demonstration, and anything else raised during the visit is presented in normal type. Comments that represent the opinion of Dr. Skolnik, including those added during the writing of the report are shown in *italics.*

The reports compiled here, as stated, covers a period through July 2001. Since then, site-visits to various project locations and the accompanying evaluations have continued. Thus, a second compilation volume should follow in the fall of 2003.

Following the compilation of reports, is an afterward that briefly discusses what has happened to some of the projects or project personnel since that particular report was written.

Technical Evaluation Report
Project: Enzymatic Conversion of Cellulose to Hydrogen
Company: Oak Ridge National Laboratory (ORNL), Oak Ridge, TN
P.I.: Dr. Jonathan Woodward
Date of Visit: February 21, 1996
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

On the above date, I met with **Dr. Jonathan Woodward** and his team consisting of **Dr. Madalena Baron** (Visiting Professor, UFPR, Brazil), **Dr. Barbara Evans** (ORNL Postdoctoral), **Kelly Turnage** (Staff Scientist), and **Maria Blanco** (Oak Ridge Science and Engineering Student) to discuss their enzymatic conversion of cellulose to hydrogen project. Briefly, the project involves the use of an enzyme system to convert cellulose (or another material such as corn syrup, starch, or lactose wastes) to glucose, and then to hydrogen and gluconic acid. During the course of the day, I was taken through their laboratory which included a short demonstration with their bench-scale reactor, and I was then given a semi-formal presentation by Drs. Woodward and Baron. Finally, Dr. Woodward concluded by answering those questions that I had sent him a week earlier that hadn't yet been covered during the demonstration and presentation.

Project Strengths:

- The process is unique in the hydrogen production arena, involving neither reforming, electrolysis nor photolytic processing.
- The project can now achieve hydrogen yields that are 100% of theoretical yields (his earlier reports had never shown any data with yields any greater than about 20%.
- They have initiated experiments using cellulose (rather than glucose) as a starting material, have run some tests with starch as a starting material and have also identified other potential starting materials (corn syrup, lactose).
- The work involving immobilization of enzymes, a requirement for a cost-effective process, is showing positive results.
- They have identified and are undergoing negotiations with two potential industrial partners.

Issues that should be Addressed:

- Dr. Woodward has not yet identified a glucose dehydrogenase (GDH) which is compatible with his hydrogenase: one that is in the same temperature/pH activity and stability regime. Having now officially discarded one GDH, and getting less than optimal results on two others, he is about to start on a new one.

- Dr. Woodward believes that the selected enzymes once identified will be able to be mass-produced cheaply. This has not yet been demonstrated.

- His hydrogen production rates and yields appear to affect each other inversely. He does not yet know what steps and processes are rate determining.

- Initial cellulose results are not extremely encouraging, and suggest that he may need either a different approach to a single reactor, a two-step (cellulose to glucose and glucose to hydrogen) reactor scheme, or (as he is now considering) a different starting material.

- Using Dr. Woodward's own numbers, it appears that any credit to be gained from a gluconic acid by-product would be tempered by the fact that this process (if it were to be a major player in the hydrogen production arena) would produce sufficient gluconic acid so as to impact the gluconic acid market.

II Discussion Topics:

Prior to the meeting, I sent Dr. Woodward a list of topics around which to base our discussion. These are listed here, and are addressed in Section III.

1. **A mass/energy balance on the process. If you were to get an optimum yield, what level of hydrogen production would you expect?**

2. **An overall pH/temperature/time/activity/hydrogen yield comparison for your best hydrogenases and GDHs on a one-to-one basis. For instance, in your 1995 Annual Review report, Figure 4 *(shown here as Exhibit 1)* seems to indicate that the activity of *Pyrococcus furiosis* hydrogenase is about .005 units per mL at room temperature, while what appears to be the same parameter as shown in Figure 2 *(Exhibit 2)* of your latest monthly report (the manuscript from the Edmonston and Woodward paper) is 3-5 units per mL depending on pH.**

3. **Stability data on your new GDHs (*Thermoplasma acidophilum* and *Bacillus megaterium*) as a function of temperature.**

4. **You plan on eventually initiating the hydrogen production process from cellulose rather than glucose. What procedure would you be using for converting cellulose to glucose, and how would this effect the overall efficiency and cost of the hydrogen generation process?**

5. **What is the availability of the various hydrogenases and GDHs and what are heir projected costs in quantity?**

6. **What is the market for gluconic acid and how does its projected cost and volume affect the cost of hydrogen production? How will the price of gluconic acid itself**

be effected by its additional availability due to the hydrogen production process.

7. **How do you envision an eventual commercial process being structured?**

III Discussion/Answers to Questions:

Enzymes:

As of last year's annual review, Dr. Woodward was primarily using a GDH which was derived from calf liver. He was showing the GDH to begin to lose stability at about 42.5°C. Since he required a substantially higher temperature (perhaps 60-80°C) to achieve sufficient hydrogenase activity (from their prime high temperature hydrogenase produced by *Pyrococcus furiousus*) to produce hydrogen efficiently, he stated that he would be working with new sources of GDH, which had increased thermal stability. As a result, he is now working with two new GDHs, produced respectively from: *Thermoplasma acidofilum* obtained from the University of Bath, England and *Bacillus megaterium* from Sigma Chemical Company . He had stated that the *Thermoplasma acidofilum* GDH, particularly possessed higher temperature stability. The data that he shared with me, however, showed stability beginning to drop off at 50°C -- not much of an improvement. *Bacillus megaterium* is even less stable. He is already starting to speak of a new higher temperature GDH from the organism *Sulfobolius*, that he is trying to obtain. He claims that this enzyme will be stable at much higher temperatures, perhaps up to 100°C. This would make it more compatible with the hydrogenase *Pyrococcus furiousus* which grows at 100°C.

Although many of the enzymes are currently expensive and not in large supply, Dr. Woodward believes that the thermofile enzymes such as those from *Pyrococcus furiousus*, *Thermoplasma acidofilum*, and the soon to be incorporated *Sulfobolius*, will be readily available and inexpensive through emerging recombinant DNA technologies. In addition, some of the research currently going on in Dr. Woodward's group involves the immobilization (stabilization) of enzymes. Dr. Madalena Baron's work involves the investigation of substrates for immobilization of the hydrogenase and GDH enzymes. The goal is to identify an inert matrix on which the aqueous solution of free enzyme is insolubilized, and is therefore able to keep its catalytic properties for a longer time. She has identified DAEA-Sephadex, an ion-exchange resin as a good immobilization substrate. Preliminary experiments show that *Bacillus megaterium* GDH, when electrostatically deposited on DAEA-Sephadex, does not lose any activity after nine uses. Of course, this does not necessarily mean that the results will be the same for the more thermally stable GDH, *Thermoplasma acidofilum*, the yet-to-be-received GDH, *Sulfobolius*, or the hydrogenase, *Pyrococcus furiousus*. These materials have yet to be tested.

Calf liver GDH, which was used in much of the early work, has now been rejected.

Thus, it would appear that Dr. Woodward is still looking to find a source for a GDH that will be stable at high temperature. He believes that he does not yet have the right enzyme.

If he finds the right enzyme, he has evidence (but not proof) that he can immobilize it. GDH identity is Dr. Woodward's current major problem for the glucose to hydrogen step.

Hydrogen Yield:

Dr. Woodward is now showing data with the *Thermoplasma acidofilum*/ *Pyrococcus furiousus* system wherein the hydrogen yield is 100% of theoretical. While this is encouraging, it should be noted that it takes about 5 hours to get the reaction to go to completion, and quantities are at the micromole level. Dr. Woodward is finding inverse relationships between hydrogen yields and hydrogen production rates. The group is still looking to understand the rate-limiting steps of hydrogen production.

There is still a ways to go as far as getting reaction rates to be sufficiently high as to co-optimize both yield and rates (activity). When Dr. Woodward switches to a new GDH, which he'll probably have to do, it may be a whole new set of conditions.

[*We should note that 100% of theoretical for the reaction just involves the recovery of one hydrogen from the glucose molecule*.]

Renewable Starting Materials:

Dr. Woodward's group is starting to obtain data using renewable starting materials. One of our major concerns was the fact that all of the data up to this point (and in fact, all the results that I have described up to now) had involved glucose as the staring material. Nevertheless, the group has been studying the cellulose/glucose system for "years". The major problem with the use of cellulose as a starting material is that since it is insoluble, it reacts very slowly. Cellulases which convert cellulose materials to glucose are relatively inexpensive (a few cents per pound) and are available commercially. Dr. Woodward's group is attempting to use metals such as ruthenium to complex with the cellulase. The metal would then attack the lignin associated with the cellulose and help break it down. Dr. Woodward defined the problem of increasing the rate of the cellulose reaction as a "key need".

Initial experiments for which I received data, in which cellulose, cellulase, GDH, hydrogenase, and nicotinamide adenine dinucleotide phosphate (NADP) (the cofactor) were all placed together in the reaction vessel resulted in only a two percent conversion from cellulose (through glucose) to hydrogen. Dr. Woodward indicated that now he is up to about five percent.

Dr. Woodward has also performed some experiments in which starches were used as the starting material rather than cellulose with about a 15% conversion to hydrogen to date. He also says that he wants to look at different starting materials such as corn syrup (an inexpensive commodity at about eight cents per pound) and lactose (a dairy industry waste product). In conjunction with Dr. Baron, he is also considering Brazilian fructose sources as a starting material.

It may be too soon to tell if Dr. Woodward will be able to convert cellulose to hydrogen. It appears to add layers of challenges, however, to an already complex system. While the use of starch, lactose and corn syrup as starting materials seem attractive, their incorporation into the project will likely result in spreading resources too thinly.

<u>The Hydrogen/Gluconic Acid System</u>:

According to Dr. Woodward, a system that is optimized for hydrogen will be optimized for gluconic acid as well. He does not currently measure gluconic acid yields, so has no data of this type. In fact, he said that the concept of considering a co-product is relatively recent in his thinking concerning project direction. If Dr. Woodward does form a team with PMP Fermentation Products, Inc. (see below), the latter will concern themselves with gluconic acid formation rates.

Gluconic acid is a rather important commodity, currently costing about $1.20 per pound. The U.S. gluconic acid market is currently about 40 million pounds annually, with an additional 5 to 6 million pounds per year of sodium gluconate. Gluconic acid and its salts are used primarily as metal sequestering/chelating agents. They are used to prevent metal scaling in aqueous systems, as a bleaching medium for pulp and paper and textile operations, and as an additive for paste cleansers for household aluminum utensils. Calcium gluconate is used as a mineral supplement, and magnesium gluconate is an antispasmodic drug.

Dr. Woodward made a rough estimate of potential hydrogen production from cellulose. He considered cellulose from newspapers having an availability of about 7.25 million tons per year. Roughly, this would correspond to seven million tons of glucose, and then seven million tons of gluconic acid. This (though understandably an extremely optimistic figure) totally overwhelms the 40 million **pounds** of gluconic acid in the current U.S. market. This quantity of cellulose would theoretically produce 37.4 billion standard cubic feet (0.013 quads) of hydrogen.

Economics for the system have not been worked out yet. The lack of an identifiable GDH enzyme (and therefore a cost for that enzyme), an immobilization system for that enzyme, and an immobilization system for the hydrogenase makes an economic assessment premature -- even for the single-step glucose to hydrogen and gluconic acid portion of the reaction. Dr. Woodward said that he expects Maggie Mann of NREL to eventually work on the economics of his process.

From a chemistry standpoint, gluconic acid is maximized when hydrogen is maximized. Stoichiometrically, it's one mole to one mole. There is not enough data yet available to determine what the practical ratio is, if it is at all different, or what parameters control it. As a first estimate, based on Dr. Woodward's figures, it would seem that if this process became **the** renewable hydrogen process or even one of the major processes, the gluconic acid market would be greatly impacted.[1]

---

[1] In a later telephone conversation, Dr. Woodward informed me that in discussions with Dr. Robert Jungk of PMP Fermentation, he found that an over-supply of gluconic acid is

Relationships with Industry:

Dr. Woodward is in the process of forming relationships with two industrial partners. First of all, he is "close to a CRADA" with Eastman Chemical Company (Kingston, TN). Eastman is the largest producer of cellulose esters in the world, and therefore they have a lot of cellulose and cellulose ester waste materials. They are looking for a way to remove acid from their esters to make the cellulose more digestible. This, of course, is an issue for Dr. Woodward as well when he starts from cellulose. In addition, Eastman is a major user of hydrogen (as a reducing gas) and could become interested in becoming a producer as well. Dr. Woodward says that they have been trying to work out a CRADA since 1992.

Dr. Woodward also has a "collaborative relationship" with PMP Fermentation Products (Itasca, IL). PMP is the largest producer of gluconic acid and sodium gluconate in the United States. Their relationship to date involves PMP providing commercial samples and analytical support to ORNL. PMP is very interested in Dr. Woodward's work as an alternative to fermentation for gluconic acid production. They may also be interested in being hydrogen producers as well. Dr. Woodward and PMP are therefore looking to expand their relationship and are planning to hold discussions in the spring.

Thus, there is apparently industrial interest in Woodward's project, and efforts are proceeding (albeit somewhat slowly) toward more formal collaboration. The identification of potential hydrogen stakeholders, who are leaders in two chemical industries (cellulose esters and gluconic acid) but were previously not considered, is a benefit to the Hydrogen Program as a whole and to the Industry Outreach effort in particular.

Other Topics:

- Dr. Woodward on several occasions both prior to and during my visit stressed the importance of projects such as this as a means of promoting education. He cited a former ORNL Science and Engineering Student, Susan Mattingly, who previously worked with Dr. Woodward and whose name appears on several of his earlier reports, as having received a full scholarship to the University of Bath. This award was a direct result of her having worked on this project.

- The discrepancy between two pieces of data showing *Pyrococcus furiousus* hydrogenase activity was due to an error in the Edmonston and Woodward paper. The activity was actually 0.03-0.05 units per ml rather than 3-5 units. This is still an order of magnitude higher than reported in the earlier Annual Review paper. The difference was that the later result was obtained under aerobic rather than anaerobic conditions.

---

not a bad thing. With an increase in availability and a decrease in price, gluconic acid could successfully compete with citrates in the beverage industry.

- Dr. Woodward sees a commercial process developing in 10-15 years based on this research if they receive "good funding".

Exhibit 1. Hydrogenase Activity (for Comparison with Exhibit 2.)

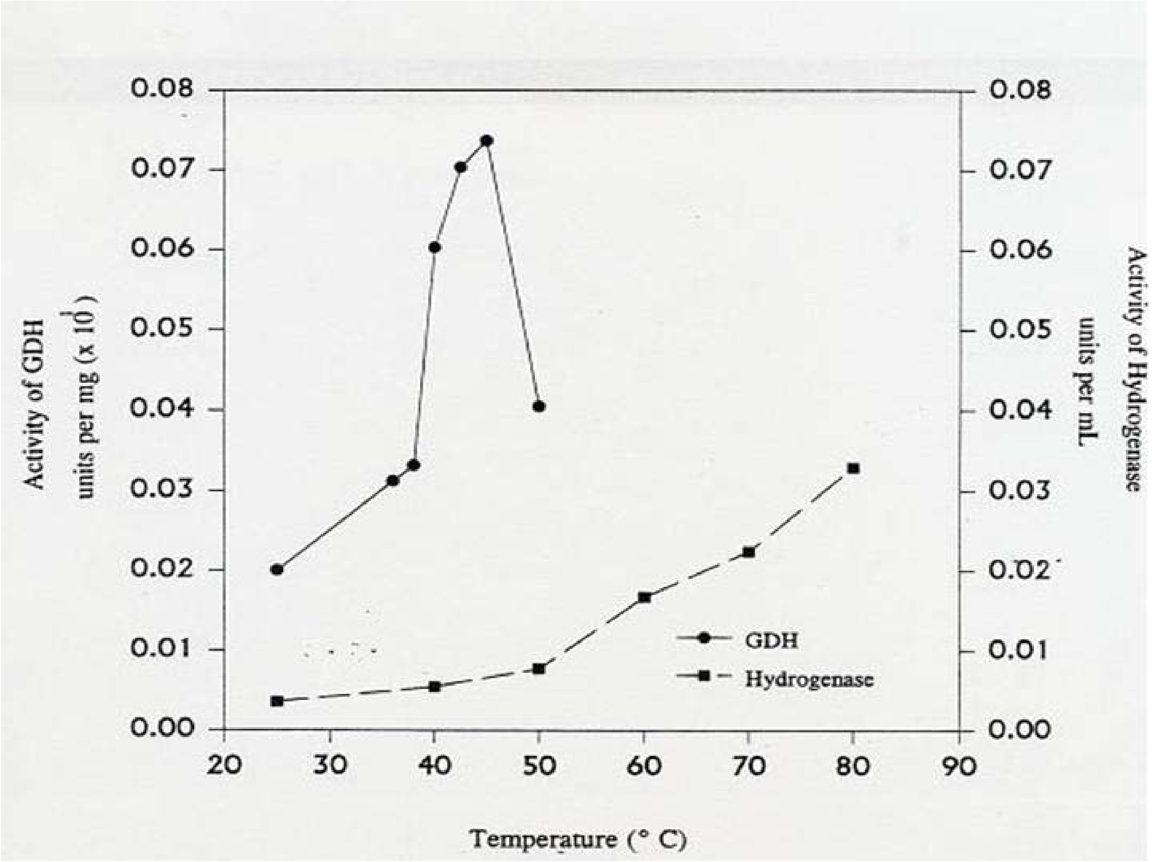
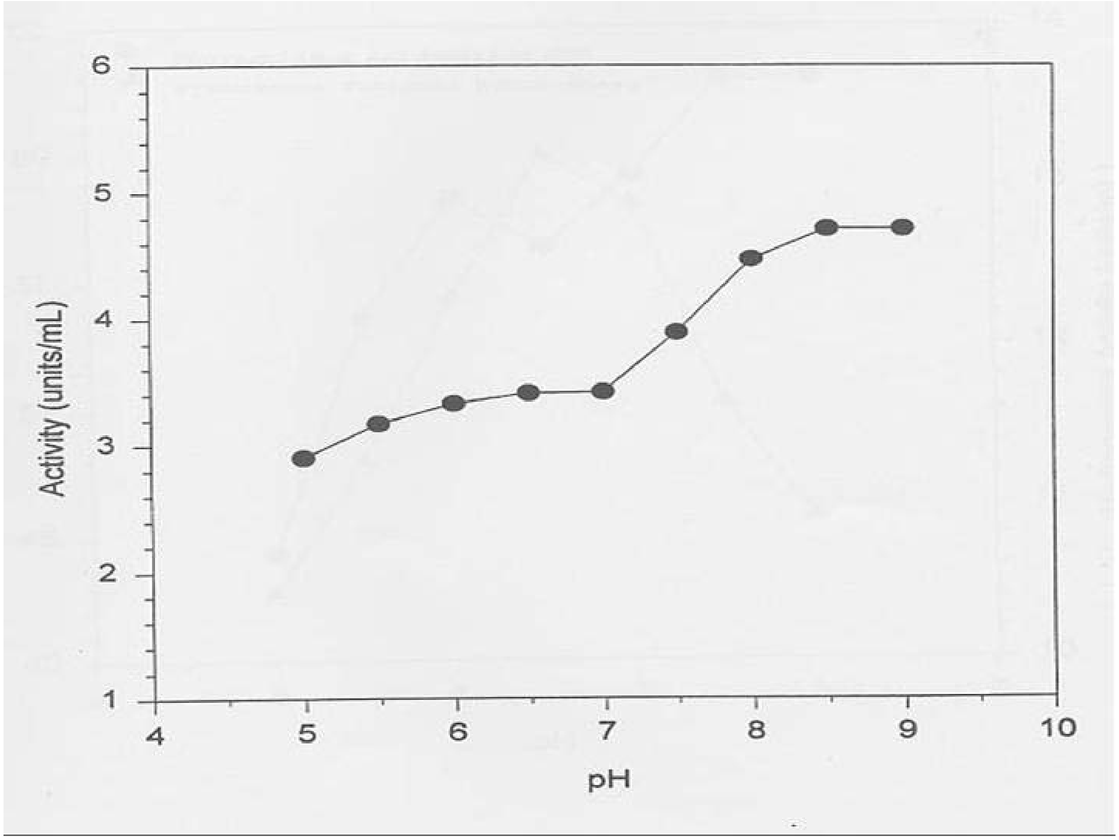


Exhibit 2. Hydrogenase Activity (for Comparison with Exhibit 1.)



Technical Evaluation Report
Project: Thermocatalytic Cracking of Natural Gas
Company: Florida Solar Energy Center, Cocoa, FL
P.I.: Dr. Nazim Muradov
Date of Visit: February 22, 1996
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

I met with **Dr. Nazim Muradov** on the above date to discuss his thermocatalytic cracking of natural gas project. Briefly, the project involves heating natural gas (or methane in the laboratory) to several hundreds of degrees, Celsius, in the presence of a catalyst. The methane is cracked to hydrogen and carbon. In the preferred process, the carbon is a recoverable by-product. During the course of the day, I was given a complete demonstration of the working bench-scale reactor and also had a lengthy discussion with Dr. Muradov on all aspects of the project including the answers to the questions that I had sent him a week earlier.

Project Strengths:

- There is the potential for a non-emitting thermal-hydrogen production process.
- If a hydrogen/natural gas blend at, say, 25/75 is acceptable, a low (400°C) temperature reaction scheme is possible.
- At small scale, there is the potential for the process to be relatively inexpensive, especially with a credit for carbon.
- The flow reactor is not complex. It could be a relatively simple process.
- The basic set-up for the bench-scale reactor appears valid. It seems to be doing what it should be doing.

Issues that should be Addressed:

- The key step for success of this project is the fact that no CO_2 is emitted in the process. Dr. Muradov appears to be straying away from this goal and evaluating carbon burn-off techniques.
- If the thermocatalytic cracking process were ever used at a large scale (that is, replacing steam reforming) the carbon formed would overwhelm the market.
- The effect of impurities both in feedstock and in hydrogen (especially with carbon burn-off) needs to be taken into account. If the product is meant as fuel cell feed, CO especially must be dealt with. This, plus the potential need for a dual reactor with one

reactor being run in the production mode while the other is in the burn-off mode raises both efficiency (losses during switching and purging) and cost questions.

- Dr. Muradov may be paying too much attention to short-term optimum hydrogen production yields rather than the hydrogen yield at steady state. I think this may be a better focus for catalyst selection.

II Questions and Answers:

Prior to my visit, I sent Dr. Muradov a list of questions. These became the focal point for our discussion.

Coking Issues:

1. **What is the length of practical reaction time before the catalyst becomes coked, and how the catalyst is recharged.**

This is probably the biggest single issue in the entire project. In order to be efficient, the catalyst must be free of carbon buildup. In addition, if the carbon is to be sold, it must be non-destructively removed from the catalyst. Dr. Muradov has indicated that he considers coking issues the biggest challenge for the current year. [*I would whole-heartedly agree.*] Dr. Muradov is currently considering how he might remove the carbon non-destructively.

However, Dr. Muradov is also now in part backing away from the non-destructive removal approach. Some of his latest reports, as well as a major portion of the demonstration that he put on for me involved the burn-off of carbon by air introduction. The demonstration was flawless, with hydrogen production after burn-off being essentially the same as with fresh catalyst. In fact, Dr. Muradov envisions an on-board or industrial system that would consist of two reactors; one in the hydrogen production (thermocatalytic cracking) mode, and the other in the burn-off mode. The process would be cyclic with ten to thirty minute periods.

I would consider the non-destructive removal of carbon rather than its oxidation to be by far the preferred process. While the thermocatalytic process may still be viable with the burn-off step, it would lose a great deal of its attractiveness. One of the major advantages that this process has over steam reforming is that it does not produce CO_2*. In addition, it provides a potentially valuable co-product – carbon. Finally, a cyclic crack/burn-off process will either need extensive, efficiency-reducing purges between steps, or will result in the inclusion of more impurities such as* CO_2 *as well as CO. The removal of the latter would be vital to using the hydrogen in a PEM fuel cell. Thus, I would consider the success of the project tightly bound to the carbon recovery mode. Dr. Muradov did say that if he could develop a carbon recovery system in the next 1-3 years, he could then begin scale-up work.*

Theoretical and Practical Hydrogen Yields:

2. **What is the amount of hydrogen you expect to get out of the system per unit energy input, including the amount of energy necessary to heat the system?**

The thermocatalytic cracking process theoretically will produce 2.12 cubic meters of hydrogen for each kWh of energy input. (Steam reforming will produce 1.94 cubic meters per kWh input). In practicality, Dr. Muradov expects "one to two" cubic meters of hydrogen per kWh for his process. It has been found that 9.4% of the methane is needed to heat the system, as opposed to about 20-30% for steam reforming. Alternatively, the system thermal requirements could be covered by 15% of the produced hydrogen. This option would be the most benign environmentally. If the process being used contains a carbon burn-off step as opposed to carbon recovery, the oxidation of 21% of the carbon would satisfy the thermal requirement for the system.

On a theoretical basis, the thermocatalytic process is slightly favored over steam reforming, but Dr. Muradov's "one to two" cubic meters of hydrogen could indicate an efficiency as low as 50%. Thus it could be inferior to steam reforming.

Feedstock and Hydrogen Purity:

3. **What are the effects of impurities (and the variation of impurities) in natural gas on your reaction and especially on your catalyst? (Your reports indicate that apparently you are using methane rather than natural gas as your feedstock in your experiments to date.)**

The effect of using natural gas rather than pure methane (which Dr. Muradov has been using in all of his experiments to date) as a feedstock would be no different - or no worse - than that expected with steam reforming. In fact, Dr. Muradov states, if the catalyst used were iron based, there would be no need for a desulfurization step prior to cracking. This could be an advantage over steam reforming.

Dr. Muradov states that the purity of produced hydrogen will typically be between 25 and 95% by volume. The major impurity (or co-product) is unreacted methane. The higher the reaction temperature, the higher the percentage of hydrogen. Dr. Muradov sees one of his potential markets to be gas-filling stations for vehicles. A blend of 25/75 hydrogen/methane could be produced at 400°C, and would result in a significant emissions reduction. For other uses, such as fuel cell feedstock, the process would be run at a higher temperature and hydrogen purities would be close to the 95% level. The major impurity is methane which would not be a problem with fuel cell utilization.

Dr. Muradov does not see a problem with using 95% pure hydrogen as a fuel cell feed. I would be concerned with CO and CO_2 impurities especially if the process being used involved carbon burn-off. While not an insurmountable problem, I would think that a purification step such as the use of a separation membrane would be necessary.

Carbon By-Product Issues:

4. How much carbon do you get out and what is the form it takes?

Dr. Muradov is not yet sure what form the carbon is taking, but preliminary indication indicates that it may either be graphitic or amorphous carbon black -- it depends on the catalyst.

5. Please provide the latest update on the potential market for carbon. How will the amount of carbon being formed in this process being let into the market effect the price of carbon?

For the answer to the question on the current market for carbon, Dr. Muradov turned to a paper that he has previously cited: L. Fulcheri and Y. Schwob, *Int. J. Hydrogen Energy*, **20**, 197 (1995). This paper indicates that the world carbon-black market is about 6 million tons per year, with a value of between $1000 and 1400 per ton. In the thermocatalytic process,

$$CH_4 \rightarrow C + 2\,H_2,$$

one mole (12 grams or 0.026 pounds) of carbon forms with each 2 moles (44,800 cm^3 at STP or 1.58 scf) of hydrogen. Thus, the formation of one trillion scf of hydrogen (representing about 1/4 of today's annual hydrogen production, and also the approximate amount of hydrogen produced by steam reforming), would result in the formation of about 8.2 million tons of carbon.

If thermocatalytic cracking with carbon recovery ever rivaled steam reforming in the United States as a hydrogen production process, it would yield more carbon annually than is currently being marketed in the world. If we were to take a niche market of a size equivalent to, for instance, the amount of hydrogen being consumed by the U.S. space program (a good analogy for a project being conducted near Cape Canaveral), about .001 quads, the associated carbon would equal about 25,000 tons, or less than one half of one percent of the market.

Hydrogen Market Issues:

6. Please conceptualize a commercially-sized system. What is your opinion as to what degree the success of your process depends on the use of product hydrogen as an emission-reducing gas when co-fired with natural gas?

Dr. Muradov does not see his process competing with steam reforming. He sees it filling niche markets, although the niche markets that he describes could be quite large. He cites two main markets: On-board units consisting of cracker/ fuel cell combinations, and gas-filling stations also for vehicular use. He sees these niche markets being serviced by the thermocatalytic cracking process in 5 to ten years. He visualizes an on-board unit to have a capacity of somewhere between 1.5 and 10 kW, and a reactor volume of the order of 15 liters. The on-board system, if run in the carbon recovery mode, might allow for taking the produced carbon to a station for credit. Dr. Muradov has not worked out a potential infrastructure for such a system.

Gas-filling stations would have on-site reactors having volumes, depending on usage from about 200 liters to about one cubic meter. Even in a carbon burn-off mode, these stations could be of value according to Dr. Muradov. They would produce hydrogen (and CO_2 during burn-off) in a suburban area, and fill natural gas vehicles with a hydrogen/natural gas blend. Thus emissions would be transferred from the city to the suburbs.

Dr. Muradov did not see his process as compatible with large utility utilization, but thought one potential scenario might include certain small electric utilities located in a place where there is a natural gas source but no infrastructure. The produced hydrogen could be used to run a fuel cell to produce electricity. This would not seem to have any advantage over a gas turbine unless one is considering CO_2 emission reductions and is running the cracker in a carbon recovery mode.

One scenario where large scale use of thermocatalytic cracking might become favorable would be if CO_2 were deemed a major problem. Under these conditions, steam reforming would become unacceptable, and thermocatalytic cracking units could enjoy wider exposure. Under these conditions, larger utilities might become users as well. Of course, this would all depend on the success of the non burn-off mode for carbon. At these large global yields, Dr. Muradov suggests, where the carbon market could be overwhelmed, carbon could be stored.

Here again, the focus appears to be moving away from a recoverable carbon mode. Dr. Muradov envisions the market now not so much as large systems that could replace steam reformers and that would be based on carbon recovery rather than burn-off, but smaller niche markets where burn-off might be acceptable. This would indicate that carbon recovery may not be doable, and that if it were doable, large scale carbon recovery would impact the carbon market.

Additional Topics:

7. **You indicated that you had to change your set up to a pulsed system to get an accurate GC response when you used the nickel catalyst. Is a pulsed reactor an option for an actual system or is it simply a means of gathering data? What would its efficiency be when compared with the CF reactor?.**

The pulsed reactor system that Dr. Muradov mentioned in some of his reports is not a real system. He has done two things: First, he has constructed a smaller reactor for his bench top process. This allows faster heat up and cool down times and, thus, means he can approximately triple the number of test conditions that he can run in a day. Second, he found that in attempting to obtain maximum hydrogen production numbers in a flow mode, the residence time within his detector (a GC) was greater than his time at maximum production. Thus, he initiated incrementally adding the methane to the reactor.

This change in procedure happened to occur simultaneously with his using the smaller reactor, making it appear that he had actually changed the process. In actuality there is no pulsed reactor, it's only a procedure being used to obtain more accurate maximum hydrogen numbers for the bench top reaction. An industrial process would use a continuous flow scheme.

8. What was the temperature(s) at which the platinum-catalyzed reactions were run? These data do not appear in your report.

The platinum-catalyzed reactions discussed in Dr. Muradov's FY1995 report were run at 900°C. Platinum, as Dr. Muradov points out, is not a good catalyst as it degrades much too rapidly when compared to iron- or nickel-based systems.

III Additional Discussion:

Currently, Dr. Muradov does not have identified industry partners. He was approached earlier by Energy Partners but they have backed off saying that they have done some "rearrangements" and are now focusing on fuel cells.

Technical Evaluation Report

Project: Hydrogen Manufacturing Using Plasma Reforming
Company: Massachusetts Institute of Technology (M.I.T.), Cambridge, MA
P.I.: Dr. Leslie Bromberg
Date of Visit: April 19, 1996
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

M.I.T. is investigating plasma reforming as a means for producing hydrogen for decentralized electricity generation and for transportation utilization both in a "gas station" mode, and, because of its compact size, as a potential on-board reformer. The M.I.T. project is comprised of theoretical modeling (thermodynamic and kinetic) and experimentation on the use of plasmas to reform hydrocarbons. The technologies being considered include plasma reforming versions of partial oxidation, steam reforming, and pyrolysis, while both natural gas and heavier liquid hydrocarbons are potential fuel sources. In this way, it presents a portfolio of potential hydrogen production scenarios. To date, much of the emphasis has been on the partial oxidation option, probably because thus far, modeling (non-optimized) is showing this to be the most efficient.

II Introduction and Background:

On the above date, I met with **Dr. Leslie Bromberg** and his team to discuss M.I.T.'s plasma reforming project. The team includes **Dr. Alexander Rabinovich**, Plasma Fusion Center, **Dr. Simone Hochgreb**, Associate Professor Sloan Automotive Laboratory, Department of Mechanical Engineering, and **Chris O'Brien**, Graduate Student, Department of Mechanical Engineering. **Dr. Daniel Cohn**, Head of the Plasma Technology and Systems Division also participated in the discussion.

I was given formal presentations by each of the team members and was shown the team's gaseous and liquid hydrocarbon reforming systems including a short demonstration of each in operation.

Project Strengths:

- It covers a lot of ground. Plasma reforming has the potential to replace several hydrocarbon conversion technologies. In addition it offers the potential of being applicable for both gaseous and liquid hydrocarbons.
- The thermodynamic and kinetic modeling provides the parametric framework that focuses the experimentation in the most beneficial directions. This is a time and money saver. It also appears to be working, so far. For instance, their kinetic model is showing a two-step reaction process for plasma reforming of methane in the partial oxidation mode. Experimentation is bearing this out.

- The short residence time necessary for plasma reforming allows for rapid start up and shut down.

- The pyrolysis mode, although currently calculated to achieve lower efficiency, provides the potential for CO_2-free hydrogen, as well as removing the need for a shift reaction. Optimization of the process including the incorporation of heat regeneration will increase overall efficiency.

- The system is small enough to have on-board potential.

- They are addressing systems analysis early-on.

Issues that need to be Addressed:

- The sheer volume of parameters, including type of reforming and type of starting fuel makes some of the approach and data hard to follow. Reporting needs to be more structured so that one can follow the researchers' logic more easily.

- In the pyrolysis mode, a means to remove particulates is needed.

- In the partial oxidation and steam reforming modes, the researchers need to address the shift reaction.

- In the next year, the project needs to have identified one or two key process/fuel combinations for further study.

- The planned incorporation of heat regeneration will be needed for the system(s) to be efficient.

III Questions and Answers:

I sent Dr. Bromberg a list of questions prior to my visit. They were discussed during our meeting and are shown here.

Product/Processes:

1. **The partial oxidation experimental work appears to be optimized for acetylene. Is there intent to maximize for hydrogen? How does this effect efficiencies? You make several references to the DuPont Process for acetylene manufacture. Is the M.I.T. experimental system modeled on this?**

The M.I.T. progress report based on work through the end of Calendar Year 1995 seemed to indicate that much of their work was focused toward acetylene production. This is not the case. They were citing some earlier acetylene production work in their survey of relevant literature. The report was somewhat confusing in that some literature discussion and current project discussion seemed to overlap. The M.I.T. research group is focused on hydrogen, however.

2. **Does quenching increase the concentration of materials such as acetylene at the expense of hydrogen? If so, how would this be overcome if the desired product is hydrogen? A slow cool down?**

They reduce (eliminate) acetylene production by removing the quench step and use a slow cool-down.

3. **Up to now, the program seems to have focused on partial oxidation of methane. Will the emphasis be moving more toward other processes (pyrolysis, steam reforming) or toward other feedstocks (heavier hydrocarbons)? Has the system yet been run in the pyrolysis mode?**

M.I.T.'s work up to now has emphasized the partial oxidation mode and methane as a starting material. This system is easier to model, having fewer reactions. The plans are to move on to both other reforming modes and add other hydrocarbons. *I am especially interested in the result of their pyrolytic mode testing, particularly with heat regeneration.*

Mass/Energy Balances, Efficiencies:

4. **Are any overall mass and energy balances available for the three processes (pyrolysis, steam reforming, partial oxidation) optimized for hydrogen.**

A lot of the numbers that M.I.T. has obtained at this point are very preliminary. They have thermodynamic models for the plasma-partial oxidation of methane showing virtually 100% conversion to hydrogen above 1100^{o}K (1520^{o}F). Some preliminary kinetic modeling shows that the process is two-step: a rapid initial combustion period where about half of the hydrogen is formed, followed by a slower equilibrating step that actually mimics steam reforming. The onset of this second step appears to depend on energy input.

M.I.T. has not yet performed energy balances yet. They wish to add heat regeneration to the model first.

Non-optimized overall efficiencies (including a fuel cell utilization efficiency of 60%) for the three modes of reforming methane were estimated at about 43% for partial oxidation, 35% for steam reforming and 21% for pyrolysis. These numbers do not include the benefits of heat reuse, which would add over 10 percentage points to each overall efficiency.

While the data to date is not earth-shattering, it is very preliminary, and many of the proposed systems have not yet been looked at. Reuse of generated heat should help significantly.

Equipment:

5. In the modeling work, what size plasmatron is assumed?

Plasmatron size is not an issue in modeling the systems. The parameter used is the ratio of the energy input to the flow of feedstock that it can accommodate.

6. Is the recent incorporation of FT-IR diagnostics into the system being done to provide a non-intrusive measurement or are there other advantages as well? How well are the FT-IR data comparing with the GC data?

The FT-IR provides in situ temperature measurements as well as gas composition.

Environmental Considerations:

7. Are reactions involving nitrogen to form NO_x significant under plasma reforming conditions?

Initial results are indicating that optimum temperature for the partial oxidation process for methane is about 1100°K (1520°F). NO_x emissions are not expected to be a factor at these temperatures. Their model shows the post-plasma atmosphere to be reducing, and the NO_x levels to be low. When they go to higher temperatures, for the pyrolysis mode, for example, NO_x may be a factor. In addition, soot removal must also be achieved in the pyrolysis mode.

Both the NO_x and particulate issues could pose a challenge to the project in the pyrolysis mode.

Commercial Applications:

8. How do you believe that a commercial process or processes for the production of hydrogen would look using these technologies?

M.I.T. sees several potential commercial application for their project. These include distributed power generation, hydrogen "gas stations", and on-board reformers. In all cases, they are looking at small-scale hydrogen production systems, which they say are easier to commercialize than large systems. The compact nature of the plasmatron system lends itself well to small scale utilization.

As the M.I.T. researchers collect more data on several different hydrocarbons in all three reformer modes, the commercialization potential will become clearer. An economic evaluation would be warranted at that time. Much of the current engineering and economic data is very preliminary.

Specific Data Questions:

9. Have any absolute measurements of hydrogen production concentrations been made yet? Data presented in the 1995 Progress Report do not include percentages for water vapor, acetylene, or ethylene. Variation in the concentrations of these substances would effect the relative hydrogen concentrations.

Their initial experimental data did not contain concentration measurements for water vapor, acetylene, and ethylene. Later reports will contain these data.

10. Referring to Figure 6.9 *(shown here as Exhibit 1),* is this saying that a scaled-up system would require significantly less energy input per unit CH_4 input? The figure shows a value of about $\zeta = 6.9$ MJ/kg CH_4 at a reactor volume of 1 x 10^{-4} m^3, but over 50% less ($\zeta = 3.8$ MJ/kg CH_4) at a reactor volume of 1 m^3.

A larger plasmatron system would indeed require less energy input per unit feedstock, but the desired system compactness would be lost, and the energy savings is not much.

11. The report indicates that the concentrations of H_2O and CO_2 are dependent on the air to fuel ratio, λ, while those of H_2, CH_4, and CO are dependent on the energy input, ζ. The experimental evidence seems to bear this out. Would the data also show the non-dependence of the opposite? That is, would it show the concentrations of H_2, CH_4, and CO to be independent of λ, etc.?

Newer analyses are showing that there is indeed little dependence of H_2O and CO_2 concentrations on the energy input.

12. In what way do the experimental data points in Figure 6.16 *(shown here as Exhibit 2)* correspond to the perfectly stirred reactor model? It doesn't appear that the value of ζ for the onset of conversion corresponds that well.

The M.I.T. researchers agreed with me that the experimental data points for the relationship between methane concentration decrease and energy input are not really well correlated with the model. The difference is that heat losses are not included in the model.

Exhibit 1. Effect of System Size on Energy Input

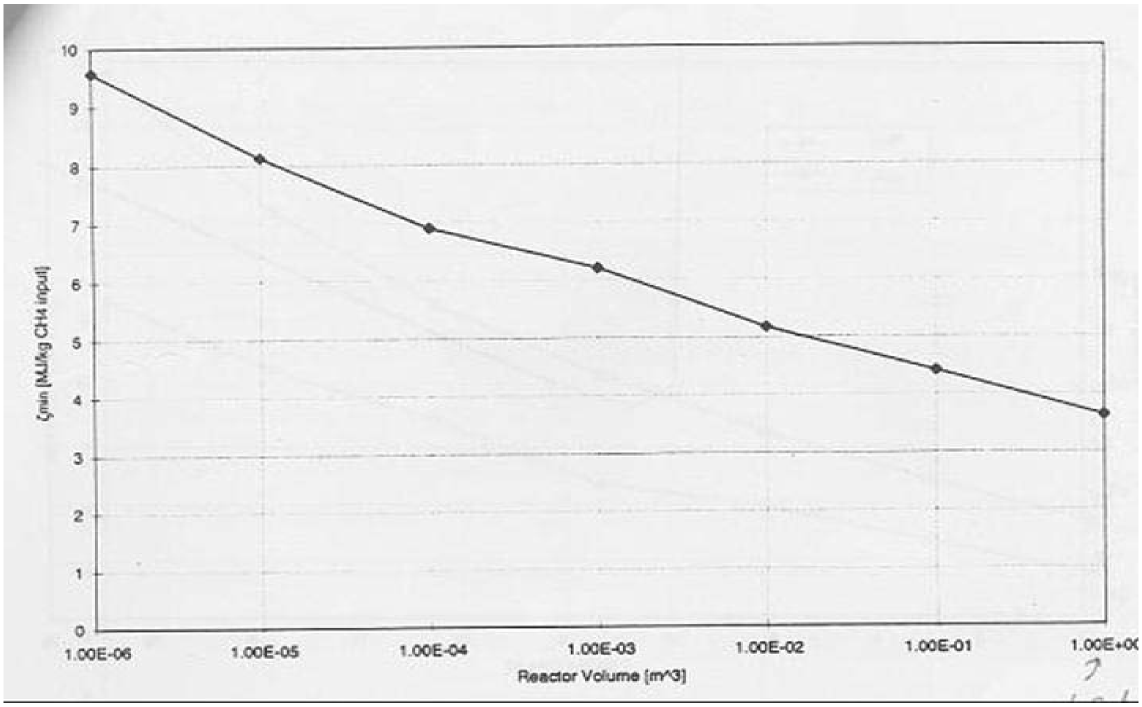
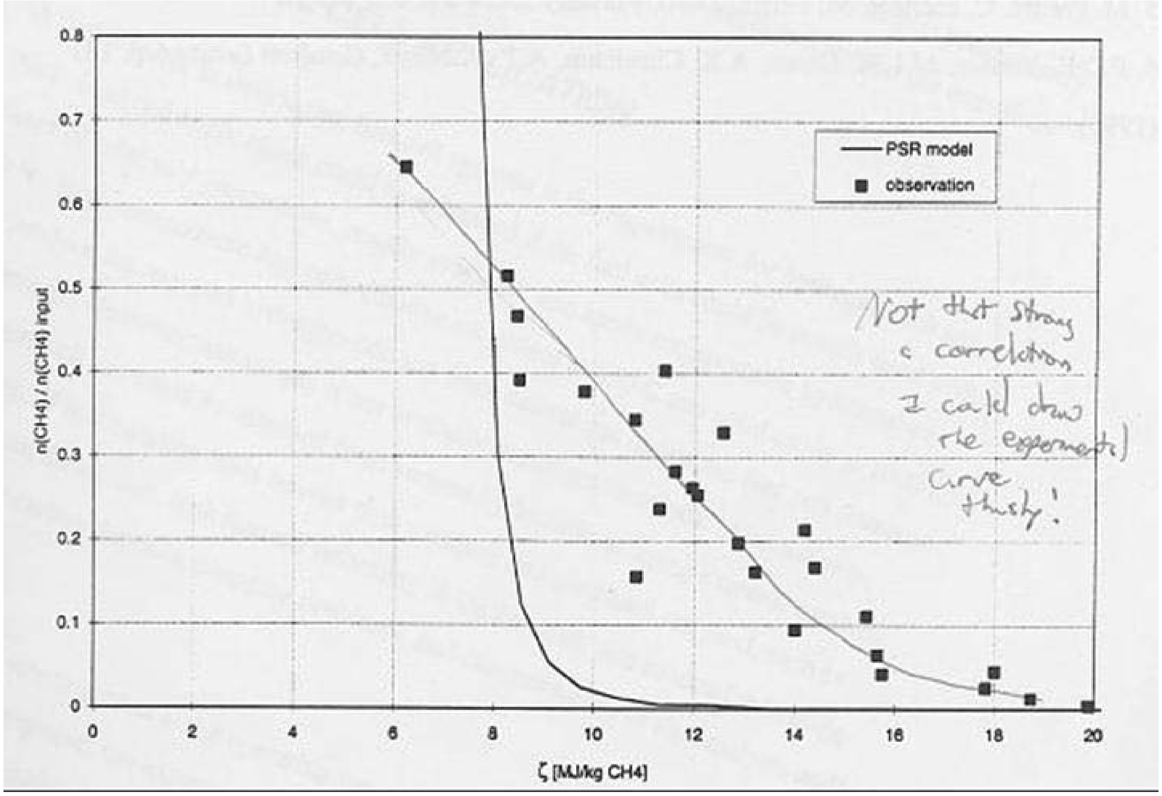


Exhibit 2. Relationship Between Energy Input and Methane Concentration



Not that strong a correlation I could draw the experiment) curve thusly!

Technical Evaluation Report
Project: Plasma Reforming
Company: Massachusetts Institute of Technology, Cambridge, MA
P.I.: Dr. Leslie Bromberg
Date of Visit: December 8, 2000
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

For the past six years, a group of researchers at the Plasma Science and Fusion Center at the Massachusetts Institute of Technology (MIT) have been conducting R&D on the use of a discharge through a plasma to enable the reforming of gaseous and liquid fossil fuels to produce hydrogen. The process is touted to be more energy efficient than conventional reforming processes, especially on small scale. It can reform both liquid and gaseous fuels, and can be run in ways that can simulate several different conventional reforming methodologies (steam reforming, partial oxidation, pyrolysis).

Project Strengths:

- The new, non-thermal plasmatron that MIT has developed has reduced electrical energy requirements for hydrogen production down to 4 MJ/kg H_2. This is a factor of about 4 better than the best results with the old, high current device and greater than an order of magnitude better than the energy requirements that were being quoted at the time of my 1996 visit.

- The plasma reforming process can provide a compact/convenient configuration as an on-board process.

- Plasma reforming offers the potential of scaling-down more efficiently and cost effectively than conventional reformers; they don't have the same heating requirements as conventional reformers, where size plays a much larger part.

- Costs and efficiencies for diesel reforming using the plasmatron appear potentially to be superior to conventional systems.

- Working with Texaco, BP Amoco, and IMPCO gives the project additional credibility.

Issues that should be Addressed:

- In my opinion, the strongest "hook" that this project had to offer was the possibility of reforming methane in a pyrolysis mode, and producing only hydrogen and carbon. This, however, has now been shown to take too much energy to be cost effective.

- The plasma reforming process is producing too much CO. That is, the water shift portion of the reaction does not seem to be working well. This needs to be dealt with.

- This project has suffered more then most from an on-again, off-again funding situation.

II Introduction and Background:

I visited Drs. Leslie Bromberg and Alex Rabinovich at the Plasma Science and Fusion Center at MIT for the second time. We discussed the progress that they had made on the plasma reforming project, including the development of a new "non-thermal" plasma reformer.

I had first visited this project in 1996 when it was still quite new. At the time, MIT had demonstrated their ability to make hydrogen and were working to develop heat and material balances for the system, and to reduce the input energy. At the time, we saw a potential bonanza for the project if they could efficiently and inexpensively create hydrogen from methane in the pyrolysis mode. Under that condition, the byproduct would be solid carbon, and no gaseous pollutants would be emitted. MIT also felt that the technology lent itself well toward on-board reforming of liquid fuels, which would allow for more or less conventional refueling.

Today, with their two plasmatron designs and their large decrease in the amount of input electricity required, the MIT team sees potential for their plasma reforming technologies in many vehicular and stationary applications.

III Initial Discussion:

Applications

The main feedstocks being evaluated are natural gas and diesel fuel. Dr. Bromberg spoke of using plasma reforming of natural gas in refueling stations, and using diesel fuel for small, decentralized power production and hydrogen production. For on-board systems, Dr. Bromberg proposes the use of plasma reforming of diesel fuel for use in spark-ignition engines for emission mitigation. Running in a lean mode will drop NO_x by two orders of magnitude. In addition, MIT is looking at on-board plasma reforming for auxiliary power units for cars and trucks and as a catalyst regeneration enabler in diesel engines. (For instance, barium carbonate is used to trap NO_x, forming barium nitrate. The reformate can be used to regenerate the carbonate.) MIT has received funding from the DOE Office of Transportation Technologies for its on-board reforming work.

IV Tour:

This part of the meeting was shorter and not nearly as involved as most. I basically got a short demonstration of the 2nd generation non-thermal plasmatron. What I saw was two vertically mounted tubes (electrodes) with a space between them. Fuel is injected through the top tube, while air is injected from the side, into the gap, perpendicular to the tubes.

Some of the air is there to atomize the fuel. With atomization there is less, or no, soot.

The plasmatron is powered by a 200 kHz, 1 kW power supply.

The reaction extension zone consists of two sections of catalyst and a heat exchanger.

This is the plasmatron that will be sent to Sandia.

V Questions and Answers:

I sent Dr. Bromberg a set of discussion questions prior to my arrival. These were discussed in detail during my visit. In addition, I was given a written set of answers for most of the questions. These are reproduced below.

1. **What mode are you using to plasma reform diesel fuel (steam reforming, POX, pyrolysis)? What percentage of the hydrogen in diesel fuel becomes molecular hydrogen? What are the byproducts? How will they be dealt with?**

"Presently, we are exclusively using partial oxidation, with O/C ratios between 1 and 1.8. For diesel, the results are shown in [Exhibit 1]. The hydrogen yield is defined as the hydrogen generated divided by the hydrogen content of the fuel. The hydrogen yield can be greater than one because of the water-shifting of the resulting CO. The maximum hydrogen yield in this case is on about 1.8. The ordinate refers to the specific energy consumption, the electrical energy required by the plasmatron divided by the lower heating value of the hydrogen produced. The old plasmatron refers to the thermal plasmatron that we have investigated in the past, the new plasmatron refers to the nonthermal plasmatron that we have been investigating since the summer of 1999.

"With the plasmatron, we have investigated single stage reforming/water shifting. For diesel, the results for several types of reactors are given in [Exhibit 2].

"The empty reactor refers to one where there is no catalyst. The ceramic catalyst is Ni-based steam reforming catalyst on an alumina substrate (a standard catalyst from United Catalyst.) The honeycomb catalyst is a rare-earth (Engelhardt proprietary catalyst) on a metallic substrate.

"Working with the non-thermal plasmatron, MIT has found that they can reform diesel fuel, (primarily using the partial oxidation approach) obtaining a high rate of conversion to hydrogen with no noticeable soot generation. One problem they are finding is that the CO concentration remains high even after water shifting. This needs further exploration.

"The best result indicate about a 6% content of CO. Further water shifting could be accomplished with a low temperature water shift catalyst. Additional CO cleanup (preferential oxidation PROX or methanation) will be required to bring the CO to acceptable levels for use with a PEM fuel cell."

MIT has not had nearly the success with steam reforming mode and pyrolysis as they did in the partial oxidation mode. Pyrolysis is proving to be too costly, and the steam reforming mode does not seem to work well. It appears that only water shifting works well if water (steam) is present.

There are some problems here. MIT retains far too much CO in the partial oxidation mode. The plasma reformer is supposed to essentially combine the reforming and shifting steps. This is not happening. If we are going to go to a major second process to bring the CO down (we're not talking about just a final purification step), the costs are going to rise – probably unacceptably.

2. Please explain the non-thermal plasmatron concept.

"The non-thermal plasmatron employs a discharge mode with non-equilibrium features allowing operation at much reduced plasma current relative to compact arc plasmatron fuel reformers previously developed at MIT. The discharge is a nonthermal plasma, with electrons at much higher temperature than the ions and neutrals, which are at near room temperature. This plasma generates relatively low levels of plasma heating. A low current plasmatron reformer is schematically shown in [Exhibit 3].

"Air and fuel are continuously injected in a plasma region provided by a discharge established across an electrode gap. The device operates at atmospheric pressure, with air or air/fuel mixture as the plasma forming gas. Neither electrode is water cooled. A variety of electrode and injection geometries are possible.

"The discharge is continuously broken by the flowing gas, followed by sudden breakdown in another place between electrodes. The discharge breaks and re-ignites at relatively high frequencies, on the order of 2 kHz."

Ion and neutrals temperatures are of the order of a few hundred degrees C (as opposed to electron temperatures in the 10,000-20,000°C range.) With the standard DC arc plasmatron, the plasma is near equilibrium, and temperatures for the electron, ion, and neutrals are all in the 10,000°C range.

The non-thermal plasmatron runs at low (~0.1 amp) current; the conventional plasmatron is closer to 20 amps. The non-thermal plasmatron removes the electrode life issue that plagues the conventional plasmatron. The electrodes are hollow, have large surface areas, and do not erode as rapidly as with the high temperature plasmatron. The older plasmatron could be run for about 50 hours, at which time substantial erosion would be noted. The non-thermal plasmatron has not yet shown any signs of erosion. MIT estimates an electrode life of greater than 3000 hours for the new version.

Two generations of the non-thermal plasmatron have been developed. The second possesses a higher power capability – up to 2 kW vs. 300 W. The lower current, higher voltage device produces a very large spark that is ideal for igniting fuels.

Working with diesel fuel and the non-thermal plasmatron in the laboratory, the researchers find a hydrogen yield of greater than 40% after 5 seconds (it takes that long to get a sample), and yields of 65-80% after 90 seconds. Once the system is warmed-up, if the plasmatron is shut off and then restarted, there is no delay in resuming hydrogen generation. Hydrogen is measured with a gas chromatograph. The low-temperature water shift mode is not working well yet.

There is a tremendous decrease in the power requirement for the low temperature plasmatron. This area has shown the most significant progress over the past few years.

3. **What do you estimate the total cost of hydrogen production to be (as $/kg) based on using diesel fuel and the low power plasmatron?**

"Using diesel, for a plant on the order of 20,000 scfm, the cost of the hydrogen generated in on the order of 14 $/kg H_2. These numbers were extrapolated from a detailed analysis carried out by MIT and BOC on the cost of hydrogen generated from natural gas using a plasma reformer, presented at the Fall Meeting of the American Chemical Society (1999).

"The cost is shown in [Exhibit 4] as a function of the cost of the diesel fuel.

"It should be stressed that a substantial cost of the hydrogen (on the order of 60%) is due to the cost of the fuel. The cost of operating a hydrogen plant is shown in [Exhibit 5] for both natural gas and diesel as the hydrocarbon fuel."

$14/ kg hydrogen is approximately $123/ MMBtu. If one looks at Exhibit 4, it shows costs closer to $14/MMBtu, which I think is what Dr. Bromberg meant, although that would be the cost with $1/gal diesel fuel. (A gallon of diesel fuel produces approximately 138,000 Btu, so $7.25/MMBtu diesel produces $14/MMBtu hydrogen.) The numbers include the use of a separate shift reactor, so they may not be too bad. I think, however, that finding a way to perform the entire reaction with the plasma reformer (as was originally intended) would be valuable.

For natural gas, Dr. Bromberg quoted about $10/MMBtu hydrogen from about $4/MMBtu NG.

4. **What do you feel is the maximum rate of hydrogen production that the low power plasmatron can handle?**

"Presently, the plasmatron operates efficiently at diesel flow rates between 0.25 g/s and 0.5 g/s (These numbers approximately represent 10 and 20 kW of equivalent thermal power).

"We are limited by the experimental facilities in using large flow rates (limited by the air flow in the hood required to dilute the hydrogen and CO concentration to levels that allows release).

"We are exploring operation at lower flow rates."

This does not really answer the question as to how high a flow rate the plasmatron can handle. The last sentence, however, indicates what types of markets the group is targeting.

5. **Please explain the "reaction extension region" that you mention in your AOP submittal. Is it a widening of the plasma region, or actually a second reactor? If the latter, what kind of a reactor?**

“The reaction extension region represents the volume immediately following the discharge, where high temperatures due to proper thermal insulation allow completion of the reforming operation. It is not a second reactor.

The reaction extension region can be seen in Exhibit 3, the schematic of the non-thermal plasmatron.

Perhaps if it were a second reactor, it could be tailored to better handle shift reactions.

6. **Some of your publications indicate that you generally use standard reforming catalysts for your plasma reforming processes. Have you ever looked at any other catalysts? Does it appear that whatever works best for conventional processes (e.g., steam reforming H.T. water shift, L.T. water shift) also works best with the plasma?**

“We have used Ni-based catalysts (for steam reforming), and water shifting Fe-Cr catalysts that are commercially available (United Catalysts). We have also used rare earth metal catalysts of proprietary nature (Engelhardt).”

With plasma reforming you generally combine several process steps. *But apparently not well, based on the remaining CO content of the product.*

The Ni-based catalysts are referred to as “ceramic” in Question 1 and Exhibit 2, while the Engelhardt catalysts are referred to as “honeycomb catalyst.”

7. **Does the non-thermal plasmatron process utilize a catalyst? Is the catalyst different than with the “conventional” plasmatron?**

“We have not carried exploration outside “conventional” process catalysts. We have used similar catalysts on both the thermal and nonthermal plasmatrons.”

8. **You indicate that you will be designing and/or building two pilot plants – one “conventional” and one non-thermal plasmatron based-plant. About what size is each anticipated to be? What will the fuel be? How complete will these systems be? (For example, will you separate out byproducts, hook the hydrogen up to a fuel cell or store the hydrogen, etc.?). What parameters will you be measuring?**

“We will be building only a pilot plant based on the nonthermal plasmatron. We will be measuring composition of the reformate, electrical characteristics of the plasmatron as a function of the throughputs, composition and nature of the catalyst.

“We are expecting to generate throughput on the order of 50 kW thermal equivalent of hydrogen rich gas, with composition that is close to low temperature water shifting.

“The fuel will be diesel and/or natural gas.

“We will not be testing systems for further purification of the hydrogen. These systems are commercially available (such as PSA, pressure swing adsorption).”

MIT appears to be concentrating on the low temperature plasmatron almost exclusively at this juncture.

9. **Going back to some of the work you were doing during my visit in 1996: You were examining (or going to examine) the pyrolysis mode reforming of methane. One premise was that potentially, you could get hydrogen and carbon – no CO_2. The question was could it be done efficiently and economically. Where did this finally lead? Was this ever tried in the presence of a catalyst?**

"We tried extensively to decrease the energy consumption in the pyrolytic conversion of methane. We tried several schemes. The methods explored included:

- Homogeneous reactors
  - No preheat
  - Preheat
  - Cyclonic soot separation with combined heat exchanger
- Inhomogeneous reactor
  - Fluidized bed with charcoal particles

"The results for the different combinations are shown in [Exhibits 6 and 7] as a function of the specific energy input of methane (electrical energy used per mole of methane).

"It was surprising that the results with the fluidized bed reactor were as negative as they turned out to be. It was understood that the fluidized bed was a very good heat transfer mechanism, cooling the gas very efficiently and reducing the yields."

It doesn't appear clear in the written response, but the message seems to be that the fluidized bed being mobile carried the heat away from the plasma lowering hydrogen production efficiency. (Perhaps if the bed were recycled, there wouldn't be as much of a loss.)

"[Exhibit 8] shows two of the results without the fluidized bed, one with the lowest specific energy consumption, and the second one with the highest yield. Hydrogen yields were as high as 60%, although at specific energy consumption on the order of 170 MJ/kg H_2. For comparison, the lower heating value of hydrogen is about 120 MJ/kg, less than the electrical power required for the pyrolysis. It was concluded that pyrolysis was impractical due to poor energetics.

"We never tried to do pyrolysis from liquid fuels. Hydrocarbon pyrolysis is being commercially explored for the production of carbon black, where hydrogen is only a by-product of the process."

When we were discussing pyrolysis in 1996, we only spoke of methane since carbon black and hydrogen would be the only products. Pyrolysis of higher hydrocarbons would also probably result in some mixed species.

When MIT tried to run in the pyrolysis mode, their best results came when they used no catalyst. When they ran with an activated carbon catalyst, results were poorer. They never tried metal catalysts. Dr. Bromberg mentioned that they might have gotten better results if they had used a metal catalyst, but they felt that they would have coking problems.

It would have been interesting to have seen some tests with a metal catalyst. Recall that Muradov at FSEC was able to produce hydrogen by pyrolysis with a metal catalyst. It's true that he did have a coking problem, but may have solved it by employing a fluidized bed. The results for the plasma reformer with a fluidized bed and a metal catalyst may have given satisfactory results – lower required energy without coking. Of course, the overly efficient heat transfer abilities of the fluidized bed may have negated the gains.

At any rate, the mass balance came out accurately, and the power consumption numbers are far inferior to those obtained with partial oxidation conditions (by a factor of about 50). The pyrolysis mode for methane plasma reforming does not appear promising.

VI Additional Discussion:

MIT is currently building and testing a plasmatron that will be sent to Sandia National Laboratories (CA) to test its ability to reform diesel fuel. Tests will include durability. The plasmatron is planned to be used for the Remote Power project in Alaska. Sandia's Jay Keller has told Dr. Bromberg to just get him the syngas, and Sandia will water shift it. (Recall that the low-temperature plasmatron was having some problems in the low temperature water shift mode.)

Dr. Bromberg recognizes that most of the work that they have done has been geared to non centralized power (distributed generation), be it on board reforming, refueling station sized reforming, or decentralized power production. None of these are conducive toward CO_2 sequestration, and therefore don't fit well into the global climate change mitigation arena.

MIT has been and currently is involved in collaborations with several industrial partners:

- MIT did a project with BOC Gases in which they conceptualized a 20,000 standard cubic feet per hour (scf/h) hydrogen generation plant, based on the plasmatron. The feedstock was natural gas. Unfortunately, BOC got bought out, and the project is defunct. A schematic for this plant is shown in Exhibit 9.

- MIT is currently looking at higher pressure hydrogen production for BP Amoco. They are trying to produce hydrogen at about 10 bar (approximately 145 psi).

- They are also involved in some high pressure work with Texaco, in which the feedstock is "real" natural gas, containing about 10 % oxygen.

- MIT will likely do some more work with Texaco that will include shipping a plasmatron to them for a refueling station.

- Finally, MIT is investigating the possibility of a collaboration with IMPCO in the decentralized power arena. IMPCO is interested in refueling stations.

Exhibit 1. Hydrogen Yield vs Energy Consumption for Diesel Reforming

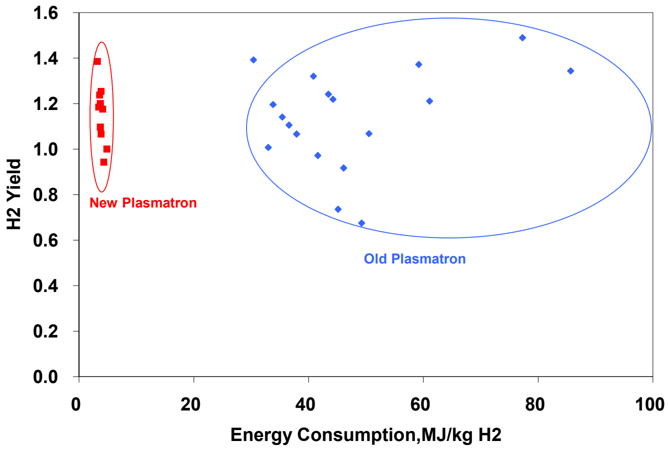


Exhibit 2. Nonthermal Plasmatron Diesel Reforming

	Initial Process Parameters				Gas Composition								
	Power kW	O/C	H2O/C	Fuel g/s	H2 vol.%	CO vol.%	CO2 vol.%	N2 vol.%	CH4 vol.%	C2H4 vol.%	H2 Yield	Power Effic (%)	Power Consump. MJ/kg
Empty reactor, no water	0.27	1.32	0.00	0.26	14	16	4.7	64	0.7	0.1	0.64	56	13.2
Ceramic catalyst, no water	0.19	1.51	0.00	0.48	14	17	4.7	64	0.2	0.0	0.75	64	4.3
Honeycomb catalyst, no water	0.23	1.33	0.00	0.31	19	21	3.3	57	0.3	0.0	1.00	81	6.1
Honeycomb catalyst, with water (2 excess)	0.15	1.24	1.78	0.31	23	17	6.2	52	1.2	0.4	1.22	87	3.3
Honeycomb catalyst, with water (4 excess)	0.22	1.57	4.04	0.22	21	10	10.8	58	0.3	0.0	1.30	72	6.3
Honeycomb catalyst, with water 2nd generation plasmatron	0.24	1.47	3.67	0.25	23	6	13.5	57	0.1	0.0	1.31	60	6.0

Exhibit 3. Non-Thermal Plasmatron Schematic

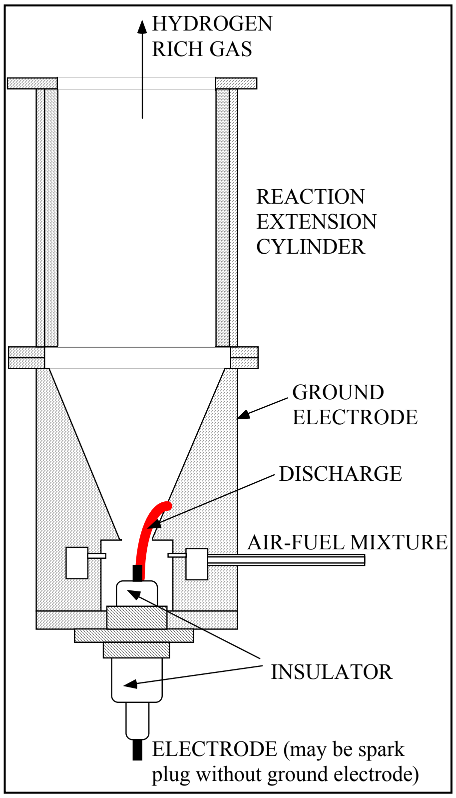


Exhibit 4. Cost of Hydrogen as a Function of the Cost of Diesel Fuel

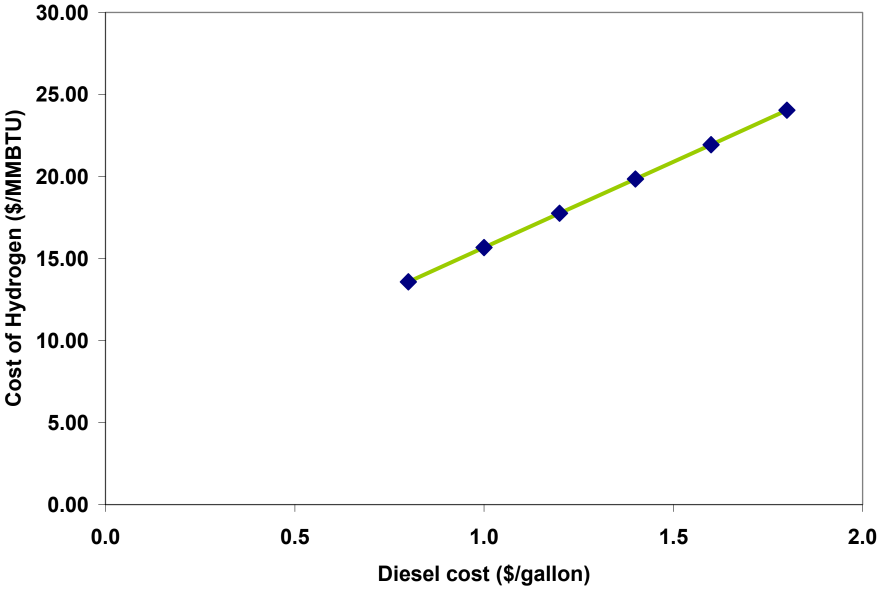


Exhibit 5. The Cost of a Hydrogen Producing Plant

	Natural gas	Diesel
Labor	$35,000	$35,000
Catalyst	$10,000	$10,000
Power	$73,636	$156,667
Fuel	$221,952	$624,128
Total Op. + Util.	$340,588	$825,795
Total cost Op+util+cap	$490,558	$1,012,960

Exhibit 6. Hydrogen Production (Yield) as a Function of Power Consumption for the Pyrolysis of Methane for Different Design Modifications

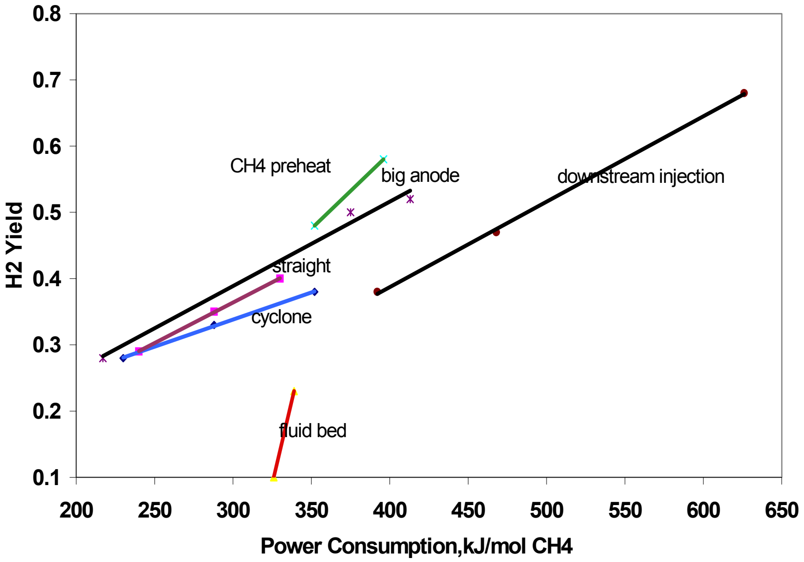


Exhibit 7. Power Consumption Comparison (Hydrogen Produced vs. Methane Used) for the Pyrolysis of Methane, Different Design Modifications.

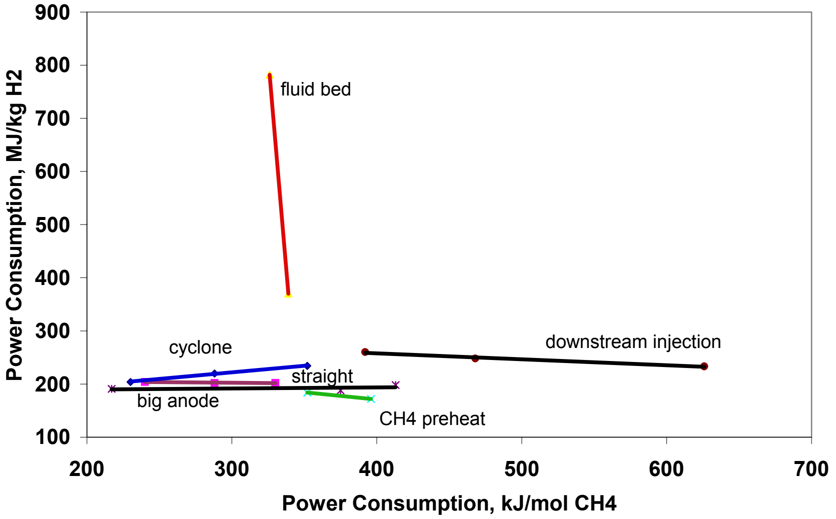
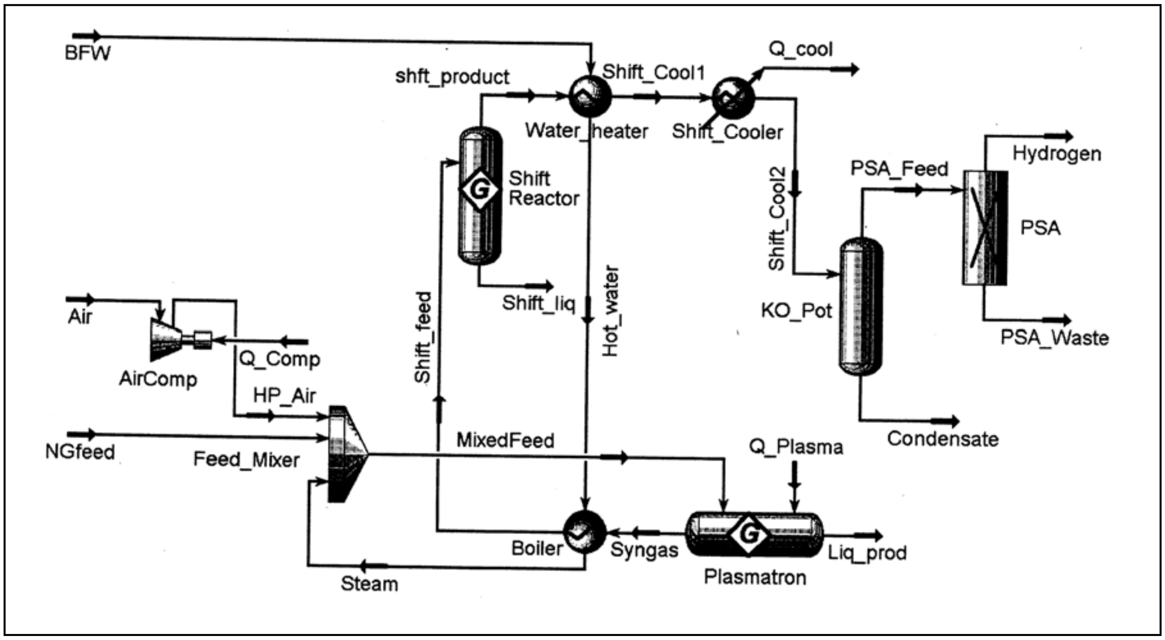


Exhibit 8. Pyrolysis of Methane "Best of the Best" (One Showing Low Power Consumption, and the Other Showing High Hydrogen Yield)

CH4,g/s	0.14	0.08
N2,g/s	0.29	0.29
OUTPUT		
H2,vo.%	23	33
O2,vol.%	0	0
N2,vol.%	41	54
CH4,vol.%	28	7
CO,vol.%	0	0
CO2, vol%	0	0
C2H2, vol%	4.7	3.2
C2H4, vol%	0.66	1.16
C2H6, vol%	0.34	0.02
Sum.	98	99
mass flowrate (g/s)	0.43	0.37
volume flowrate, STP (cm3/s)	543	457
INPUT (g/s)		
H2	0.04	0.02
C	0.11	0.06
Power consump, MJ/kg hydroger	169	231
H2,vo.%	0.23	0.33
Hydrogen yield	0.32	0.68
Specific power, kJ/kg total	4390	8465
Power consumption, kJ/mol CH4	217	626

Exhibit 9. Conceptual Design of Plasmatron-Fuel Converter Based Hydrogen Generating Plant (20,000 scf/h plant)



Technical Evaluation Report
Project: Improved Metal Hydride Technology
Company: ECD Corporation, Troy, MI
P.I.: Dr. Krishna Sapru
Date of Visit: August 21, 1998
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

The hydrogen storage group at Energy Conversion Devices, Inc. (ECD), have an excellent understanding of metal hydrides, how to make them, and how to use them. In addition, they have available to them an abundance of diagnostic equipment, making the obtaining of timely data in house possible. This makes ECD a very good place for the undertaking of applied R&D leading to commercial products. **Dr. Krishna Sapru** and her team seem to have approaches toward developing a hydrogen storage system that is well thought out, and multifaceted. The metal hydride R&D, however, seems to be pointing toward a conclusion that one cannot have both a high weight percent hydride (over three percent on a H/(M+H) basis) and a low dehydriding temperature material (below about 100^{o} C).

ECD does not appear concerned with <3% H/(M+H), which works out to about 2% system weight. They say that Ron Sims of Ford finds this level quite “adequate”, and that Ford “loves metal hydrides.” *There are many niche markets where 2 weight percent system weight is reasonable, but I would think, this would not include mainstream applications, that is, for use on board light-duty vehicles.*

The magnesium work does not appear to be progressing sufficiently. Its use may be likely limited to niche market applications. ECD has not investigated the transition metal hydrides in nearly as great a degree; low temperature systems will most likely be achievable, but their theoretical hydride loading is limited greatly by the high atomic weights of the metals in question. ECD is currently concentrating on market identification for their magnesium and transition metal hydride systems. There is still a possibility, however, that ECD will achieve a more widely useful system. They have recently produced some ultra-fine (under 100 nm) size alloys that may lend themselves better to hydriding/dehydriding kinetics. This in turn could lead to a lower temperature system for a given composition.

II Introduction and Background:

On the above date, I visited Dr. Krishna Sapru and her team at Energy Conversion Devices, Inc. (ECD), in Troy, MI. I was given a tour of their United Solar unit and their Ovonics Batteries unit as well as a tour/demo of their metal hydride work. There were also several hours of discussion with Dr. Sapru and five members of her staff. I also met briefly with ECD President Stan Ovshinsky, mainly a courtesy visit, and even got a ride in an EV.

ECD and its subsidiaries are about 400 people strong. Their United Solar (PV) and Ovonics (Nickel Metal-Hydride Batteries) divisions, including their General Motors-Ovonics Joint Venture, seem to be going full speed ahead. (United Solar is owned jointly by ECD and by Canon of Japan.) They also have an "information" division that looks at materials that store information by undergoing physical and/or chemical changes.

ECD got into the hydrogen business in 1980 through a contract with ARCO when the oil company was investigating alternative fuel options during the energy crisis. At that time, they investigated aspects of hydrogen production, storage, and utilization. This respectively involved alkaline electrolysis (developed thin film electrodes), disordered materials (sputtered thin films), and alkaline fuel cells. Although this was only a three-year project, it provided the knowledge that ECD used to develop their nickel metal hydride (NMH) battery business. NMH technology was first investigated by Daimler-Benz, but it was ECD that led the way to commercialization. Nearly every battery manufacturer in the world has licensed some part of ECD's NMH technology. Their current NMH activities concentrate on batteries for vehicles.

III Questions and Answers:

I had provided Dr. Sapru with a list of questions and discussion topics prior to my visit. She and her staff compiled answers to these questions prior to my arrival, and these answers formed the basis for our extensive discussion. These questions and answers are discussed below:

Materials:

1. **Do you plan to look only at magnesium based alloys or will you look at other materials as well?**

ECD is and will continue to look at Mg systems, but is also approaching the goal of high-capacity low-temperature storage from the other direction by investigating low-temperature transition metal hydrides (e.g., Ti-V-Zr). They combine elements by examining pressure vs. temperature profiles. Currently, they are beginning to achieve hydride weights of about 1.5% at room temperature, and indicate that these levels are applicable for certain niche markets.

ECD believes that the "current goal", stated as 3 wt% hydride 2 wt% system is achievable, and are the type of systems that have many applications. ECD has spoken to Ford's Ron Sims, who believes that 2 wt% system is perfectly adequate and is a desirable system due to its high safety. Dr. Sapru also pointed out that these 2 wt% systems have applicability in context with small, stationary fuel cells. ECD admits that improvements to the magnesium hydride systems present a challenge, but feel they are making "slow but steady progress."

It appears to me that ECD considers these magnesium hydrides as being of limited value. They are talking about niche markets and special cases. Their work with the transition metal hydrides may work out better, but these are weight percent-limited by the weight of the metals.

2. **What role does Mo play in the Mg/Ni/Mo alloys?**

Molybdenum, acting more like a dopant than an alloy, serves as a catalyst for both hydrogen dissociation and for the absorption/desorption process. It forms oxides that are more conductive than resistive. Levels of 1 wt% Mo are sufficient. The use of Mo for this purpose arises from ECD's work in the early '80s. At that time, ECD showed that the addition of Mo to Mg-Ni electrodes improved the hydrogen evolution reaction by reducing cell overvoltage.

3. **Are any data available for systems in which you use the four-part alloys that you have spoken about?** *This refers to Dr. Sapru's presentation at the 1998 Annual Peer Review, where she alluded to Mg-Ni-Mo-C alloys.*

In fact, most of the data presented during 1998 involve these kinds of systems. Results for these four part systems are quite reproducible. Recently, ECD has even been working with five and six part systems in order to lower the desorption temperature.

Alloy preparation:

4. **In particle size experiments, what characteristics are you looking for to optimize a system? (For example, narrow or wide or multimodal distribution, high surface area, regular/irregular shape, introduction of eccentricities, etc.)**

Kinetics are improved by the use of high surface areas, that is, a high percentage of fines. Thus, the goal is a narrow particle size distribution with most particles between 1 and 10 microns in diameter. When measurements are made, the powders are sieved first, and measurements are made on only the <45-micron fraction. In addition, measurements are rarely taken prior to about five hydriding/dehydriding cycles. These cycles act to break particles (hydrogen embrittlement) and improve the kinetics. The system is stabilized after 5-10 cycles.

Particle shape is not controlled; particles are generally spherical. Mechanical alloying introduces stresses into the particles, which lead to disorders. These disorders are preferred for improved storage properties.

The need for several hydriding cycles, or a "breaking in" process will, of course, need to be accounted for in any demonstration/commercial venture, or simulation.

5. **How reproducible by chemical structure are materials that are made by a mechanical alloying process, and how reproducible are their properties?**

Chemical composition is “generally reproducible,” while properties, especially kinetics can vary in some cases. Dr. Sapru cited Mg-Ni-Mo-C as a very reproducible system both in composition and in properties, while Mg-Ni-Cu-Fe-Mn-Si-C has reproducible composition, but varies from run to run in properties, especially kinetics.

6. **When you refer to “yield” following a grinding process, what exactly does that mean? Is it yield of a particular alloy … or any alloying? When the yield is less than 100%, and especially when the yield is very low, what are the other materials present?**

Yield is simply percentage of powder recovered after milling. Some of the material sticks to the walls of the mill or to the grinding media. Dr. Sapru indicated that these fractions are recoverable. *Aside from the efficiency/cost considerations of low yields, there is the additional R&D concern that testing done on low yield fractions are not representative of the system as a whole.*

7. **When grinding is done with a lubricant, how is it proposed to separate the lubricant from the alloy?**

Lubricants used are graphitic carbon and/or heptane. Heptane evaporates during processing, while the carbon becomes part of the alloy. It is also believed that the carbon acts as a catalyst and a kinetic aid for the hydriding/dehydriding cycle.

8. **How does a large number of catalytic hydriding sites lead to a high tolerance against surface poisoning?**

Dr. Sapru states that sites due to such phenomena as dangling bonds, unfilled orbitals, and surface dislocations act as catalytic sites. As more sites are available, losing a few (i.e., poisoning) does not significantly reduce the material’s activity.

9. **Did you ever look at a dispersant to reduce agglomeration of fines?**

Heptane (see Question 7, above) acts as a dispersant and reduces agglomeration. However, its use requires that the materials undergo a longer grinding time.

It may be advisable to investigate the use of dispersants to increase yields, that is, getting the materials off the mill walls.

10. **Would you expect that a high grinding speed at a shorter time is more efficient from a power consumption point of view as well as a time saver, or doesn’t it matter?**

Dr. Sapru pointed out that mechanical alloying is basically a low cost process. With the R&D batch mixes, time and speed are basically interchangeable. ECD believes that in a practical process, the higher speed/shorter time scenario would lead to a more economic process, but efficiency evaluations have not yet been performed on this aspect.

ECD is not yet sure what the process will be, but they do not believe that scale-up will be difficult, and they feel that if they get good yields, the process will not be expensive.

Hydriding and De-hydriding:

11. What do you project as the "ultimate" hydrogen concentration you could achieve at temperatures compatible with PEM fuel cells?

For the magnesium system, MgH_2 is 7.8% theoretically. Dr. Sapru stated that a Mg based alloy operating at less than 100^oC would have a capacity of no more than half that (3.8%). *Based on the overall conversation, 3.8% would seem optimistic.*

The theoretical maximum weight percent for a transition metal based system, say VH_2, is a little under 4 percent. The concept of high weight percent at low temperature with a transition metal is a "new problem" for ECD. They have never worked in the direction of high weight percentage before. They want to increase state-of-the-art transition metal systems form 1% to 2% in the short term, and think that they can get to close to 3% eventually.

12. Your papers at the NHA meeting spoke of using hydrogen as a heat source to dehydride your storage materials. I don't recall any reference to this either during the annual review or during the World Hydrogen Energy Congress. Are you still considering this as an option?

That particular work was not DOE funded, but was done under a now completed SBIR supported by DARPA. That work involved the construction of a laboratory prototype metal hydride hydrogen storage unit. Dr. Sapru indicated that she would not be opposed to receiving DOE funding to optimize this prototype.

13. I have heard/read at various times that melt spinning produces a more homogeneous material that increases the level of hydriding. However, I also heard that hydriding is improved by disorders in the matrix. Please explain.

The homogeneity is on a more macroscopic level. It does not effect the matrix disordering level. ECD has not done a great deal of melt spinning trials. They have found, however, that rapid quenching (based on wheel speed) leads to a highly disordered system. The limited use of the melt spinner is due to the fact that it is the property of their battery people, and there is concern about poisoning the equipment.

14. Do the same alloy/particle properties that favorably effect desorption kinetics also favorably effect hydriding rate?

The activation energies are the same in both directions, and the rates are mutually effected the same way by material parameter changes.

I am surprised that this would be the case universally, unless diffusion rate were the rate determining step, which Dr. Sapru says is not the case.

IV Tours:

Tour of Hydrogen Storage Technologies Area:

ECD's mechanical alloying studies are performed in attritor mills, using twenty-gram samples for research. They generally mill in an argon atmosphere, although they have also looked at 5% hydrogen in argon. They classify the ground material using sieves in a glove box, and then use the –325 mesh (<45 micron) material for hydriding tests.

While the "conventional" Mg systems are made by the mechanical alloying method, the non-magnesium transition metal systems are generally made by induction melting. Processing is done with a 15 kW induction heating system, with the materials in graphite crucibles.

I was also briefly shown a system in which transition metal mixtures are subjected to plasma discharge, producing particles that are under 100 nm via gas-phase condensation. Dr. Sapru is quite excited about this material, which can lead to much more favorable kinetics. (I'm not sure that it would lead to any increased loading; probably not. Perhaps with the Mg systems, it may make lower temperatures more practical, however.)

Testing of metal alloys and metal hydrides include kinetic measurements and pressure-composition-temperature (PCT) measurements. Testing is performed on 1-2 gram samples. Typically, a magnesium-based sample is heated to 300^{o}C, and then soaked in 500 psi hydrogen for two hours before the pressure is relieved. The pressure is cycled four times before any measurements are taken. The reason for this is that the first couple of hydriding cycles results in an overall decrease in the particle size of the alloy, resulting in a change (improvement) of kinetic properties.

Tour of Other ECD Areas:

The tour of the United Solar facility consisted primarily of a showcasing of their PV panel production PDU. This unit produces triple-junction amorphous silica PV panels that will produce in excess of 2 volts, making them capable of splitting water. The nine layers (pin,pin,pin) of this material, some less than a micron thick, are formed by plasma arc-induced chemical vapor deposition upon the substrate. This is accomplished by robotically-controlled operations forming the various layers at different stations. (Very impressive!) The unit runs continuously, producing one-half mile long rolls of PV panel. Five MW of panel can be produced annually. ECD estimates that when scaled to an annual production of 75 MW, the cost for these panels will be under $1/watt.

At the Ovonics NMH development facility, I was walked through the process of making NMH batteries. An ingot consisting of an alloy of nickel, vanadium, titanium, zirconium and chromium is produced in the furnace, and is then broken into fine powder by using hydrogen to embrittle the material. It is then melted into the substrate to form a negative electrode plate. The positive electrode plate is made of nickel foam with a paste of nickel hydroxide and other materials painted on. The plates are alternated with foam separators between them, and inserted into a metal can.

Similar processes are carried out on a larger, partially automated scale at the GM Ovonics facility. Overall, 800,000 linear feet of electrode material per month are made by this and other GM Ovonics plants.

ECD also has quite extensive analytical capabilities, and runs these as a separate section within the organization. Since much of their work involves surface conditions of their materials, one of their most important analytical tools is a system that provides thin film surface analysis. It is a four-function system that incorporates Auger Spectroscopy, Electron Spectroscopy for Chemical Analysis (ESCA), Auger Sputtering, and Secondary Ion Mass Spectroscopy (SIMS). With these techniques, surface thickness, composition, and impurity identification and depth can be determined.

Among its other analytical equipment (not including the tools discussed in the tour of the hydrogen storage area) are a scanning electron microscope, and an inductive coupled plasma spectrometer. The latter system is used to obtain detailed composition measurements of metal alloys, down to the parts per billion range in cases. The ingot is dissolved in acid, diluted, and subjected to plasma discharge, to obtain emission spectra.

As mentioned above, ECD also has an “information” division, but this area was not toured.

This page intentionally left blank.

Technical Evaluation Report
Project: Photolytic Hydrogen Production
Company: University of Miami, Miami, FL
P.I.: Dr. Homer Hiser
Date of Visit: May 3, 1996
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

On the above date, I met with **Dr. Homer Hiser** of the Remote Sensing Laboratory at the University of Miami to discuss the photolytic hydrogen production project. Dr. Hiser and I spent about three hours discussing the project, during which time he elaborated on his Annual Review presentation and also answered several questions (attached) that I had forwarded to him earlier.

The photovoltaic hydrogen project at the University of Miami is somewhat of a misnomer. In fact, the most recent title used by Dr. Hiser (for his Annual Review presentation) is "Solar Hydrogen Production via Hybrid Collectors" It is indeed only partially a PV project. The goal is to optimize the collection and utilization of both PV and thermal solar energy. The composite energy will ultimately be used to run one or more electrolyzers, at least some of which will be of the high temperature steam variety. High temperature storage of the thermal portion is also a critical consideration. The bulk of the work performed to date is on the solar side: determining the degree of insolation in various parts of the country with differently configured collectors as well as adding solar thermal collection to standard PV collection. Dr. Hiser has not yet begun incorporating high temperature electrolyzer data into his model. This is the next step.

The U Miami team aspires ultimately to model overall pathways for converting solar energy to hydrogen. Three potential scenarios, taken from Dr. Hiser's presentations and papers are shown as Exhibits 1-3. The models will be both engineering- and economic-based, and will be geared for "large-scale" hydrogen production. Some data from the models will also be applicable for assisting the Pakistanis with a demonstration solar hydrogen house. This, of course, will be of much smaller scale. The Pakistanis are currently designing their demonstration facility.

The project's other thrust is in the design of a thermal storage system. Not much consideration has yet been given to the high temperature electrolyzer or the remainder of the hydrogen production system. Dr. Hiser, however, does consider this a hydrogen production program.

Project Strengths:

- It will provide an overall optimized system(s) for utilizing both PV and solar thermal energy, including a high-temperature storage option. Although there is nothing particularly unique in the modeling of the system components, the overall system model will be of value.

- If the tie-in with the Pakistani project can be clarified, it will lend a valuable international flavor to the program.
- It has the potential for leading to a relatively short term purely renewable hydrogen source. The high temperature electrolyzer and thermal storage aspects probably push commercialization out to at least mid-term, however.

Issues that should be Addressed:

- Much of the project is not really focused on hydrogen, but on solar efficiencies and thermal storage. The project could easily be rescoped as a solar/renewables project, with electricity as its end product.
- The key hydrogen tie-in is through high temperature electrolysis, which will be difficult to model with its lack of data. Dr. Hiser plans to talk to the Germans. Perhaps he should also talk to Westinghouse and Brookhaven for some older data, and to Clovis Linkous at FSEC for any tie-in with his high temperature materials.
- The Pakistani connection is not clearly defined.
- There is a plan to incorporate hydrogen storage into the model, but it has not yet been thought out, and does not appear to be an integral part of the project.

II Questions and Answers:

I sent Dr. Hiser a list of questions that we discussed during our meeting.

Tie-in With Pakistani Project:

1. Is the model that you are producing for system efficiency and cost universal or specific to a location(s) in Pakistan?

Dr. Hiser's team is collaborating with the Pakistanis, but does not see the Pakistani project as being strongly connected to the current DOE project. The Pakistani project, being performed by the National Institute of Silicon Technology in Islamabad, is looking to design and build a solar/thermal building that would serve as a demonstration for future village homes in remote areas where there is no centralized power. Hydrogen would be produced and stored as the basic energy supply. The model for hydrogen production for the DOE project is large scale.

Although no numbers were presented, the goal is a hydrogen production resource for merchant hydrogen, refineries, etc.

2. **Does the initial design of the experimental system in Pakistan include electrical storage?**

There is no plan to incorporate thermal storage into the Pakistani project. Right now, at least, they are looking at PV only. They may incorporate battery storage, however, as a means to overcome intermittency.

Information gleaned from the DOE project can be used by the Pakistanis, but Dr. Hiser does not see a direct connection. *In fact, if you look at the U Miami contribution to the AOP, their monthly reports, and their annual review presentation, there is no mention of the Pakistani project. The only mention I have seen in writing on Pakistan is the original NSF proposal, dated 1993.*

There are some similarities and overlaps between the U Miami and Pakistani projects, but if anything they seem to be drawing farther apart, with the incorporation of the thermal collector and storage vessel in the U.S. project.

Thermal (or Electrical) Storage System Sizing:

3. **Is the energy storage subsystem meant to smooth out seasonal as well as daily energy input variations?**

It is of interest that some of the documents connected with this project (from the proposal to NSF in 1993 right up to the contribution to the FY 1996 AOP) indicated a PV-only system with the potential for an "energy" storage system (a generic term, but almost certainly not a thermal storage vessel). My question on smoothing seasonal as well as daily energy input variations was based on the generic system, but fits even better for the thermal storage system. The answer was that they are now allowing for an intermittency smoothing of their model over a weekly period, but there would still be a seasonal bias.

Efficiencies:

4. **What are emerging as controlling functions for insolation variation and then for PV efficiency?**

U Miami's initial analyses were showing that the efficiency of the PV subsystem was indeed a large contributor to overall system efficiency. Now that they have added a thermal component, PV efficiency is less of a factor.

5. **In the calculation for E_s (annual insolation), how does the effect of a concentrator get factored in -- is it just as a change in the effective PV area?**

In the PV mode, the effect of the concentrator is factored into the overall PV efficiency.

6. **With recent emphasis on the concentrator selection -- has the PV subsystem efficiency portion (η_1) been shown to be a major factor in overall conversion efficiency (η_0)**

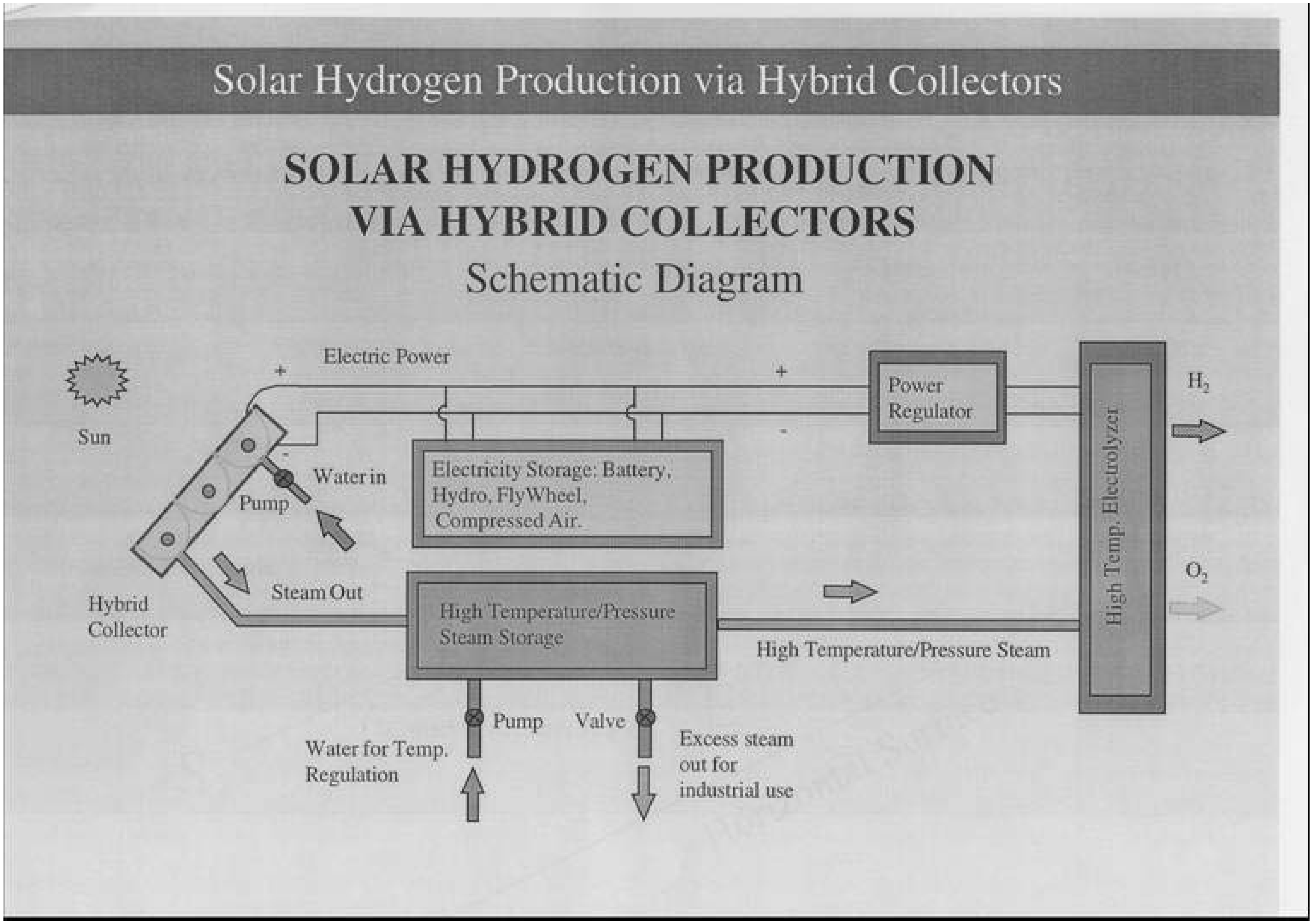
My questions on this issue were based on what I read in U Miami's 1993 NSF proposal. With their initiation of a thermal subsystem, the PV factors become less important. The major new player that is of concern to us is the high temperature electrolyzer, and as we already mentioned, they have not addressed this yet.

III Final Thoughts:

The project is an interesting exercise in optimizing solar thermal and PV processes as well as utilization of thermal storage. The relevance of the project to hydrogen, however, is not that certain. The work is called a hydrogen production project, but its only connection to hydrogen is that the electricity that is produced directly and indirectly from solar energy is used to run one or more electrolyzers. Under some scenarios some or all of the energy goes through a high temperature electrolyzer to make hydrogen.

Dr. Hiser's team is collaborating with the Pakistanis, but does not see the Pakistani project as being part of their effort in the current DOE project. For one thing, the demonstration in Pakistan is small-scale. They will be building a "solar house" and producing hydrogen as a base fuel. According to Dr. Hiser, the DOE project is large scale, with the model for hydrogen production being on the megawatt level.

Exhibit 1. Solar Hydrogen Option 1

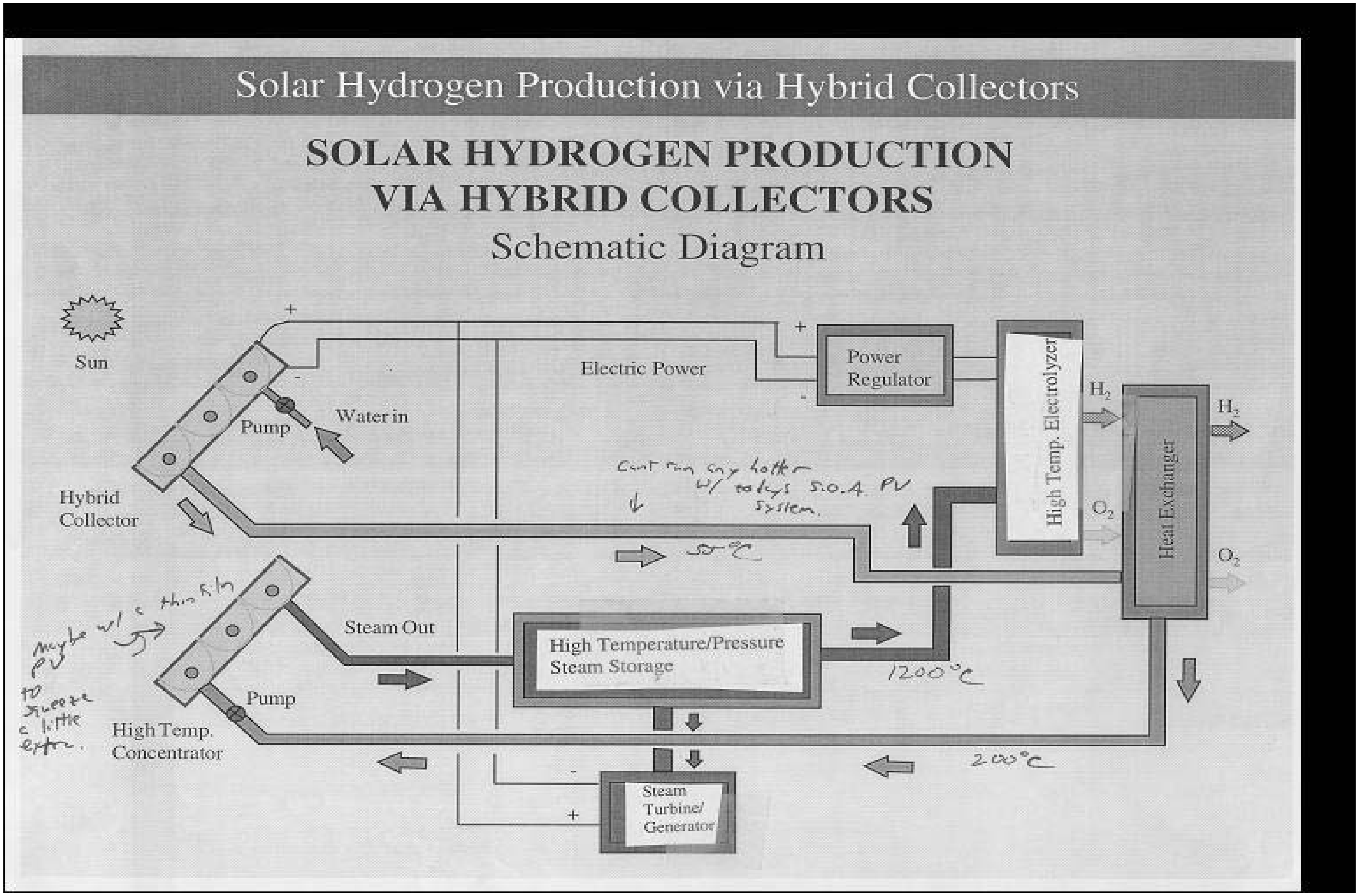


Solar Hydrogen Production via Hybrid Collectors

SOLAR HYDROGEN PRODUCTION
VIA HYBRID COLLECTORS

Schematic Diagram

Exhibit 2. Solar Hydrogen Option 2



Solar Hydrogen Production via Hybrid Collectors

SOLAR HYDROGEN PRODUCTION VIA HYBRID COLLECTORS

Schematic Diagram

Cant run any hotter w/ todays S.O.A. PV system.

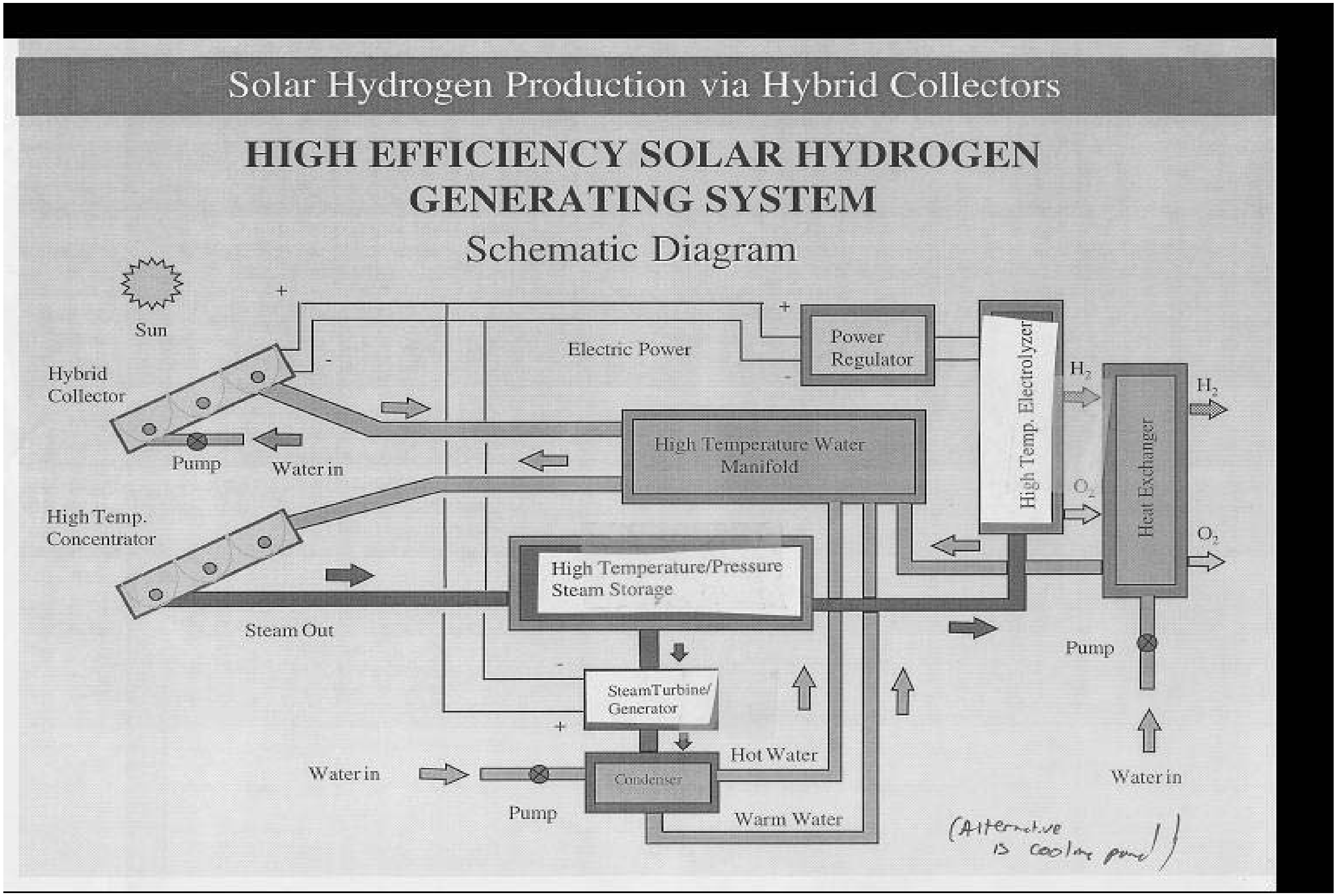
50°C

1200°C

200°C

maybe w/ a thin film PV to squeeze a little extra.

Exhibit 3. Solar Hydrogen Option 3



Solar Hydrogen Production via Hybrid Collectors

HIGH EFFICIENCY SOLAR HYDROGEN GENERATING SYSTEM

Schematic Diagram

(Alternative is cooling pond!)

This page intentionally left blank.

Technical Evaluation Report

Project: Biomass-to-Hydrogen
Company: National Renewable Energy Laboratory (NREL), Golden, CO
P.I.: Dr. Esteban Chornet
Date of Visit: December 22-23, 1998
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

NREL is developing a process in which they are looking to convert biomass waste into hydrogen by means (usually) of a two step process. In the first step, the waste is converted into one or more products by means of a fast pyrolysis reaction. This product, a "pyrolysis oil," can then be separated using water, into an aqueous and non-aqueous fraction. In the second step, the aqueous fraction (or possibly the whole pyrolysis oil) is subjected to steam reforming to produce hydrogen. The potential success of the project is tied heavily to both technical and economic issues, in a fairly complex and feedstock-sensitive manner. An important part of the project is the plan to offset process and feedstock costs by making a salable co-product of the non-aqueous, or pyrolytic lignin, fraction. To date, the co-product of choice has been an adhesive that could take the place of a phenolic resin used to join layers of plywood or particleboard. They are also investigating fuel additives as co-products. The major technical challenges at this time are the charring that occurs during the reforming process, causing fouling of the catalyst, and issues dealing with the robustness of the system to differing feedstock.

Exhibit 1 shows a schematic of the overall fast pyrolysis/reforming process.

Project Strengths:

The major strengths (and potential weaknesses) of the project all lie in the robustness of the concept and the systems. The project has been thought out in much detail, and is strong in chemistry, engineering and economic analysis. The researchers have a mind toward multiple products, usage of multiple waste materials, and both niche and large markets. The project has a real conservation, "use everything" ring to it. Even the char that is formed during the fast pyrolysis step is combusted to provide heat for the reactor.

One key strength may be the concept of being able to transport liquid, pumpable, pyrolysis oils, the intermediate product, rather than biomass or hydrogen. This is likely the least expensive way to go, lacking a hydrogen infrastructure.

Unlike some other projects, this one is approaching the coking problem during the second step, in what I believe to be the correct manner – a fluid-bed catalyst system.

Issues that should be Addressed:

A potential drawback is that there is so much going on, so many potential feeds, products, and co-products, that it would be easy to lose sight of the fact that this is a hydrogen project. There are many scenarios under which this project can become a real winner: inexpensive or free feedstock to the pyrolysis system, co-products that will reduce the cost of hydrogen to a competitive level, inexpensive or free feeds to the reformer system, small localized pyrolysis reactors, etc. All of these scenarios, however, have a sub-scenario where hydrogen production becomes unneeded or unwanted. I do not believe that this is happening, but it is something for which we should keep our eyes open. For instance, a focus on a lucrative pyrolysis co-product could lead to the wrong optimization parameters for hydrogen. In another example, the scenario discussed below in which the aqueous fraction or the whole oil is reformed at a refinery in conjunction with natural gas or naphtha does not lead to hydrogen as an energy carrier.

In all, (the potential for the project to veer to a non-Program goal aside) this is, in my opinion, one of the strongest projects in the Program, with the greatest potential for inexpensive, renewable hydrogen.

II Introduction and Background:

On the above dates, I visited **Dr. Esteban Chornet** and **Dr. Stefan Czernik** at their laboratory in the Field Test Laboratory Building (FTLB) at NREL. On the afternoon of December 22, Dr. Czernik gave me a tour of the fast pyrolysis and reformer facilities. Dr. Czernik and I also spent some time with **Maggie Mann**, discussing the life-cycle aspects of some of my questions. On the morning of December 23, I met with both Dr. Chornet and Dr. Czernik, and we discussed the project in detail. I had previously sent Dr. Chornet a list of questions to be discussed during our meeting, and these formed the basis for much of our discussion.

The NREL project by which fast pyrolysis is used to turn biomass into materials that can be processed has been around in one form or another since the early ‘80s. The goal was to make liquid hydrocarbons. This particular project, to make hydrogen, started in 1994.

The objective of this project is to use fast pyrolysis as a means to convert various biomass waste materials into handleable oils (as opposed to tars) and to reform some of these oils into hydrogen. In order to help offset the cost of hydrogen, other pyrolysis products are tailored to be sold in other markets.

III Tour:

Dr. Czernik walked me through the entire pyrolysis/reforming setup. The fast pyrolysis system occupies much of a large multi-leveled laboratory [I would really call it a Process Development Unit (PDU)] within the FTLB. It is a multifunctional system, used for some gasification studies (with a different reactor) as well as the present work. The fixed- and fluid-bed reforming systems are located in an area on the upper level of the laboratory. These systems are considerably smaller.

Fast Pyrolysis Process:

The fast pyrolysis reaction occurs by means of an ablative process in a vortex reactor. The cylindrical, stainless steel reactor is 26 cm in diameter, and is capable of a heating rate of about 2000^{o}C/sec. The feedstock, generally 2-5 mm in diameter, is dry, but possibly containing up to about 10% moisture, is introduced tangentially. Either steam or nitrogen is used as the carrier gas, which is preheated. The residence time for one pass through the reactor is about 0.5-0.8 seconds. The temperature at the reactor walls is nominally 650^{o}C, while the gases in the center are about 500^{o}C. The particles do not totally react with one pass-through but are recycled some 10-20 times through the reactor. Unreacted particles are separated from product gases by centrifugal force for recycling. Byproduct char will eventually fall out of the reactor along with the product gases. The products contain about 10-15% by weight char (note that it is a char and not a pure carbon), which is then separated from the product using two cyclones and a baghouse, the latter for small (< 5 micron particles). The baghouse is held at 400-420^{o}C. This provides for a balance between purity and yield; at a higher temperature, they would get a lower yield. As it is, they probably lose about 10% of product for the sake of purity. The pyrolysis system can operate in this manner for about 9-10 hours before the baghouse becomes clogged, if periodic back-flushes are used to clean the flexible ceramic or sintered baghouse filter.

The product gases then go to a condensation train. Two scrubbers and coalescing filters are used to collect the product. Scrubbing is a difficult process, probably due to the aerosol nature of the product.

The overall pyrolysis system can also be run in a gasification mode. In that case, a second Inconel reactor is used, and the reactor temperature is nominally 800^{o}C. This is not part of the current project, but shows the versatility of the system.

Reforming Process:

The feed for the reformer can be either the aqueous fraction of the pyrolysis product, or the entire pyrolysis oil. Alternately, the group is looking at feeds from other sources – primarily waste streams that would provide an economic benefit.
The initial reformer reactor for this project (still set up) utilized a fixed-bed configuration. The reactor used generally standard nickel catalysts in packed tubes. Superheated steam (600^{o}C) and the biomass feed was introduced co-currently. The furnace area itself was three-zoned; the top (inlet) zone had a temperature of no less than 600^{o}C, the middle zone 750^{o}C, and the bottom zone 700^{o}C, but the temperatures could be varied. Shifting as well as reforming took place in the reactor, but the system was not efficient for converting all the CO to CO_2.

The fixed-bed reactor worked well for model compounds, but was less successful for actual pyrolysis oils. When the oils were vaporized (to allow better contact with the catalyst bed) to feed into the reactor, they tended to form a char material especially in the pre-catalyst portion of the tube furnace, where it would clog the reactor. The char could be removed by reaction with CO, but the regeneration cycle was unacceptably long. Feeding the pyrolysis oil as a fine mist reduced the charring problem, but made the oil/catalyst contact less efficient.

The group therefore has recently moved to a fluid-bed reactor. Again, there is a three-zone furnace around the Inconel reactor, but the catalyst particles have to be ground (300-500 microns) in order to be mobile. Superheated steam is used as the fluidizing gas. The reactor can be operated up to 800^{o}C. The feed is sprayed into the fluid bed in liquid form through a 0.2 mm nozzle immersed in the bed. The system products are hydrogen, CO, CO_2, and a few ppm of methane. As the catalyst deactivates, methane concentration increases to, perhaps, 0.01%. The system is all computer-monitored, and the product gas is analyzed every five minutes. One problem with the current configuration is that some of the catalyst fines winds up in the steam condensate system.

Presently, about 90% of the carbon goes to product, with the remainder ending up as coke on the catalyst. Overall, a 95% mass balance closure is being achieved.

IV Initial Discussion:

The success of the project on a large scale is tied to the diversity of feedstocks that can be used and the cost to acquire and use these feedstocks. To date, much of the work has involved either model compounds or poplar. Currently, the group is beginning to investigate peanut shells (from a collaborator in Georgia, consisting of a municipality and a utility), southern pine, and bagasse (sugar cane stems), as inexpensive – or free – feedstock. They have estimated that the cost of hydrogen from feedstock such as these, with the assumption that the feedstock is free, is \$7-12 /GJ hydrogen. This does not include any revenue that might be generated from a co-product. They want to be more than niche market suppliers.

The co-product is made by the addition of water. (A higher quality material can be made by using ethyl acetate extraction rather than water, but this would be more expensive). This creates an aqueous fraction, which is reformed to make hydrogen, and a non-aqueous fraction that can be tailored to be a substitute for a phenolic adhesive that is used to bind plywood or particle board. If this adhesive material is mixed 50/50 with a real phenolic adhesive, there is no decrease in physical properties for bonding plywood or particleboard. No long term repeatability or aging data is available yet. Maggie Mann estimates that this "biophenol" would cost about half as much as phenol. This would lower the net cost of hydrogen to about \$5/GJ. There is one major drawback to this product, however. According to the researchers, people who use it complain about the smell; therefore, industry has lost interest (perhaps only temporarily) in this material. This is part of the reason that the Chornet group is also looking at alternative products –

primarily fuel additives that will boost the octane rating. The group is also receiving funding from the Ethanol Program to investigate this type of gasoline additive.

A strategy being investigated would be to locate the fast pyrolysis system at the feedstock site, and then transport the pyrolysis oil. The reforming step would be performed at either the hydrogen use site, or where a hydrogen infrastructure existed. This would be a less expensive alternative to having to transport either biomass feedstock or hydrogen – at least without a hydrogen infrastructure. Dr. Czernik pointed out that this type of strategy is not an option for a biomass gasification project where either feedstock or hydrogen would have to be shipped.

Dr. Chornet envisions a scenario where fast pyrolysis could be performed in a local region, like, for instance, an agricultural community. Such a community could buy a fast pyrolysis system to process their communal agricultural waste, and sell the pyrolysis oils.

Fast pyrolysis is a low-dollar investment technology. If you have a co-product, the cost decreases even more. If you team with a refinery to reform the aqueous fraction, the infrastructure already exists.

The Chornet group is expecting to announce an agreement on fast pyrolysis of peanut shells with the aforementioned Georgia group, sometime within the next few months. Since Georgia also has a plywood industry, this may be an especially good match. At this point, however, no names are being disclosed.

Although the vortex reactor works well at the size (PDU?) being used at NREL, it may not scale well. A circulating or bubbling fluid bed may be needed for commercial fast pyrolysis units.

Another issue is the effect of the biomass on the nickel catalyst. Since the biomass material contains considerable oxygen, it can attack the nickel catalyst, forming nickel oxide. Dr. Chornet's group is trying to work with ICI and with United Catalysts to develop a new catalyst that would be more suited to the oxygen-containing biomass.

V Questions and Answers:

A major part of our discussion centered on the questions that I had sent to Dr. Chornet prior to our meeting.

1. **Have there been any attempts at non-oxidative methods of removing coke materials after fast pyrolysis, and thus reduce/eliminate CO_2 emissions during this step? Alternately, have there been any attempts to alter the system configuration to limit coking of the catalyst in the first place?**

The fast pyrolysis process does not produce a coke; it produces a char. This is considerably more oxygenated than coke. There is no attempt to remove the char at all during fast pyrolysis. It is an integral part of the balanced system. The char is burned to provide some of the heat for the pyrolysis process. In fact, the process is tailored to produce the right amount of char.

2. How are the biomass feedstocks to the pyrolysis process prepared for handling?

You need a fairly dry material as a feed; you don't want to use the fast pyrolysis system as a drier. Ideally, the feed will be 10-15% water. You could use char combustion as a means of drying the feedstock. You would have to balance the need of drying with the need of char combustion to provide heat for the fast pyrolysis. Alternately, an agricultural commercial drier could be used. The feedstock is then ground or milled. In the case of lightweight materials, such as peanut shells, it may be advantageous to pelletize the particles as well. You generally want about 2 mm particles.

3. What is the chemical composition of the coke that is evolved during the pyrolysis and reforming process? Is it close to pure carbon for any natural feedstocks?

The fast pyrolysis char contains 15-20% oxygen, 1-2% hydrogen, about 10% "ash", and the rest carbon. Dr. Chornet indicated that some of the ash might be amorphous silica, which may be salable to the semiconductor or tire industries.

The material formed during reforming, is indeed coke. It is nearly all carbon, and creates a problem for the catalyst.

4. Are the pyrolysis oils generally handleable and pumpable at room temperature, or do they have to be heated?

The oils have viscosities of about 50-100 cps at room temperature; the pour point is below the freezing point of water. The pyrolysis oils are pumpable and easily handleable.

5. How does the reforming process compare to conventional (refinery-based) steam methane reforming or catalytic naphtha reforming? What reforming temperatures are used? Do the processes involve conventional shift and purification steps?

The process is very similar to conventional reforming methods. In fact, one concept was that the process could actually be performed in the refinery one day, perhaps co-reforming the pyrolysis oil with natural gas or naphtha. The group's goals include compatibility with present industry and infrastructure.

Here is one example of where the project's goals could be incompatible with that of the Hydrogen Program.

6. You showed a Figure in your 1998 annual review paper that indicated that the aqueous bio-oil fraction is either directly steam reformed, or goes through a "thermal depolymerization and/or stabilization" step prior to steam reforming. What is the advantage of the additional step?

The pulp and paper industry has a refuse stream that is similar to the aqueous fraction of pyrolysis oils, and may be a good candidate for reforming. However, it is quite polymeric. The reformer handles monomers easier than polymers. Thus, the thermal depolymerization may be needed to utilize this type of material. The aqueous fraction of the "standard" pyrolysis oil produced by fast pyrolysis has little polymeric content.

7. During the reforming process, how does coking vary with the different partial or whole oil feedstocks?

If there is no aqueous separation step, meaning that the whole oil is reformed, there is a higher tendency to coke. This is due to the higher oligomeric content of the whole oil. The hemicellulose (non-aqueous) fraction is highly oligomeric.

The need to remove coke from the reforming system was recognized as a problem early in the project. One of the first things that was done was to demonstrate the ability to regenerate the catalyst by removing coke with steam or CO.

This is admittedly a tedious process, and should not be the final answer. It does appear that it will be the final answer, as the rate of catalyst contamination should decrease dramatically with the use of the fluid-bed catalyst system.

8. Have there been any attempts to tailor a process for minimal CO_2 emissions (resulting in net negative CO_2 when including the growing of the biomass)?

In order to best consider CO_2 emissions, one must look at the entire life of the carbon materials – a life cycle analysis (LCA). The net CO_2 emissions are near zero. The only time that the net CO_2 becomes negative is when the carbon can be tied up in a non-combustion mode. For instance, if a co-product is made from the fast pyrolysis process, and that product is the adhesive material, the carbon is tied up. This scenario would result in a net-negative CO_2. If the co-product is a fuel additive, the carbon is soon combusted. The only other source of non CO_2 carbon as determined by LCA is what is sequestered in the soil during the biomass growing period.

Basically, the amount of overall CO_2 emissions is not sensitive to starting material.

9. What are the net overall CO2 emissions in the "standard" pyrolysis/reforming process?

As stated above, negative net CO_2 emissions are realized if the co-product is used in a non-combustion mode. Barring this, the net result is a slight positive CO_2 emission.

The reformer system in a commercial process would use pressure swing adsorption (PSA) to separate the hydrogen and concentrate the CO_2. As with any other system, concentrated CO_2 is superior to combustion-formed diffuse CO_2 for sequestration or for possible use. [Dr. Chornet also mentioned the potential to use CO_2 with ammonia to make urea for fertilizer. Urea is $(NH_2)_2CO$.]

The low net CO_2 emissions is a strong positive attribute of the process.

10. Are there any results yet available for the reforming of whole pyrolysis oils with a fluidized bed configuration?

There are now some recent results. Charts are attached for a reforming run that was performed on a whole bio-oil using a steam to carbon (S/C) molar ratio of 1.6. The hydrogen yield compared to the stoichiometric yield (Exhibit 2), and overall gas composition (Exhibit 3) are shown. Hydrogen yield can be seen to be dropping off from a maximum of a little under 80% after about one hour. In this case, regeneration of the catalyst was not included. About 10% coke was obtained, and the drop-off was attributed to this. In addition, the S/C is not ideal; it should be higher – perhaps 3 to 5. Dr. Chornet believes that under these conditions, the drop off should not occur until, say, 50 hours.

As a first run, the results are not bad, although I am not sure as to why they used such a low S/C to begin with. I'll be interested to see what they get when they improve the ratio.

11. How do the costs of using purchased pyrolysis oils compare with those of pyrolyzing biomass, and using these oils?

When doing an economic analysis on a "bought oil", Maggie Mann uses a price of \$80/ton. Information that Dr. Chornet received from a Canadian company indicates that pyrolysis oil will be available for something between \$70 and \$200/ton, but the product is not yet marketable.

The assumed cost for a dry feedstock is \$40/ton. At an energy density of 16 GJ/ton, this works out to \$2.50/GJ – about the same as natural gas. Even if the feedstock is free, you have to transport it – maybe \$20/ton. That is why the co-product concept is important, as is the need for an environmental driver.

This shows why the concept of localized fast pyrolysis and shipment of a liquid intermediate is attractive.

12. Have you looked at all at the feasibility of using waste biomass as a feedstock?

Sludges are not good feedstocks for this kind of process. They generally contain too much moisture (75-80%) and are too expensive to dry, unless a special case exists where waste heat can be used. Forest wastes (i.e., sawdust, etc.) containing 50-60% water may be able to be dried economically.

Exhibit 1 Hydrogen from Biomass Schematic

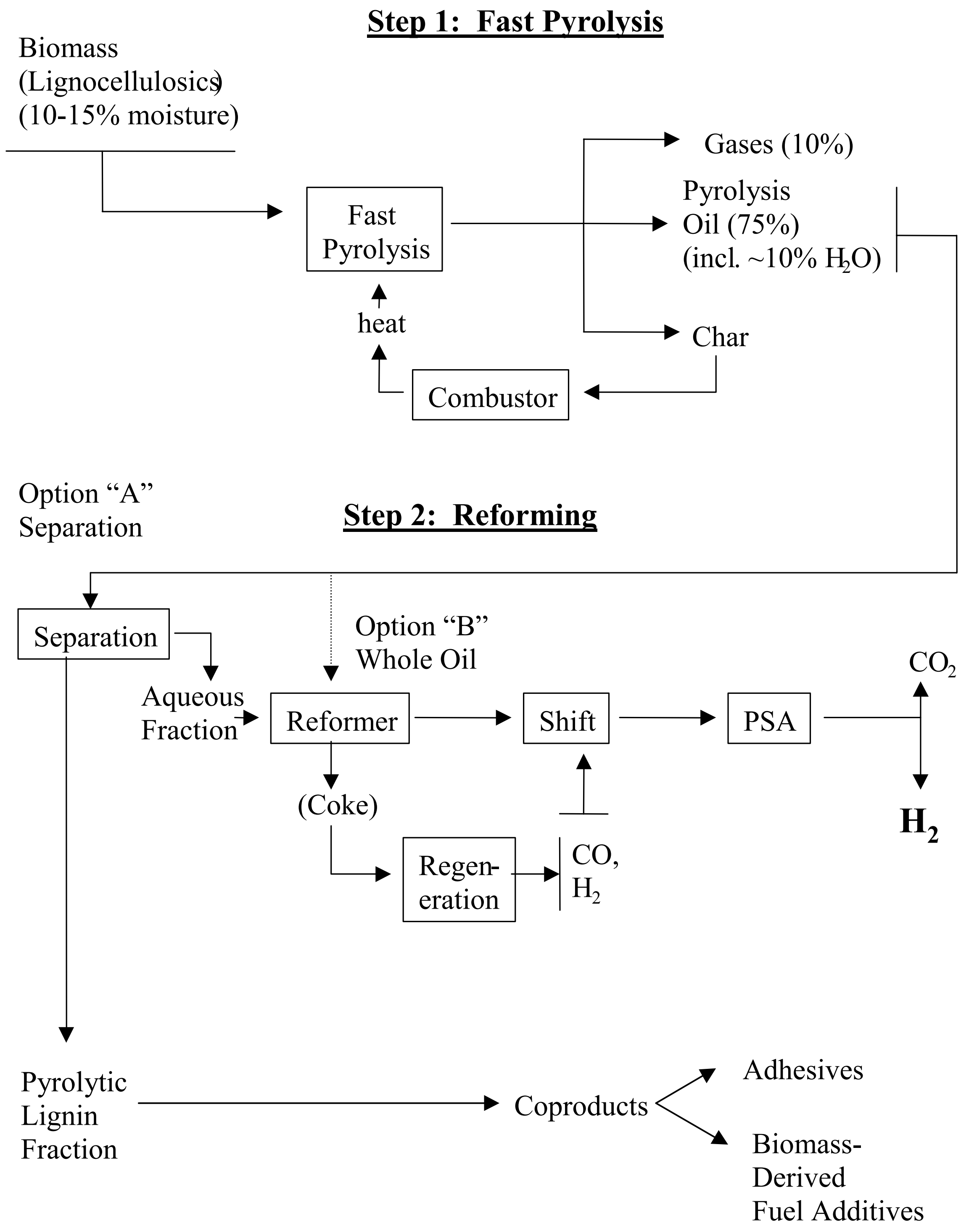


Exhibit 2. Hydrogen Yield from Bio-oil Reforming

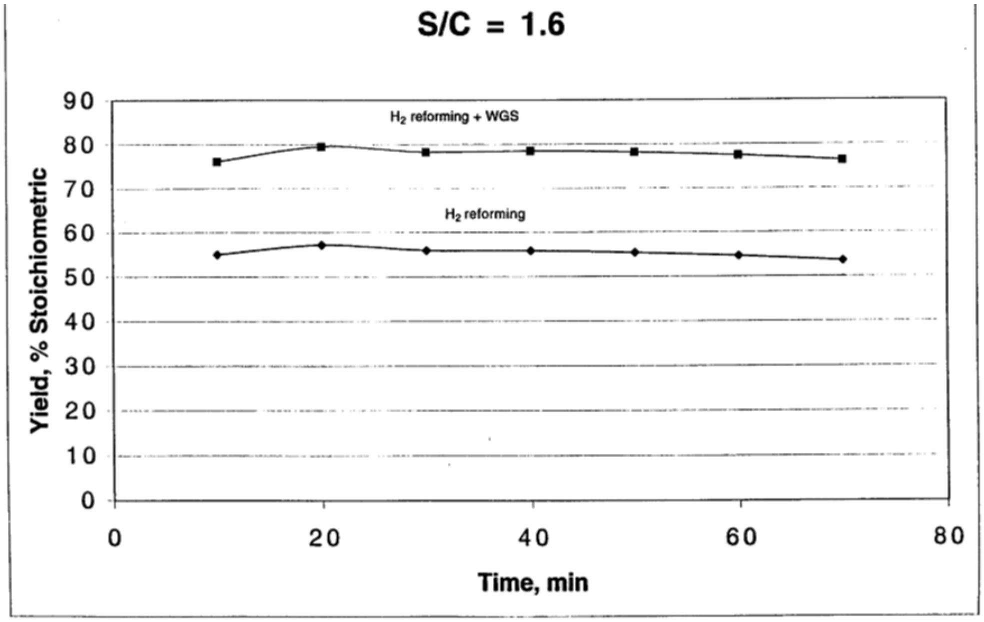
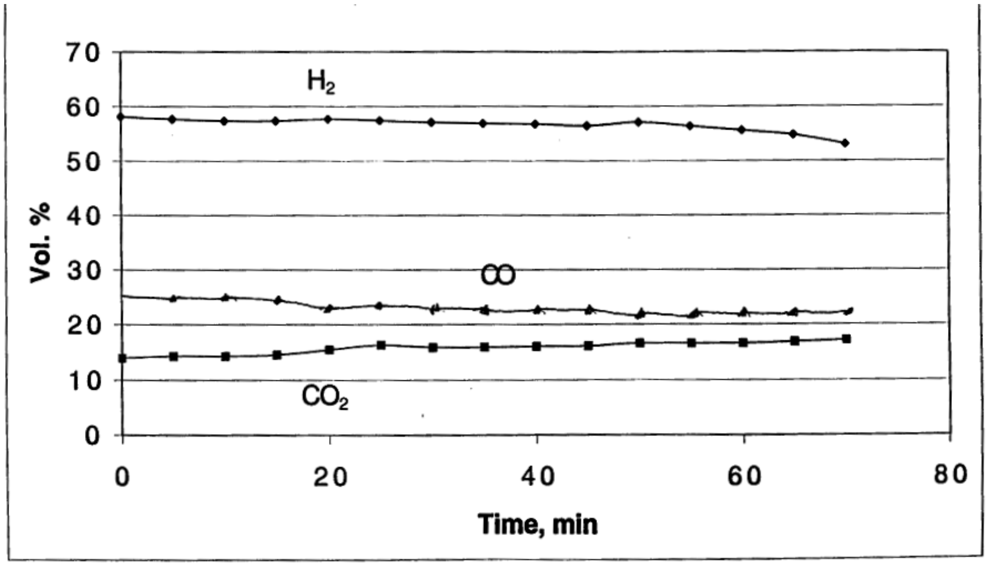


Exhibit 3. Overall Gas Composition from Bio-oil Reforming



Technical Evaluation Report

Project: Membrane Separation Technology
Company: Savannah River Technology Center, Aiken, SC
P.I.: Dr. Myung Lee
Date of Visit: March 23, 1999.
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

The membrane separation project being carried out at the Savannah River Technology Center (SRTC) is headed by **Dr. Myung Lee**. The project basically involves the development of a sol-gel processed glass that has a tailored porosity that will selectively pass hydrogen. The material, applied by a dipping and drying process, appears as a two-micron thick coating either on a porous inert substrate such as Vycore, or on a reactive metal hydride. The fact that two quite different systems (with very different separation mechanisms) are being studied with the two different substrates is not extremely clear from Dr. Lee's various reports and submittals. Regardless of the substrate, however, the properties of the coating have been the focus of much of the project to date. The goal is a coating with a very narrow pore-size distribution, with an average measurable pore diameter of about 40 Angstroms.

Over the past couple of years, Dr. Lee and his group have examined sol-gel materials, mixing methods, and drying times and temperatures in order to optimize coating properties. They have demonstrated that they can selectively collect hydrogen through the membrane, and have measured some take-up rates as a function of pressure.

What has not been done yet is to create a robust system that can be recycled repeatedly – except if a metal hydride substrate is used (more on this later.) They do not yet have hydrogen collection efficiencies and purities measured as a function of their input parameters. Consequently, they do not have material and energy balances for their system(s), nor are there any rough cost estimates available.

Project Strengths:

- The addition of membrane separation technology to the portfolio of available hydrogen technologies is important in that it provides the potential for less expensive and more efficient recovery of high purity hydrogen compared to pressure swing adsorption. It specifically provides a better system for removal of CO from hydrogen, decreasing the likelihood of fuel cell catalyst poisoning. Although a few years ago, several laboratories were slated to begin R&D on various metal or ceramic membranes for hydrogen separation, all but the SRTC project was cancelled. The Hydrogen Program currently funds only the SRTC project as a separation technique.

- The concept and methodology of this project is credible, once one can dig down and determine what it actually is.

Issues that should be Addressed:

- The amount of progress made so far is not great. The accumulated data to date is heavily weighed toward pore size distribution. There is little in the way of hydrogen take-up data, and nothing in the way of hydrogen purity and recovery percentage.

- This project should begin to generate "practical" data. Their metal hydride system is ready for this now. (They have built a bench-scale reactor that has the versatility to provide rate, purity, and efficiency data for both types of membranes.)

- Getting 1 or 2 more membrane projects in the portfolio would be beneficial.

II Introduction and Background:

I visited Dr. Myung Lee at SRTC to discuss his project involving the development of membrane systems that selectively filter hydrogen. His project is one of several under the SRTC hydrogen umbrella, which is more or less spearheaded by the SRTC tritium work, mostly funded by DOD. Among the DOE/EE funded projects, Dr. Lee lists only his own project and the Westinghouse Bus Project.

III Tour:

I was given a tour of the three laboratories in which Dr. Lee prepares his membranes, dries them, and tests them for hydrogen permeability.

The key element of Dr. Lee's membrane is a polymeric ringed silica material having alternating silicon and oxygen atoms, with the average ring containing 6-7 silicon atoms. In a typical mix, Dr. Lee combines a solution of tetraethylorthosilicate (TEOS) in ethanol with a separate water-ethanol mixture that has been adjusted to a pH of 1.6 by hydrochloric acid addition. The proton provided by the acid prevents premature agglomeration of the polymer.

As the mixture just begins to form a gel, the substrate is dipped into it and allowed to partially dry about four times. This results in a two micron-thick coating. The coating is allowed to dry under ambient conditions for about two days, and then subjected to oven drying at various temperatures. Dr. Lee stated the drying temperature as being 200-600°C. The ambient, slow dry tends to narrow the pore size distribution, while the high temperature finish removes the large pore size "tail" from the distribution. The finishing temperature range is very wide. I was not able to get a good answer from Dr. Lee as to why this range has not been narrowed as yet. Recently, Dr. Lee has recently begun testing the effect of microwave drying as opposed to oven drying. No conclusions have yet been made from this – it's very new.

There are two different systems being developed here. The sol-gel material is coated on the substrate. The first involves a passive substrate such as Vycore (a porous silica-glass), or a stainless steel frit. In this case, hydrogen would pass through the sol-gel and the substrate to a collection point, while other gases would not pass through the sol-gel coating and be pumped away. The second case involves a metal hydride substrate such as LaNi (V), the current material of choice. Here, again the hydrogen selectively passes the sol-gel coating, but it reacts with the substrate forming a metal hydride. Other gases do not pass through the coating and are pumped away. The hydrogen is later recovered by a pressure/temperature operation. SRTC is currently using the composite metal $LaNi_{4.7}Al_{0.3}$ because it "is available". It will typically store about one percent by weight hydrogen. Dr. Lee offered that the identity of the metal could be changed if desired, to accommodate some of the higher temperature, higher storage capacity hydrides.

One advantage of the metal hydride substrate is its self-sealing ability. If a defect (i.e., large pore) occurs in the sol-gel coating at a particular site, allowing CO passage. The reaction of the CO with the metal poisons and seals that site. Thus, the coating localizes and minimizes metal hydride contamination. Dr. Lee states that mixtures with as much as 10% CO have been used without contaminating the hydride. In addition, the coating extends the cycling life of the membrane, preventing breakdown due to contamination. On the other hand, a large pore defect (i.e., hole) present with a passive substrate renders the membrane ineffective.

Dr. Lee has built a bench scale reactor system that will handle both the passive (Vycore) and active (metal hydride) substrate systems. He provided me with a schematic of the system, a copy of which is attached as Exhibit 2.

There is nothing special or unique about the reactor design. It appears to be a reasonable system with with which to gather hydrogen separation effectiveness and efficiencies. Hopefully, SRTC will start to collect meaningful hydrogen data.

IV Questions and Answers:

Prior to my visit, I sent Dr. Lee a series of discussion questions. These questions and answers are included in the general discussion below, in the appropriate section.

1. What is the desired pore size distribution? How do pore size results vary with temperature?

One cannot measure pore sizes any smaller than about 15 Angstroms, while hydrogen separates from other small gas molecules (e.g., CO) at about 3-4 Angstroms. Dr. Lee believes that the pores have "bottlenecks" within their structure. Measurable 20 Angstrom pores, he believes will contain the 3-4 Angstrom bottlenecks through which hydrogen will pass, but CO will not. *This is somewhat roundabout, and not conclusive in itself, but Dr. Lee has shown correlations between 20-Angstrom average pore size and selective hydrogen take-up.*

Dr. Lee believes that pore size distribution should be narrow. This can generally be accomplished by a slow room temperature dry, followed by the 200-600°C bake.

2. **How is the pore size measured? How reproducible is the pore size distribution?**

Pore sizes in the gel are measured using the B.E.T. (Bruner, Emmett, Teller) adsorption method. Dr. Lee has much data showing pore size as a function of mixture parameters. Data show very good reproducibility for a given mix.

3. **Does the evaporation process effect pore size?**

Yes, as does the drying time and temperature. Exhibit 1 shows the effect of drying temperature on pore size distribution.

4. **How is the thin layer thickness controlled? How uniform is it? How reproducible is it?**

Thickness is controlled by the number of times the substrate is dipped in the gelling material. Four dips produce a two-micron coating. Uniformity is often a function of the uniformity of the substrate. *In other words, uniformity and reproducibility is somewhat limited. The correlation between performance and thickness properties is unknown.*

5. **Metal hydrides are generally a long term storage medium for hydrogen. What is the role they will play in the separation process? If they are actually capturing hydrogen, it seems that a complex temperature/pressure cycle would be needed to keep the purification going on a continuous basis. – or is it a batch process?**

The use of a passive (e.g., Vycore) substrate would result in a continuous process mode, while the metal hydride process is by nature a batch process. For the latter, Dr. Lee envisions having two membrane systems, one collecting hydrogen in the metal hydride while the other recovers the hydrogen, thus creating a pseudo-continuous process.

The fact that there are two far different types of substrates and two quite different processes is something that should have been revealed long ago. It's probably a communication fault.

Currently, typical runs using the Vycore substrate involves putting hydrogen into a calibrated volume at a fixed pressure and then exposing it to the inside of a Vycore tube which has a sol-gel outer coating. The tube is simply set in a hood and the hydrogen is allowed to pass through the tube walls and vent through the hood. Rate of hydrogen take-up is measured by monitoring the pressure decrease in the calibrated volume.

For the metal hydride substrate, the hydrogen is generally pulled into the metal by a vacuum. Hydrogen can later be reclaimed by heating the system; the hydrogen recovery pressure is a function of temperature at the time of release.

6. **Are there any data showing selectivity of the filter to hydrogen? What concentration of CO passes through the filter?**

Dr. Lee states that with the metal hydride system, no CO passes through the sol gel coating, and if an imperfection exists, the flaw is quickly sealed, as stated above. A perfect Vycore system is also impervious to CO. However, this system appears to be much lest robust. (See next question).

Other than one piece of data that showed that with the best sol-gel (noted as "Mix E" by Dr. Lee), a 90/10 H_2/CO mixture had a "100% hydrogen capacity" no selectivity data is given. In addition, Dr. Lee shows concern that if hydrogen sulfide is present, it may corrupt the system.

I think we can say that no real separation efficiency/effectiveness data exist.

7. Do any recycling data exist? Does any degradation of the system occur?

Dr. Lee's group has recycled the metal hydride system through "hundreds of cycles" with out any apparent degradation of the system. No long term aging data are available, however. The Vycore system is not nearly as robust. After exposure to hydrogen, many membranes begin to grow cracks. Dr. Lee believes that the cracks are forming in the substrate and then propagating into the coating as well. He also thought that moisture might be involved in the process. At any rate, this is a serious problem for the non-metal hydride system, and is one that Dr. Lee is currently concentrating on solving. The Vycore type system is expected to be a much lower cost system than would be the metal hydride system. One thing that Dr. Lee is considering is the use of an alumina substrate instead of Vycore. It is obviously a serious problem.

Although, cracking is a serious problem, hopefully not a great effort will be spent on trying to solve it if this means putting off getting the efficiency/effectiveness data. These data can and should be obtained for the metal hydride system now. They can also work with the Vycore system, getting the data on the first cycle or two, prior to cracking. The material is not expensive, at least at the small scale, and a large number of membranes could be made for this purpose. We need to see if the system is worthwhile to begin with, before we try to fix the cracking problem.

8. In the written report for the 1998 Annual Review, a Figure is presented as indicating flow rate for hydrogen as a function of feed pressure. How does purity compare with the Pd/Ag membrane? What is the hydrogen regeneration rate?

No measures for purity comparisons or hydrogen regeneration rate are available.

9. What is the identity and concentration of metal hydride in the ceramic membrane? How is it dispersed?

My question presents a good example of the communication problem. Dr. Lee's reports are not clear on the two systems. It appeared from some of his writing that metal hydride particles were dispersed throughout a sol-gel ceramic matrix. As is obvious now, the metal hydride is a substrate in one of two basic membrane configurations. SRTC has submitted a patent application on the coated metal hydride design.

10. What temperature range do you anticipate using to run the filtration process?

It depends on the process. You could use the membrane on a reformer output, running at 400-500°C, or you could run at room temperature. With a metal hydride system, you could run at room temperature to collect the hydride (remember this is a LaNi system) and then use heat off the reformer to later recover the hydrogen at a high pressure.

11. Your contribution to the 1999 Annual Operating Plan (AOP) shows that you plan to construct a "large filter". How large? Is it expected that most of the membrane material issues will be settled prior to construction?

SRTC has used 1 cm^2 and 20 cm^2 filters for their tests. For scaling up to the "large" filter, they will just use several of the 20 cm^2 filters. Membrane issues have not been settled for the Vycore system, and will be addressed in parallel.

This is obviously not a production scale filter about which SRTC is talking. It is to be used in the bench scale reactor. Hopefully, good metal hydride membrane data will be developed now, and Vycore membrane data will follow soon thereafter.

12. The AOP also shows a rather ambitious schedule involving the construction and testing of a reactor. What size is this expected to be? Is its construction on schedule?

The reactor in question, is of course, the bench scale system that we have already discussed. It has already been built and vacuum-tested.

13. Do any projected mass/heat balances and system costs exist?

Not yet. They have to get the data first.

VI Additional Discussion:

Dr. Lee has found that if he takes two metal hydride substrates, coats only one of them, and exposes both of them to hydrogen, the coated substrate will adsorb twice as much hydrogen as the uncoated one. (About 2% by weight as opposed to 1%.) The take-up rates are not affected by the coating. Dr. Lee does not understand what is actually occurring here, but thinks that some hydrogen might actually become trapped within the sol-gel coating itself.

Dr. Lee believes that the membrane would be "much less expensive" than pressure swing adsorption (PSA) if the single step (Vycore) membrane is used. If the metal hydride system is used, and a heat source exists off which the membrane could tap, the system would also be cheaper than PSA. If no "piggyback" source exists, the cost would be about equivalent to PSA. *I do not believe that these statements are based on any real calculations, and are just rough estimates.*

The cost and simplicity of system are the reasons that SRTC is pushing for the single-step membrane. – But they will have to solve the cracking problem.

Dr. Lee is expecting a group from Mississippi Chemical Company to visit his laboratory in the near future. They make ammonia, and are apparently very interested in the SRTC process. *Dr. Lee is quite excited about this prospect, as it represents the first industrial interest in his project.*

Exhibit 1. Effect of Drying Temperature on Pore Size Distribution

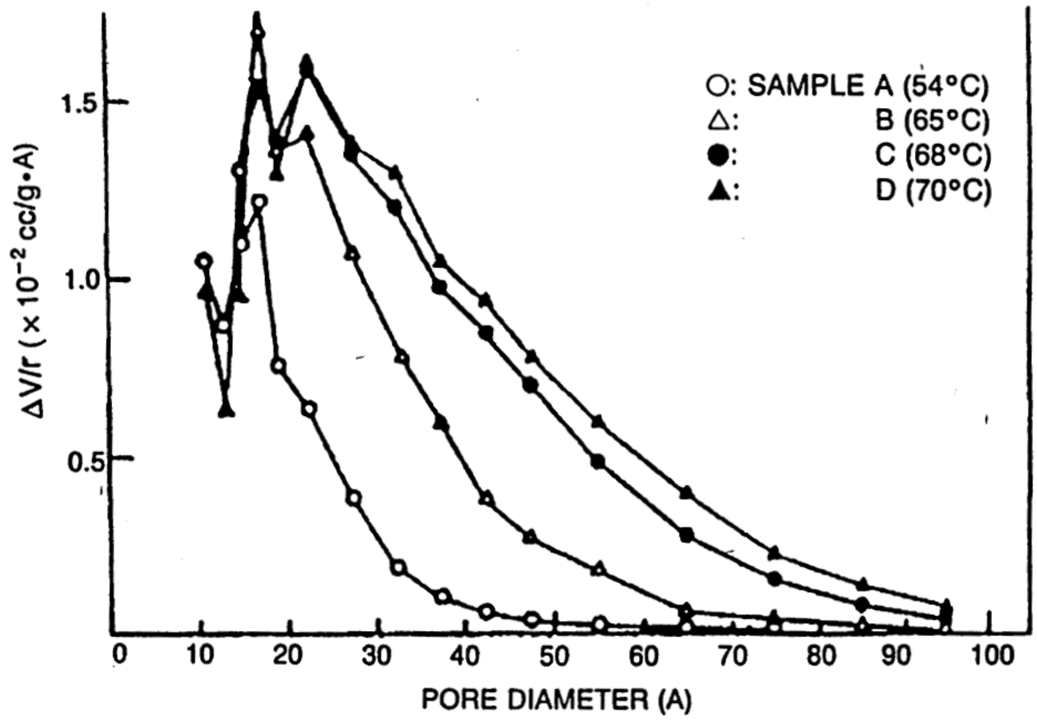
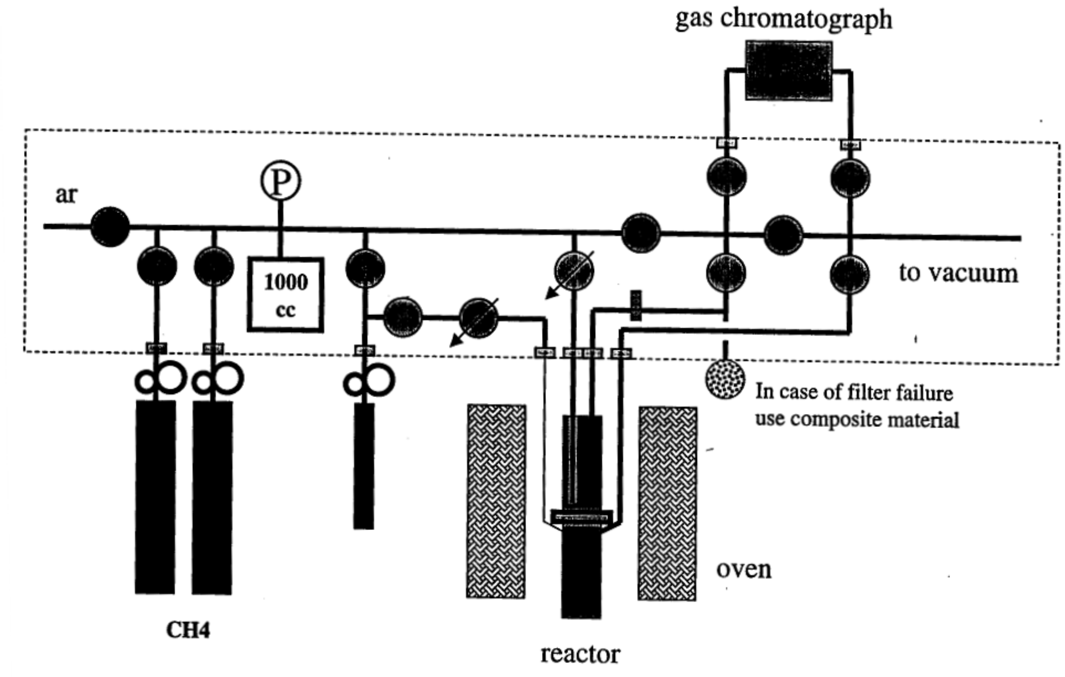


Exhibit 2. Bench Scale Reactor System



This page intentionally left blank.

Technical Evaluation Report
Project: Photosynthetic Water Splitting
Company: Oak Ridge National Laboratory, Oak Ridge, TN
P.I.: Dr. Elias Greenbaum
Date of Visit: March 30, 1999
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

At the 1998 Hydrogen Program Peer Review, the Photosynthetic Water Splitting project being headed by **Dr. Elias Greenbaum** at Oak Ridge National Laboratory (ORNL) received some criticism from the reviewers. This criticism was based on the alleged failure of the project to concentrate on the proper avenues to lead to efficient hydrogen production, while addressing issues relating to the possibility of the existence of algae mutants that operate in a single photosystem process. In the past several months, however, Dr. Greenbaum has changed the course of this research to emphasize the development of algae that can produce hydrogen from water at a rate and pressure that would be commercially attractive. He is also addressing the decrease of the ratio of chlorophyll antennae to photosynthesis reaction sites thereby increasing the efficiency of the photobiological reaction. *Dr. Greenbaum is therefore showing himself to be both responsive to the reviewers' concerns, and, I believe, is on the right track.* We must, however, keep in mind that this type of research is long-term; we should not expect a precommercial-scale reactor based on these systems within, say, the next decade or two..

Project Strengths:

- Dr. Greenbaum was quite concerned about last year's review, and has been as responsive as anyone I have ever seen in this position. His shift of focus back to hydrogen production seems both sincere, and to date, effective. He is now looking at an alga that can produce hydrogen against a 1 atm. hydrogen head pressure, and is also now addressing antenna size. The fact that the research is refocused was clear to me during my visit, and is also, I believe, further proof that the Annual Review system works!

- In the past year, however, Dr. Greenbaum has moved his effort toward the alga *Scenedesmus* D_3, which, he has found, can produce hydrogen against at least a one-atmosphere hydrogen head pressure. This is more in line with following a path that could lead to usable hydrogen production.

Issues that should be Addressed:

- There is no doubt that Dr. Greenbaum is still interested in the "one vs. two photosystem" work that he had been immersed in over the last couple of years. He still plans to pursue it, only not for the Hydrogen Program. Care should be taken that this is not part of the Program Work.

II Introduction and Background:

I visited Dr. Elias Greenbaum at his laboratory at ORNL, Dr. Greenbaum's work is based on the development of algal systems that can synthesize hydrogenase. Certain algae can synthesize hydrogenase in an anaerobic atmosphere. No larger organism can do this. The hydrogenase enzyme is reversible; it can produce or consume hydrogen, and its reactivity is not inhibited by the presence of nitrogen (as the enzyme nitrogenase is). Some of the problems that incur with the use of the hydrogenase enzyme to produce hydrogen include:

- Hydrogenase will lose its ability to function in the presence of oxygen, generally at levels of 100-1000 ppm.

- The corresponding oxidation reaction is inhibited by the presence of hydrogen

- In the presence of CO_2, the photosynthesis reaction prevails.

Another problem is that the rate of photon excitation is uncontrollable. The excitation sets electrons in motion at a kinetically limited rate of about 100 electrons/second. Since there are a multitude of receptor sites for the photons (i.e., antennae), there is an imbalance between photon excitation and electron motion. It is thus necessary to reduce the antennae size, limiting the number of receptors, and thus "controlling" photon excitation.

Dr. Greenbaum, for the past several years has been conducting research on defining/creating algae that will make hydrogen (and oxygen) from water. His research, up until last year had focused on the alga *Chlamydomonas*. This was largely based on the fact that Dr. Greenbaum had some results indicating that the system required only one light reaction rather than the normal two to make hydrogen. This single photosystem mechanism (requiring only one photon) offered the possibility that the conversion of light energy to hydrogen for *Chlamydomonas* could be twice as efficient as that for other algae systems. In addition, *Chlamydomonas* is quite suitable for genetic manipulations that could decrease the antenna size.

The number of photosystems involved in the mechanism of water splitting by *Chlamydomonas*-produced enzymes then became a matter of some controversy, and the ORNL group devoted a great deal of effort trying to prove their one photosystem theory. The jury is still out on the answer to that, but it appears that the mechanism consists of at least partially the more common two-photosystem variety. Dr. Greenbaum believes that the one-photosystem mechanism is still partially correct too, however.

The bigger problem as far as the DOE Hydrogen Program was concerned, however, was that this debate was slowing progress toward a robust, efficient hydrogen-producing system that could eventually lead to a commercial product. This year's effort, however, has seen more of a hydrogen focus. Dr. Greenbaum has found that the alga *Scenedesmus* D_3 may be the "production hydrogen" alga needed. It can produce hydrogen against a one-atmosphere head pressure.

Much of our discussion, delineated below, centered on the *Scenedesmus* D_3 vs. *Chlamydomonas* options.

III Questions and Answers:

I provided Dr. Greenbaum with a series of discussion questions prior to my visit, and these formed a major part of our talk:

1. **How does *Scenedesmus* D_3 compare to *Chlamydomonas* as a hydrogen producer? Your note says that *Scenedesmus* D_3 may be an "industrial grade" hydrogen producer. What were the factors that had you emphasizing *Chlamydomonas* up until this year? What technical factors caused you to change your emphasis to *Scenedesmus* D_3?**

Scenedesmus D_3 was the alga that was actually the one with which hydrogen production was originally discovered in 1942. The production rates of hydrogen from *Scenedesmus* D_3 and from *Chlamydomonas* are similar, but the former can produce hydrogen against a one-atmosphere hydrogen head pressure, thus making it more suitable for higher pressure hydrogen production. Up until now, the concentration was on *Chlamydomonas* because it was a better understood system. It was attractive from a genetic engineering perspective. That is, it was a good alga to work with in the task of reducing antenna size.

If ones goal is high pressure "industrial" hydrogen production, one would think that this would be a criterion from day 1, and that algae screening and development would have included this test, thereby identifying Scenedesmus D_3 *earlier. This obviously did not happen. Dr. Greenbaum was caught up in the* Chlamydomonas *phenomenon of a single photosystem mechanism. This could have led to a higher conversion efficiency, and was obviously of importance for this reason. The fact that the hydrogen production reaction for* Chlamydomonas *was inhibited by hydrogen was not given enough importance at the time. This was probably a mistake, but maybe understandable in the light (no pun intended) of the single photosystem phenomenon. At any rate, the fact that Dr. Greenbaum has refocused his work toward* Scenedesmus D_3 *is more important.*

2. **How would you envision a commercial process in which *Scenedesmus* D_3 (or some other alga) would produce large quantities of hydrogen? What would you consider the biggest challenges to this effort?**

The process would be based, of course on solar-driven biotechnology. The reactors would be glass tubes, and the algae would generate hydrogen at relatively high positive pressures. Design features would address issues such as gas separation and oxygen-induced reaction inhibition.

The "designer alga" would have small antennae (perhaps 1/10 size), would be oxygen insensitive (this would be based on NREL's contribution), and would be thermodynamically driven.

The biggest challenge, according to Dr. Greenbaum is obtaining adequate funding to complete the research phase and move the process out of the laboratory and into the marketplace. The important problems that must be solved include:

- the development of the high-pressure hydrogen producing system
- linearization of the light saturation curve of photosynthesis (*it reaches a plateau)*
- development of an oxygen tolerant hydrogenase enzyme

3. **Your FY 1999 AOP submittal indicated that you were also doing some testing with *Chlorella*. How does this compare as a hydrogen producer?**

Chlorella is yet to be tested. It is the third of the "rugged alga" that produce hydrogen along with *Scenedesmus* D_3 and *Chlamydomonas.*

4. **You also indicate that you intend (or already have) to check the indirect measurement of hydrogen formation via oxygen concentration measurements by seeding the hydrogen atmosphere with 350 ppm CO_2. I assume that this will lead to the production of oxygen via photosynthesis. How will this serve as a check on the thermodynamically driven reaction? I assume that the formation of oxygen via photosynthesis will result in inhibition of subsequent hydrogen formation. However, you can't measure hydrogen formation in a hydrogen atmosphere, so are you looking for a reduction in overall oxygen concentration? How does the oxygen concentration from the hydrogenase-catalyzed hydrogen evolution reaction compare with that from photosynthesis in the presence of 350 ppm CO_2?**

The rates of oxygen evolution coupled to hydrogen production are typically 5 to 10 percent of the rate of oxygen evolution coupled to CO_2 reduction. This is because of the photosystem II requirement of CO_2/HCO_3^- for optimum oxygen evolution activity. The bicarbonate effect is one of the limiting aspects of biohydrogen production. (Light saturation is another).

You can simply measure the concentrations of CO_2, oxygen, and hydrogen.

5. **What is ORNL's role(s) in working with Melis' group?**

Both laboratories are part of the DOE biohydrogen production team. Dr. Greenbaum stated that ORNL is the leader in systems designed and constructed for measuring simultaneously photoproduction of hydrogen and oxygen, and CO_2 assimilation.
Aside from the quantitative measurements, Drs. Greenbaum and Melis hold interactive critical dialogues on antenna sizes and sulfur issues. Sulfur deprivation could reduce the oxygen sensitivity of the hydrogenase enzyme.

6. **What are the limiting factors as to the amounts and types of solutes and contaminants allowable in the water being split?**

These algae are quite forgiving as far as water conditions are concerned. The basic rule of thumb is: if the algae can grow in the water, they can split the water.

7. **If CO_2 inhibits hydrogen generation, what is the maximum amount of CO_2 allowable in the system? How would a practical system be purged of CO_2?**

The degree of inhibition of hydrogen generation by CO_2 is dependent on temperature and light intensity. It is a good idea to keep the CO_2 levels below 10 ppm, by pumping on the system.

IV Additional Discussion:

Dr. Greenbaum believes that there is a 10-20 year "grace period" in developing a method of splitting water. He feels that the requisite research will take about that long. *I don't know about a grace period being available other than in the context of it probably taking that long to develop something of a realistic hydrogen infrastructure. Nevertheless, the time needed to develop the photosynthetic water splitting technology is probably accurate. Dr. Greenbaum contends that the time can be shortened by infusion of funds, and while this may be the case, the major message may be to keep the core research alive. It's probably the most important part of the Program.*

One aspect of the mechanism for hydrogen production that I was previously unaware of is the fact that if no CO_2 is present (i.e., no normal photosynthesis can take place), the photolysis results in the dehydrogenation of some of the starches within the alga's carbohydrate structure. In fact, 80% of the evolved hydrogen comes from the water being split, and the other 20% comes from the starch. *I would think that this would be a limiting factor, reducing the activity of the algae, unless the starch is rehydrogenated at some point.*

Dr. Greenbaum defines process efficiency as the Gibbs Free Energy of the produced hydrogen divided by the energy of the input light, and multiplied by 0.47 to account for the fact that only about 47% of the light energy is in the visible (and therefore useful) range. Input light energy is measured simply by focusing on algae on a known area of filter paper, and using photodetectors.

Dr. Greenbaum mentioned that Dr. Laurie Metz at the University of Chicago is investigating genetically reducing antenna size.

This page intentionally left blank.

Technical Evaluation Report

Project: Bioreactor
Company: University of Hawaii, Honolulu, HI
P.I.: Dr. Rick Rocheleau **(Acting)**
Date of Visit: July 8, 1999
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

The bioreactor project at the University of Hawaii is at a critical point of its existence. The project has a fairly large (200 liter) working bioreactor, an organism that produces hydrogen under anaerobic conditions and is fairly easy to work with, a competent program manager who has recently taken the program under his wing, and several biologists and bioengineers associated with the program to varying degrees. On the other hand, the project's principal investigator (PI) resigned several months ago, and no new PI has been identified. In addition, the identified cyanobacteria, *Arthrospira*, while it produces hydrogen readily in the dark, does not produce hydrogen in the light (photolytically). The anaerobic hydrogen evolves from the carbohydrate matter itself, resulting in partial (note: not total) dehydrogenation of the cyanobacteria. It leaves a partially dehydrogenated biomass waste material. This is not the anticipated process, and seems less efficient and inferior to other biohydrogen systems. The identification of a light induced reaction process with this or another organism resulting in hydrogen from water would be preferable.

Project Strengths:

- The most valuable commodity associated with this project is the bioreactor. The reactor should be made available for collaborative efforts. The identification of a good, water-splitting, hydrogen-producing organism either from the Mitsui collection or elsewhere would be a bonus.
- The Mitsui collection itself is a very valuable asset.

Issues that should be Addressed:

- The continued use of *Arthrospira* as only a low-level, anaerobic hydrogen producer should be discouraged unless one can demonstrate the regeneration of the byproduct, resulting in a steady-state biomass concentration.
- A suitable PI needs to be identified.

II Introduction and Background:

I visited **Dr. Rick Rocheleau** and his team at the University of Hawaii's Hawaii Natural Energy Institute (HENI) on July 8, 1999. Dr. Rocheleau is currently managing the bioreactor project, and is acting as principal investigator at least until a new PI can be put into place. This is a result of the resignation of Dr. Oskar Zaborsky, the previous PI, from the project several months ago. Currently Dr. Rocheleau's team includes biologist **Dr. Yasuyuki Nemoto**, bioengineer **Dr. Scott Turin**, and visiting biologist **Dr. Youji Wachii**. Drs. Nemoto and Wachii were present at our meeting; Dr. Turin was away on travel. I also met **Dr. JoAnn Radway** who formerly was Dr. Zaborsky's primary hands-on researcher. Dr. Radway is still performing research at UHawaii through the university's Marine Bioproduct Engineering Center (MarBEC). Dr. Radway recently resigned from the biohydrogen project. Through MarBEC, she is still actively involved with the bioreactor, and also is responsible for the maintenance of the Matsui Collection.

During my visit, I spent several hours with Drs. Rocheleau, Nemoto and Wachii, during which time I was given an interactive presentation on the history of and the planned future of the Hawaii biohydrogen project. Included in this presentation was a discussion of the set of questions that I had sent to Dr. Rocheleau about two weeks prior to the meeting. Following the presentation/discussion, I was shown the outdoor bioreactor and the laboratory facilities as well as the Matsui Collection.

III Tour:

I was given a tour of the biohydrogen facilities by Dr. Radway and her staff. Most impressive was, of course, the bioreactor. Its dimensions and capacity are discussed below in the "Initial Discussion" section. While I was there, the reactor was being calibrated for flow characteristics. A concern was the fact that regardless of how the system had been configured, all the small (high surface area) bubbles were coalescing into large bubbles with low surface to volume ratios while flowing up the tubes. This was hindering transfer properties. It appeared (at least at the time) that the problem would not be solved mechanically, but a chemical solution might be needed. Dr. Radway and her group were conducting the flow tests. Dr. Rocheleau did indicate to me that the two groups would share the data.

I also was taken through the laboratories, which contained a good assortment of smaller reactors, diagnostic equipment, and the Matsui collection of organisms. All of this is being maintained by Dr. Radway and her people. In fact, one of Dr. Radway's technicians probably spends about four hours each day just tending to the Mitsui collection.

IV Overview and Initial Discussion:

The goal of the HENI Bioreactor Project is to develop a sustainable bioreactor for hydrogen production. The process consists of two major stages: growth of the cells, and production of hydrogen. HENI plans to use a marine organism for this work. This is because marine organisms are more abundant, are easier to grow due to ease of nutrient uptake, and hold a much more dominant position in U Hawaii's photobiological history. *Surprisingly,* however, the current organism of choice is *Arthrospira sp*., a fresh water organism. The organism is equivalent to *Spirulina sp*., a cyanobacteria that is being used by a company called Cyanotech as a source of beta-carotene extraction. The HENI team is trying to identify a marine organism with properties similar to *Arthrospira sp*. The organism physically is long and stringy in structure, being one cell wide, but about *1* mm in length. These dimensions make *Arthrospira* easy to work with as material can be concentrated easily by sieving. In addition, *Arthrospira* grows well under alkaline conditions (an unusual situation) and is not very susceptible to contamination.

The FY 1999 proposal which had been put into place by former P.I. Oskar Zaborsky was comprised of a mechanism in which the cells grew under light conditions (photosynthesis) in stage one, and then produces hydrogen in a three-step second stage that was comprised of:

- concentrating the cells and adapting them to hydrogen production under anaerobic, dark conditions;
- producing hydrogen under light conditions; and
- recycling the cells to regrowth (stage 1)

Although literature data indicated that this scheme had worked with some types of green algae, it did not work here. The anaerobic "adaptation" step actually resulted in the production of hydrogen. Hydrogen was formed by metabolizing the cells' own carbohydrate. Hydrogen was not produced in the light; the photosynthesis process of Stage 1 proved dominant in this step.

Perhaps the most significant feature of the project to date is the utilization of the outdoor bioreactor to grow the organism. The bioreactor (*which was being used to determine flow mechanisms on the day that I visited*) consists of eight tubes, each twenty meters in length and 4 cm in diameter. This provides for a total volume of 200 liters and a total surface area of 6.4 square meters.

The growth of *Arthrospira* in the bioreactor was measured at 0.43 g/liter/day. (86 g/day for the 200 liter reactor.) The *Arthrospira* concentration in the reactor is typically 3000-5000 mg (dry)/liter.

Hydrogen was produced in the dark at a rate of about 22.4 ml in 12 hours for each gram of *Arthrospira.* If the reactor produces 86 g /day biomass, this works out to a total of about 2 liters of hydrogen produced in 12 hours. No hydrogen was subsequently produced in the light. *The actual data shown never actually reaches the 22.4 ml per 12 hours bioreactor time. Under various conditions, the graph I was shown indicated production rates of 50 to 80 percent of that amount.*

Dr. Rocheleau and his team propose for 2000 that the "Old Hawaii" process be modified to reflect what was actually happening: hydrogen production in the dark followed by recycling of the biomass. They claim that concentrating the *Arthrospira* to go from an aerobic to an anaerobic environment would be easily accomplished by screening the long, thin *Arthrospira* material. They need to engineer the process, however, to make it continuous. The Cyanotech process would be a good model for this. The group may also try to look at light catalyzed hydrogen again if they can find a proper alga to work with. One of their goals might be to find a green alga that would produce hydrogen in the light, but would be easy to concentrate like *Arthrospira*.

The direction that the research appears to be going is questionable. A light-catalyzed hydrogen production process with an easy to concentrate biomass (as Arthrospira *appears to be) would have been preferable. It would have (similarly to other projects) likely resulted in hydrogen from water splitting rather than biomass depletion. What we appear to have here is a project where a small amount of hydrogen is stripped off of a large molecule leaving a large amount of questionable byproduct. I have my doubts if the direction that the project is taking is therefore the right one. An attempt to use the bioreactor with materials that could produce light-catalyzed hydrogen might be preferable.*

V Questions and Answers:

A significant period of time was used to go over the series of questions that I sent to Dr. Rocheleau prior to our meeting. These questions and responses are discussed here:

1. **What properties of *Arthrospira* make it superior to other bacteria strains in hydrogen generation? Have other systems been looked at? For example, how well did *Chlamydomonas* perform?**

As stated earlier, *Arthrospira* is filamentous, making it easy to concentrate by screening. The concentrating step is important in that it makes it easier to achieve the anaerobic conditions needed for dark hydrogen production. *Chlamydomonas* produces hydrogen in the dark at about the same rate as *Arthrospira*, but when it is moved into the light, it starts producing oxygen (photosynthesis), inhibiting further hydrogen production. The main problem with *Chlamydomonas* is that it is difficult to concentrate.

Since we know that Chlamydomonas *will produce photolytic hydrogen in the absence of* CO_2 *and with small antennae, it seems to me that it would be advantageous to examine the possibility of improving the ability to concentrate the alga so as to use it in conjunction with the bioreactor. Either that, or find a marine organism that will work. It's the bioreactor that is HENI's strength, not the* Arthrospira.

2. **Does hydrogen actually get produced during the "dark step", or what is meant by "turning on the biochemical machinery?"**

"Turning on the biochemical machinery" means creating physiological changes inside the cells that will make it possible to produce hydrogen by reversible hydrogenase activity. As we have seen, hydrogen is produced during the dark step, although this wasn't the original intent.

What I see as the problem is that the mechanism for dark hydrogen production is not really water splitting, it's biomass degradation.

3. **If *Arthrospira* has an activity of 1 micromole hydrogen per mg of dry cell under dark conditions, what production rate would be expected in the light-dependent step (step 3)?**

As stated, no hydrogen is produced; photosynthesis prevails. HENI has indicated that they plan to look for an organism that has an oxygen-tolerant hydrogenase system that would allow photolytic hydrogen production to occur.

If HENI is going to do anything other than provide the bioreactor, the oxygen tolerant organism approach would be a good idea. Concentrating on a marine organism would be a good idea also. Alternatively, HENI could simply provide the bioreactor for systems being developed in other laboratories.

4. **Explain the "exogenous electron carrier".**

This is an artificial electron donor that is used to measure enzymatic activities of materials such as hydrogenase.

5. **It appears that U Hawaii has addressed steps 1-2 (growth of cyanobacteria and dark activation) of the four step process. Have steps 3 and 4 (hydrogen production in the light, and recycling) been evaluated? Is this going to be folded in to the new fiscal year task of making a sustainable bioreactor?**

The plan has been modified to allow for dark hydrogen production, as already stated.

6. **Eli Greenbaum at ORNL has been evaluating systems that he believes can produce hydrogen against a one-atm. hydrogen head pressure. In other words it has the potential of producing hydrogen in usable concentration under real world, industrial conditions. What is the potential for the *Arthrospira* system under real-world conditions?**

They have no experimental data on this. They stated, however, that since they are concentrating the cyanobacteria and forcing anaerobic conditions, they would have very little headspace.

7. **In what manner does the culture collection maintenance play into the bioreactor work? Is the collection being co-funded by other sources as well?**

HENI plans to look to the collection to find other filamentous species and check them for hydrogen production activity. They will also look for Hawaiian marine filamentous cyanobacteria strains.

The collection is being co-funded by MarBEC. This is being accomplished by having Dr., Radway, who is being funded by MarBEC, maintain the collection.

I am not sure that "filamentous" should be the key screening parameter. Although concentrating potential is important, I believe that the ability to produce hydrogen photolytically is more important. This should be a key criterion for selecting new species.

8. At what production rate/ reactor size was the preliminary production cost of $15/MMBtu established?

This number was apparently an "old John Benneman number." Dr. Rocheleau was unsure of its history, but planned to get back to us on this. (*Dr. Benneman formerly collaborated with Dr. Zaborsky on this project.*)

9. What efforts are being made to interact with the other Hydrogen Program photobiological P.I.s? What are (will be) the contributions of other labs to the U Hawaii Project? What are (will be) the contributions of U Hawaii to projects in other labs?

Other labs would contribute to the Hawaii project by providing better strains or species for hydrogen production. These would likely be engineered to contain oxygen-tolerant hydrogenase. Hawaii would contribute to other projects by testing these strains in a "real-world bioreactor," providing hydrogen production information.

For some of this work, Dr. Rocheleau and his staff believe that the bioreactor is too large. They would want to use a smaller reactor to test other organisms and engineering parameters.

None of this type of interaction is happening as yet. I would think that this could be the most important contribution that the Hawaii biohydrogen project could make to the Hydrogen Program.

10. How would you envision a commercial process in which a bioreactor system would produce large quantities of hydrogen? What would you consider the biggest challenges to this effort?

The HENI group identified many technical challenges:

- The need to find a more suitable marine organism
- Addressing the recycling step so that essential nutrients can be reused
- The need for an automated "anaerobification" step that will allow the cells to be concentrated and put into a closed chamber with very little head space, where the cells can quickly consume all the remaining oxygen. This will provide for anaerobic conditions where hydrogen can be produced in the "dark" reaction.

This did not really address commercialization. I am also concerned about too large an effort on dark hydrogen. That process does not seem very efficient.

11. What are the plans as to restaff the bioreactor project?

The current plan is to allow Drs. Nemoto, Wachii, and Turin to run the project. A new post-doctoral fellow will also be hired to run the experiments on the "New Hawaii Process".

I am not sure that this is the entire answer. A single strong PI needs to be identified either from within the project or elsewhere. If Dr. Rocheleau can spend more time directing the project (which he probably does not have time to do) this would help. I'm not sure this issue has been completely thought out yet.

VI Final Thoughts:

The presence at the University of Hawaii of the bioreactor, which will likely be of great value to the overall biohydrogen segment of the Program, is by far the project's major asset. I do not believe that the project is headed in the right direction by concentrating on "dark" hydrogen production. The lack of a permanent PI is another serious problem. There is also the question as to what equipment belongs to the Hydrogen Program and what is the property of the MarBEC project and what is jointly owned and shared. Given his track record in other UHawaii projects, Dr. Rick Rocheleau should be given a chance to straighten these problems out.

The project should also move in the direction of providing bioreactor testing for the organisms of other laboratories, and looking for a marine organism that will produce photolytic hydrogen.

The need to efficiently produce hydrogen needs to be stressed. Interaction with other labs needs to be stressed. The role of Dr. Radway needs to be defined.

If the Hawaii biohydrogen project is to succeed, it has to be centered on the bioreactor.

This page intentionally left blank.

Technical Evaluation Report
Project: Hydrogen from High Moisture Biomass in Supercritical Water
Company: University of Hawaii, Honolulu, HI
P.I.: Dr. Michael Antal
Date of Visit: March 9, 2000
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

The group of researchers at the University of Hawaii who are developing a method of gasifying biomass in supercritical water to produce hydrogen are led by **Dr. Michael Antal**. The project is several years old, and to date, Dr. Antal's group has developed a working reactor that is capable of accepting carbohydrate-based biomass and converting it to a syngas which is primarily CO_2 and hydrogen with some methane and a small amount of CO by reacting it with pressurized (4000-5000 psi) water at temperatures between 700 and 800°C in the presence of inexpensive carbon catalysts. They have found that that they can produce the gas with very little coking, and have developed a process by which the coke and biomass-based ash can be removed from the reactor walls. The reactor is made of cast-alloy, a nickel/molybdenum based material that can withstand the high reactor pressure.

Dr. Antal's group have demonstrated that they can handle dry biomass such as sawdust by suspending it in starch gel, and can handle wet biomass such as potato processing wastes directly. They have shown that while the gasification process works well on cellulose and sugar-based carbohydrates, it does not work on other types of biomass such as sewage sludge. In fact, Dr. Antal questions whether sewage sludge can be classified as a biomass at all.

Presently, Dr. Antal is trying to obtain funding to further develop the process using potato wastes. A potato processing company in Richland, Washington, Lamb-Weston Corp., is interested in a way to get rid of their processing waste, and view the supercritical gasification process as a means to eliminate waste disposal costs and produce a usable, combustible gas as a bonus. The improved process would use a different composition reactor tube (likely zirconia, titania, or alumina) that would allow a somewhat higher temperature (and therefore higher hydrogen concentration) environment with less likelihood of corrosion than the nickel alloy. Since the proposed reactor materials will not adequately resist 4000-psi pressure, Dr. Antal proposes to encase the tube (or perhaps several tubes) in a carbon-steel pressure vessel. Dr. Antal claims that both the pressure vessel and reactor tubes are "off-the-shelf" items. *Dr. Antal, stating the above claims of off-the-shelf technology, took exception to analyses performed at NREL that indicated that the pressure reactor system would be prohibitively expensive. (I am not sure about the off-the-shelf feature. The pressure vessel itself may be off-the-shelf, but Dr. Antal has not either down-selected to a reactor tube type or even started testing choices.)*

Project Strengths:

- Dr. Antal is a dedicated, well-organized researcher. He has built systems that work. He has learned how to process slurry feedstock in a more or less generic manner so that they can be fed efficiently into the reactor; he has built, and proposes to build progressively more efficient reactor systems.

- Dr. Antal has the proper facilities for carrying out his objectives. His laboratory is a model of efficient use of space.

- The supercritical water experiment provides a medium that produces a minimum of unwanted byproducts such as coke. Furthermore, Dr. Antal has developed a process that will oxidize away the little bit of coke that does form without harm to the production gases or the catalyst. The other unwanted byproduct, ash, such as the alkali oxides that form upon gasification of potato wastes can be removed by brushing them out of the reactor (they are not fused to the reactor walls.) Dr. Antal has successfully demonstrated this process in small scale.

- The catalyst is simply carbon, not even necessarily activated. Charcoal works fine. Replacement of the catalyst bed is an inexpensive, easy process.

Issues that should be Addressed:

- First and foremost, the project has evolved in such a manner that I would no longer consider it a hydrogen project. Dr. Antal's arrangement with Lamb-Weston involves producing syngas from potato wastes, and then burning the syngas. Lamb-Weston is mainly interested in getting rid of the wastes. Getting a combustible material is a bonus. The syngas contains about 30 mole percent of hydrogen (presently, although the new design should increase this), but this does not make it a hydrogen project. It's a biomass project. Dr. Antal has asked Lamb-Weston to come up with ways that they could use actual hydrogen. Apparently there is a nearby refinery to which they could sell hydrogen, but this appears a bit of a stretch. There is no talk of how they would separate out the hydrogen. Maximizing (which is being proposed by Dr. Antal) and purifying hydrogen should be a major concern of any future work. Besides, Lamb-Weston is "perfectly happy" to burn the syngas.

- The coke and ash removal process, while effective at small scale, could become unwieldy in a larger, multiple reactor tube operation. Temperature control could be difficult.

This is, in my opinion, a good project; it's just not going down the road that parallels what the Hydrogen Program is looking for. A company such as Lamb-Weston will likely solve a major problem by employing Dr. Antal's reactor. There are very likely scores of other food processing companies, agricultural industry segments, and others who could benefit from this system.

Biomass contains a relatively small amount of hydrogen. As such, it is difficult to justify a project such as this if its primary goal is producing hydrogen. This particular program has evolved into one where hydrogen has become the afterthought. The entire Lamb-Weston concept is not a hydrogen-based concept.

II Introduction:

I visited Dr. Michael Antal and two of his co-workers, **Stephen Allen** (Junior Researcher and Member of the U Hawaii Faculty) and **Deborah Schulman** (Research Associate) on March 9, 2000, spending a full day with them, discussing the project and getting a tour of their laboratory including a dry run on each biomass reaction system present.

III Tour/Demonstration:

I was not given a demonstration of the supercritical gasifier in operation. Dr. Antal told me that it would take nearly a week to get it up and running at this point, and there was no funding to do so. *I'm sure he was trying to make a point, but it's a point well taken, and the meeting did not suffer greatly from the lack of the active demonstration. The dry run-through served nearly as well.*

The laboratory is very compact, and well set up. Half of the lab is set up for computers, analysis equipment, storage, and chemistry related tools. The other half of the laboratory contains four reactor systems.

The analysis equipment includes a Gas Sorption Analyzer that provides BET porosity measurements. This is rarely used for the hydrogen work; it is primarily for activated carbon studies. In addition, there is a GC/Mass Spectrometer and another gas chromatograph. There is also an HPLC that is used primarily for Dr. Antal's ethanol work.

The series of reactors include:

1. Their "old" reactor that operated at less than 1000 psi and at about 250^{o}C. It is currently being refurbished to be used in the making of activated charcoal from the reaction of biomass in hot water.

   In its original use, the reactor was used to make ethanol from sugar cane bagasse (stems), sugar cane leaves, corn fiber, southern pine, pine bark, or aspen wood chips. The batch reactor is about two inches in diameter; biomass (10 – 30 grams) is placed in a cage, and lowered into the hot water. Product can either be emptied from the reactor bottom, or pumped into a tank.

   This reactor was the precursor to reactor #3 (below).

2. A reactor that is used to make charcoal from biomass. It operates at about 300^{o}C and 150 psi (but can be used at pressures up to about 1000 psi). It includes a power boiler

and power reactor, built to code. This reactor produces theoretical yields of charcoal – about twice what industry gets.

3. A reactor that is used for the ethanol work. This work is being funded by the National Science Foundation (NSF), the Consortium for Plant Biotechnology (CPBR), and BC International (BCI). The work is being performed by U Hawaii, and Dartmouth College. Dr. Antal's group does the biomass pretreatment work in this reactor, and Dartmouth does the fermentation.

   The premise here is that if the temperature and pressure is high enough, you can use water alone to run the pretreatment step. Dr. Antal's group runs the reactor at 210-220°C and 335 psi, immersing the biomass in the water for one or two minutes. This dissolves (but does not react) all of the hemicellulose and about half of the lignin. This pretreatment product is then sent to Dartmouth for fermentation.

   This reactor was built to have the features of a commercial process. Instead of a hot water tank, a full-scale boiler is used. (All safety issues are met.) Steam from the boiler preheats the 8-inch diameter reactor. The feed can be up to 2 kg in weight (wet), but is generally run with about ½ kg.

   One kg of dry bagasse will eventually produce about 400g ethanol.

   Both the charcoal reactor and ethanol reactor are run in semi batch mode to make the feed process easier.

4. The "present" hydrogen reactor. It is based on a design by Modell at MIT who used this type of reactor to burn Department of Defense generated waste in supercritical water. Dr. Antal states that in the U Hawaii case, they are using the reactor to "synthesize, not destroy." Originally, Dr. Antal used the reactor to convert ethanol to ethylene for the National Science Foundation. During that study, Dr. Antal discovered that the supercritical water dissolved biomass without char formation. Thus started the wet biomass project.

   The system does not use a boiler – just a high-pressure reactor (a ¼-inch tube), so no permitting is needed (the boiler people are not interested – there is not enough material here to constitute a safety concern.

   The feed system is simply an open cylinder. A piston is placed into the chamber, and a combination of sawdust and starch gel (or potato waste without the starch gel) is placed into the upper chamber. Water is pumped into the lower chamber, or for ease of handling at this scale, the cylinder is flipped over, and the water is filled from the top. The overall feedstock is 15% solids – 10% sawdust and 5% starch gel.

   The cast-alloy reactor is heated by a three-zone furnace to about 700°C. Additional heaters are used at the entrance and exit of the reactor tube to get a quick temperature rise, and to minimize heat loss. Fifteen computer-monitored thermocouples are mounted on the outside of the reactor. The catalyst bed extends about ten cm into the reactor on the aft end, with air also entering through an aft end annulus.

The feeder is pressurized to 4000 psi with water, as is the reactor. The process starts by just running the pressurized water through the reactor until the temperature profile is stable. At this point, the water is turned off, and the feeder is opened.

A sixteen-port gas-sampling valve provides gas samples to a gas chromatograph (they monitor CO_2, CO, hydrogen, CH_4, and light hydrocarbons. They also monitor CO_2, CO and CH_4 by infrared detection.

A typical feed cycle is 1-2 hours, and is finished by switching off the feed, and back to water to react the residual feed, and then bring the pressure down, still holding the temperature at 700^{o}C. They then burn out carbon deposits with low-pressure air, monitoring the CO_2 concentration. When that value is down to about 0.2%, they insert a brush manually to break up ash deposits, then blow air through the system again.

They have made runs lasting up to about eight hours (6-7 cycles) and were still going strong when they stopped. There was no evidence of catalyst degradation. Gas yield does not decrease between the cycles, but does decrease within a cycle probably because the deposits on the reactor walls reduce heat transfer.

IV Questions and Answers:

A large portion of our discussion time was spent going over a series of questions that I had sent Dr. Antal prior to our meeting. Dr. Antal sent back a series of answers prior to my trip. These are shown below, as is the additional discussion we had on each of them.

1. **With a much-varied set of biomass raw materials being proposed, what differences do you see rising as potential technical problems? How do the differences in type, availability, and cost (positive or negative) of biomass mesh with potential markets**.

"Our proposal only concerns the gasification of potato wastes. We are interested in other food processing wastes, other wet biomass, and biomass in general (e.g. wood sawdust), but our focus for the next few years is the gasification of potato wastes".

Dr. Antal at first was looking for a representative biomass, and thought of wood sawdust as being representative of a biomass that would be difficult to work with. How do you feed dry sawdust into a reactor at 4000-5000 psi? Dr. Antal also pointed out that sawdust has large markets already such as the particle board market and the charcoal market. There are not a lot of people trying to find a way to get rid of sawdust. *Then why pick sawdust? I suppose if you find that you can feed sawdust, you can feed anything with a little preprocessing. So it's probably a good technical choice, albeit a poor economic one.*

In trying to find something that people are trying to get rid of, Dr. Antal's group then focused on sewage sludge. This is a good economic choice, but turned out to be a bad technical one. Sewage sludge (and most non cellulose-based materials) does not gasify by the supercritical water process. Therefore, the group turned to vegetable food wastes. They are carbohydrates, and people usually need a way of disposing of them. They settled on potato wastes, mainly because they had a customer – Lamb-Weston.

2. **What are transportation costs of wet biomass? Do you foresee a centralized gasification plant or dedicated distributed plants?**

"Potato wastes are available in Lamb-Weston's factories. We foresee a gasifier located in each factory. There is no transportation."

It is expensive to move biomass, especially very wet biomass such as the potato wastes. This is why Lamb-Weston cannot sell potato wastes to hog farmers, for instance. It costs too much to ship.

3. **Starch gel – does this produce hydrogen as well? How much? If you are using a feedstock that is 10-20% solids, doesn't much of the hydrogen come from the carrier?**

"The gasification of starch gels is thoroughly described in our paper. Our proposal does not concern the gasification of starch gels."

Of course I knew that starch gels would produce hydrogen. I was trying to get Dr. Antal to tell me that a significant portion of his hydrogen is from starch gel. When he has to use starch gel, such as with sawdust, his feed is nominally 10% sawdust, 5% starch gel, and the rest water. If he tries a higher solids loading, he cannot pump the material, and he cokes the reactor as well.

Of course, Dr. Antal's present (and proposed future) work concerns potato wastes which don't require an additive.

Dr. Antal considers the applicability of starch gel for biomass suspension as somewhat of a "miracle". Oily additives such as coconut oil do not gasify.

Dr. Antal also commented that there is no plan to use starch gels in the future. It was just part of a proof of concept experiment with sawdust. It's not an economically viable option.

So what is it, a miracle or a curiosity?

4. **Does the starch gel basically serve as the only additive you need for most biomass systems? How generic is the processing of the feedstock?**

"No additives are needed for potato wastes. Starch gels are needed to deliver sawdust to the reactor."

If you do need an additive, starch gel appears to be more or less generic. No additional additive is needed. The only stipulation for successfully using starch gel is that the feed must have an essentially neutral pH.

5. **You indicate that you can perform steam reforming using this process at temperatures below 800°C, but state that the process will produce more hydrogen at temperatures above 750°C. – Would they produce even more hydrogen at temperatures above 800°C? – or is the process maximized at some temperature between 750 and 800?**

"Thermochemical equilibrium calculations indicate that higher temperatures improve hydrogen yields. The reactor described in our proposal can easily be run at temperatures above 800°C to determine how much improvement is realized at higher temperatures."

The problem is that their cast-alloy reactor cannot withstand the higher temperatures. It loses its strength and "balloons" as well as corrodes more rapidly. Dr. Antal's new proposed reactor tubes will not corrode at the higher temperatures, but cannot withstand the 4000-5000 psi pressure. Thus, the carbon steel pressure vessel to maintain the tube integrity is needed.

6. **Releasing the air into the region in front of the carbon bed so that it oxidizes char at reactor entrance rather than oxidizing the bed – how close to 100% is this? Is any catalyst lost?**

"We are unable to measure any loss of bed carbon. The gas in the bed is stagnant. Little oxygen should be delivered to the bed by the airflow. In any case, in a practical reactor the catalyst would be charcoal, which is very cheap."

The material that is being formed is coke (from condensed reaction gases), not char. It burns off very easily. Dr. Antal does not know, however, if the process is practical. This is something he hopes to learn from the Lamb-Weston work.

Both the coke and the ash form near the reactor entrance because it is a somewhat cooler region. The gases condense to coke at the lower temperatures, and the ash precipitates out of the steam, being less soluble at these temperatures. If it did happen to carry down to the catalyst, it's not a big problem. Charcoal is inexpensive.

7. **How will the carbon deposit and ash removal described for the reactor translate to real world sizes and situations? Do you visualize a modified batch mode process using a bank of reactors where a reactor is shut down and cleaned every few hours on a staggered basis?**

"This is the most important issue that we face. Potato waste is about 10% ash (dry basis). If we feed 100 lb. of potato waste (on a dry basis) to the reactor, we will accumulate 10 lb. of ash. So we must remove this ash from the reactor. Our idea is exactly what you describe. Several reactors will operate in parallel within one large pressure vessel. When one reactor plugs, it will be shut down, cleaned, and restarted while the others continue to operate. This cleaning will be done in a sequential manner.

"I understand that the panel of reviewers was skeptical of this approach. In response, I emphasize that life could have been tougher. We were delighted to discover that the carbon (coke) accumulation in the entrance of the reactor is extremely reactive and burns quickly and easily in flowing air. If the carbon accumulation had not burned easily, I would have abandoned this work! Likewise, we were delighted to discover that the ash is trivially removed from the reactor by a light brushing, followed by a burst of air. If the ash had fused to the side of the reactor, I would have abandoned this work! In summary, we could hardly have hoped for a better situation."

This is indeed a batch process that would be made pseudo-continuous by having multiple reactor tubes (about one inch in diameter each) located parallel to one another inside the one foot diameter, 30 foot long pressure vessel. It may be necessary to water-cool the pressure vessel if it is affected by the heat of many reactor tubes, but the resultant hot water would perhaps be usable. Dr. Antal visualizes a situation where one (or more) tube(s) can be in a burn-out or brush-out phase while the other tube (or tubes) is in reaction mode.

The one-inch diameter reactor tubes is probably a limiting factor. Any larger, and they are no longer off-the-shelf. In additional, larger tubes would probably be less efficient from a heat-transfer standpoint. Heat transfer time is proportional to the square of the radius of the reactor. If you heat the biomass too slowly, you'll make charcoal.

I am not too confident of being able to manage such an unwieldy system, especially with a manual "brush out" component. I think temperature control may be a nightmare.

8. **One of the key "hooks" of this project is the minimization of char and tar formation in the presence of superheated water. Yet char cleanup still appears to be a major issue. Where is the gain?**

"The gain is carbon gasification efficiencies that approach 100%. The formation of "tar" and "char" is very small relative to any other gasifier. This point is discussed at greater length in our paper."

Dr. Antal also pointed out that since ash will be formed, a clean-out step is necessary anyway.

9. **Explain change in catalyst BET and packing density after run. If you assume that the loss in surface area occurs throughout the run, you would expect hydrogen yield to decrease correspondingly. Yet hydrogen yield per <u>cycle</u> does not change even though you would expect a much lower BET for, say, cycle 5 than cycle 1. Please explain.**

"As emphasized in all our papers, the surface area of the carbon is inconsequential. Biomass charcoal is a better catalyst than activated carbon. The outer surface area of the charcoal (which has virtually no pores) is more than adequate to catalyze the tar gasification reactions. We only use activated carbon because it is convenient: it is homogeneous, and already ground to a convenient size for us."

Then, I guess, it's not really necessary to measure BET or other surface measurements.

10. If the catalyst surface and density characteristics change so much after one eight-hour run, how will this be dealt with on a practical level? Change out the catalyst for each run? Recharge it?

"As mentioned above, the change in surface area of the carbon is inconsequential. If our proposal is funded, we will test the life of charcoal catalysts with potato waste feed. In any case, charcoal is cheap, and can be burned for disposal and energy recovery. If it is necessary to clean the reactor of ash every few hours, it will not be difficult to replace the charcoal catalyst once a day (for example)."

This is a little out of phase with Dr. Antal's statement that he couldn't show me an active system, because it would take a week to get it running. Perhaps it would be a bit harder to clean the reactor ash and to change the charcoal than anticipated.

11. What percentage of hydrogen present in the waste material do you expect to recover from the new reactor both before and after consideration of recycled hydrogen to provide heat to the system?

"We estimate that about 30% of the combustible gas products must be burned to run the gasifier. Thus, about 70% of the energy content of the feed will be available. It is possible that none of the hydrogen will be burned. If a gas separation system is employed at the exit of the reactor, combustion of the methane product may be enough to fuel the gasifier."

This is the only mention of gas separation. If we are going to deal with hydrogen instead of syngas, we need a separation system.

12. I understand that in some of your earlier work, there was a controversy regarding some sampling and storage techniques. While it appeared that the storage techniques were not compromising the results, I am not as sure as to the sampling techniques. I recall seeing several data tables indicating that air might have been leaking into the system during sampling. If this were occurring at high temperature, there is the possibility of additional oxidation occurring. Was any attempt made to quench any reaction in the sampler and/or has the system or technique been modified so that air no longer leaks into the sampling system?

"The gas sampling has always been done at room temperature. Air is not a problem at room temperature. If our proposal is funded, we will be using a 36 port sampling valve to take gas samples at room temperature. Air will not leak into this valve."

This puts to rest the only concern I had with leakage.

VI Additional Discussion:

- We have been talking about materials that can be successfully gasified by the supercritical water process as being carbohydrates. Dr. Antal likes to consider successful materials as those that can be fermented to ethanol, that is, it contains sugars. *This ties in well with one of Dr. Antal's other projects which we talked about earlier – his preparation of fermentation precursors.*

- The FY 1999 Peer Review Team stated about this project, even if it were fully successful "it still would run up against the same 5% hydrogen from biomass barrier." That's life; dry biomass contains nominally 5% hydrogen by weight. Dr. Antal reports his yields in grams of gas produced per gram of dry biomass solid, and in mole fractions of the product gases. He has reported total gas yield of up to about 1.3 g of gas per gram of feed solid, and shows nominal relative product mole fractions of 0.3, 0.02, 0.44, and 0.23 respectively for hydrogen, CO, CO_2, and methane. (*Mole fractions always make hydrogen look better!)* If we perform the calculation to convert to grams of hydrogen, we find that Dr. Antal is recovering about 0.032 grams of hydrogen for each gram of biomass feedstock, or about 65% of the hydrogen present. I have attached an appendix with the details of this calculation. If Dr. Antal can produce hydrogen at a higher temperature using his corrosion resistant reactor encased in his pressure jacket, he could recover more of the biomass hydrogen, and perhaps actually pull some of the hydrogen off the water (with the proper catalyst).

- Dr. Antal mentioned that the Codes and Standards (C&S) situation in Hawaii is rather unusual. For boiler-related work (and some of the reactors have boiler components) only boiler inspectors are allowed to have the C&S books. It is difficult for his group to maintain a proper collection of C&S literature.

- Potato waste is one of the more difficult materials to work with because of the amount/type of ash – it's high in alkali content.

- Dr. Antal is concerned about the NREL process analysis that was based on a commercial plant, and did not consider the fact that a cast-alloy reactor is low-cost.

VII Final Thoughts:

Using typical values supplied by Dr. Antal in some of his reports, we calculated approximate efficiency of converting biomass to hydrogen.

1.3 grams of gas evolved from 1.0 grams biomass solid.

Mole fractions of gases evolved: H_2: *0.3*
CO: *0.02*
CO_2: *0.44*
CH_4: *0.23*

A total of one mole of gases would mean:

H_2: *0.3 moles x 2 g/mole = 0.6 g*
CO: *0.02 moles x 28 g/mole = 0.56 g*
CO_2: *0.44 moles x 44 g/mole = 19.36g*
CH_4: *0.23 moles x 16 g/mole = 3.68 g*

Total weight of one mole of gas would be 24.20 g

So 1.3 g of gas is equal to a composite 1.3/24.20 = 0.054 moles of gas, of which 30% is hydrogen. Thus, 0.054 x .3 = .0162 moles of hydrogen. At 2g/ mole of hydrogen, this equals 0.324 g of hydrogen produced for each gram of biomass processed. If the biomass composition includes 5 % hydrogen, the hydrogen production efficiency is about 65%.

This page intentionally left blank.

Technical Evaluation Report

Project: Solar Photocatalytic Hydrogen Production From Water Using A Dual Bed Photosystem
Company: Florida Solar Energy Center, Cocoa, FL
P.I.: Dr. Clovis Linkous
Date of Visit: September 22, 2000
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

The Florida Solar Energy Center (FSEC) is investigating a photoelectrochemical hydrogen production process in which hydrogen production and oxygen production occur in two separate containers linked by a mediator fluid. For several years, the FSEC group concentrated on inorganic semiconductor materials, settling on TiO_2 to evolve oxygen and InP to evolve hydrogen. Over the past year, FSEC has switched to organic pigment-based photocatalysts due to instability in the inorganic-based system.

FSEC believes that since these pigments can utilize a wider range of the solar spectrum, they can evolve hydrogen (and oxygen) more efficiently. They also should not be subject to the same instabilities that beset the inorganic materials. FSEC uses ionization potentials as initial screening tools for the pigments, and then continues the down-selection process via actual gas evolution experiments.

Gas evolution results to date have been disappointing. The best hydrogen-evolving pigment generated just over 100 microliters of hydrogen after irradiating a 6 cm^2 surface of immobilized pigment for six hours with a xenon lamp. This is about 3 orders of magnitude less than theory predicted. Oxygen evolution with its best pigment appeared to be about 4.4 milliliters under the same condition. Subsequent investigation, however, revealed that much of the oxygen was likely coming from photodecomposition of the redox mediator IO_3^-. The mediator was being photolyzed by ultraviolet radiation that was being transmitted through the new quartz reactor.

Currently, FSEC is trying to regenerate oxygen evolution data using a UV filter to prevent mediator decomposition, and to identify better hydrogen generators. The work also includes improved distribution/immobilization techniques for the photocatalysts and cocatalysts.

Project Strengths:

- The dual bed method has the potential of lower cost hydrogen production than other photoelectrochemical processes.
- If pigment-based photocatalysts prove successful, there will be many more candidates than with standard semiconductors. If FSEC can start producing acceptable levels of hydrogen, it will likely be easier to “tweak” the system to improve results.

Issues that should be Addressed:

- FSEC does not appear to be producing acceptable levels of hydrogen. Distribution techniques to blend the photocatalyst and cocatalyst as well as to uniformly spread and immobilize the blend must be developed. This is very likely the source of the low levels of hydrogen. However, there is no data that indicates that the pigments themselves are the proper ones.

- The results to date for the entire oxygen-evolution side of the process (since FSEC started using pigments rather than semiconductors) is flawed. The errors resulted from ultraviolet photolysis of the redox mediator when a (ultraviolet transparent) quartz reactor was used. It was unfortunate that a large amount of data (Exhibit 2) was generated using the quartz reactor.

- The 6-10 acre site needed to produce adequate hydrogen for a refueling station (assuming an 8% solar conversion efficiency) may make the whole concept unfeasible except under special conditions.

II Introduction and Background:

I visited **Dr. Clovis Linkous** and his associate **Dr. Darlene Slattery** at FSEC in Cocoa, FL to observe and discuss their dual bed photoelectrochemical hydrogen production system.

The dual bed photosystem project has been a part of the DOE Hydrogen Program intermittently for the past several years. The premise is that water can best be split into hydrogen and oxygen photoelectrochemically if the two half reactions are physically separated from one another in separate containers, connected by a redox mediator. Thus, each half- system can be tailored to utilize a wider range of the solar spectrum including low energy photons so that they each half can better produce its respective product (hydrogen or oxygen). The two beds also facilitates the separation of the product gasses.

The project has recently shifted from using the inorganic photocatalysts TiO_2 (for oxygen evolution) and InP (for hydrogen evolution) to organic pigments. FSEC was concerned about the lack of stability of the inorganic semiconductors, especially InP. In addition, the use of organic pigments will allow one to take advantage of the visible portion of the solar spectrum. While some of our discussion involved general information on the dual bed system, a major portion of the day was spent on the organic pigment concept.

III Initial Discussion:

FSEC went through a screening process in order to pick the organic pigments best suited to oxidize water and to evolve hydrogen. This involved an investigation of the band-edges of the pigments – looking at the highest occupied molecular orbital and the lowest unoccupied orbital for the pigments. Thus, electron affinity and ionization potential (IP) levels are the key parameters.

FSEC is still screening pigments; they want to make sure that they have the best pigments before they scale up. They hope, in FY 2001, to identify the best pigments, and perform a modeling effort to see what their system can do realistically. They believe that they need 8% efficiency to be successful, and will use the model to develop a sensitivity correlation between that efficiency level and kinetic and design parameters.

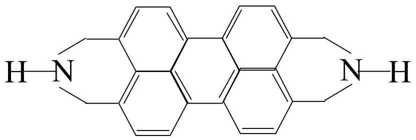
Since oxygen evolution ($2\ H_2O \rightarrow 4H^+ + O_2 + 4e^-$) is a more complicated, four electron/mole O_2 process compared to the two electron/mole H_2 ($2e^- + 2H^+ \rightarrow H_2$) process for hydrogen evolution in the other bed, FSEC decided to tackle the oxygen side first.

Oxygen Evolution:

FSEC used IP to chose pigment candidates for oxygen evolution first by conducting a theoretical screening and then measuring IP using ultraviolet photoelectron spectroscopy at the University of Arizona. Based on this, they zeroed in on about twelve different organic pigments, all of which contained fused ring structures with oxygen and nitrogen either in a ring, or attached to a ring. The pigment color comes from the conjugated electrons. These π electrons also determine the bandwidth; the more π electrons, the smaller the bandwidth. The presence of the "hetero" atom (O or N) lowers the highest occupied molecular orbital and increases its ability to split water.

FSEC uses a xenon lamp (strong ultraviolet component) to irradiate a vessel with quartz windows to evolve oxygen. Earlier, they had been using a pyrex system. Pyrex, however, filtered out the high energy (< 330 nm) ultraviolet radiation. When they switched to the quartz system, they found that they were irradiating the redox mediator (IO_3^-), causing evolution of oxygen, and giving a falsely high reading of this parameter. They have since inserted an ultraviolet filter, which eliminated the problem. *We will address this in more detail later in this report.*

Drs. Linkous and Slattery have found that the best oxygen-evolving pigments are based on perylene structures. *Perylene is a derivative of anthracene, and contains a high degree of pigment-enhancing conjugated electrons.* Specifically, FSEC is considering perylene diimide (*generic structure shown*) derivatives, and is currently looking at structures containing fluorinated side chains. A fluorinated alkyl side chain will increase the conductivity of the pigment by introducing enough molecular disorder to force the π electron clouds closer to one another. FSEC is waiting for results of the latest experiments involving the fluorinated system. Dr. Linkous considers this type of study (investigation of side chain effects) as one of the key upcoming tasks that FSEC should be doing.



Perylene Diimide Structure

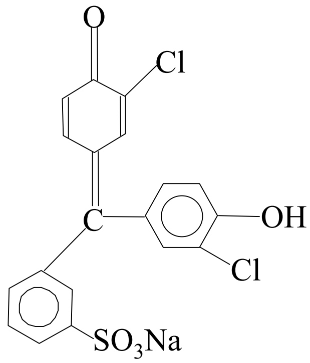
While evolution of oxygen is of course important, a demonstration showing high hydrogen evolution efficiency would be a stronger statement.

Hydrogen Evolution:

Early in the pigment selection process, FSEC considered the same pigments for hydrogen evolution as for oxygen evolution, but they were "not the best". Better hydrogen-evolving pigments were found from the photography industry. These are generally soluble, but can be precipitated as barium salts.

One group of materials that FSEC is looking at closely for hydrogen evolution is triaryl methines. These can have colors complementary to the oxygen producers, that is, they don't absorb the same wavelength light. Therefore, one is able to increase efficiency by stacking one bed atop the other.

By changing the positions of the attached halogens and hydroxyl group or the number of sodium sulfonate groups, Dr. Linkous says that they can change the pigment's color (thereby increasing efficiency) without reducing the amount of hydrogen that will be evolved.



Typical triaryl methine

FSEC, at the time of my visit, had not yet tested this family of pigments for hydrogen-evolution. (*In fact, much of the earlier work that was done and reported on hydrogen-evolving pigments involved a totally different class of materials – phthalocyanine compounds.)*

IV Tour:

Drs. Linkous and Slattery took me through their photolab where they were running an oxygen evolution experiment. The photocell is a 1-inch diameter, 3-inch long cylindrical vessel with a "bump" at the top as an oxygen collection area. Lexan (a polycarbonate) is used to immobilize the pigment particles. They soften the Lexan with methylene chloride, and stir in the pigment particles. (Dr. Linkous indicated that they would have to look at scale-up options for this.) The reaction vessel is static (sealed). The pigment is irradiated with a xenon lamp; ultraviolet radiation is filtered out. FSEC runs the oxygen evolving photolysis under an atmosphere of helium, and the hydrogen evolution counterpart under argon.

I was also shown a reactor in which they are fluorinating a perylene diimide. Dr. Linkous indicated that if the fluorinated species does not produce the desired results (a satisfactory oxygen-evolving species), FSEC might next consider a dye-sensitized system next. Alternately, they may want to look at making photoelectrodes (ala NREL and U Hawaii) out of the pigments. *It would appear that FSEC may believe that no other options for* *pigment based dual bed photochemistry exist.* Dr. Linkous did indicate that they are not "asking for a license to screen pigments forever."

In a separate area, I was also shown a solar simulator that FSEC has recently acquired. It has the power of about one and one-half suns (1.5 kW/m^2). The mixed gas/xenon lamp simulates the entire *(middle of the)* solar spectrum from the infrared to the ultraviolet. It runs off of a power supply of several hundred amps.

V Questions and Answers:

Prior to our meeting I sent Dr. Linkous a group of questions/discussion topics. In addition to the oral answers provided by Drs. Linkous and Slattery, Dr. Linkous also provided me with written answers.

Many of my questions were based on the relatively high reported oxygen yield compared to the hydrogen yield, the apparent emphasis on oxygen evolution to begin with, and the use of ionization potential as a pigment screening tool.

1. **Please discuss how you obtained an 8% solar to hydrogen efficiency estimate, and a $13/MMBtu cost for hydrogen based on that efficiency.**

"This was done by making current and future (10 years) estimations of materials costs and combining them with realistic solar conversion efficiencies. The original work appeared in the proceedings of the 12th World Hydrogen Energy Conference. I supplied a few of the numbers, but most of the work was done by Dave Block.

"Assumptions are:

Desert Southwest (6.44 kWh/m^2)
Glass paneling: $10/m^2
Balance of system to collect H_2 and O_2 and to hold the cells at the correct latitude tilt angle: $120/m^2. This value is the same as that which is commonly used for photovoltaic systems.
Capital cost is depreciated at 6%/year over 20 years.
Operating cost/year is taken as 10% of the initial cost.
Photocatalyst cost: $50/g (this gives us plenty of leeway for synthetic intricacy)
Photocatalyst loading: 5 mg/cm^2 (actually some of our earlier work would suggest as low as 2 mg/cm^2)
Solar transmission losses (through glass covering and water layer): 11 % and 5%, respectively.
Fixed latitude tilt angle (modules not heliostated).

"The conclusion is that if you can operate a dual bed system at 8% efficiency, the H_2 could be sold at $13/MBtu. There are literature citings where the conversion efficiency of semiconductor particulates for H_2 evolution has been as high as 40%, but that was done with the use of sacrificial electron donors. Our value is based on using water as the ultimate electron donor. In the next phase of the project, our task will be to sum the various optimized structural and material attributes of the system to show how the 8% value can be reasonably achieved."

The 8% number is a "reasonable guess" based on what other semiconductor photoelectrochemical systems have obtained. Dr. Linkous considers the pigments to be, essentially, semiconductors.

The reference for the Dave Block paper is: "Comparative Costs of Hydrogen Produced from Photovoltaic Electrolysis and from Photoelectrochemical Processes" by D.L. Block, in Hydrogen Energy Progress XII, Proceeding of the 12th World Hydrogen Energy Conference*, Buenos Aires, Argentina 21-25 June 1998, J.C. Bolcich and T.N. Veziroglu, Editors, International Association for Hydrogen Energy, pages 185-194.*

It should be noted that Dr. Block's analysis assumed the use of the inorganic semiconductors that FSEC was using two years ago, not the organic pigments. It also shows the higher efficiency and lower cost that can be derived from the dual bed process.

2. **Has your previous work shown significant reverse reaction problems? Would you expect this phenomenon to be more or less of a problem with organic pigments?**

"We have run experiments where we stacked the deck toward the reverse reaction as much as possible (continuous O_2-purging, high iodide concentration) in order to look at the worst possible case. Even then, we could not halt water-splitting; the rate of O_2 consumption was only a small fraction of our measured rates of production. Furthermore, there is no reason to believe that the organics would promote the reverse reaction to any greater extent than the inorganics. If anything, it would be less."

Dr. Linkous uses the term O_2-purging to mean adding oxygen, not removing oxygen.

3. **Why do you believe that pigments will work better than semiconductors. What properties of pigments led you to consider them? For what reason did you abandon semiconductors?**

"In our view, the pigments are semiconductors. The properties of semiconductors are enabled by their segregated distribution of filled and empty electronic energy levels. Under these conditions, conductivity must be achieved by creating charge carriers (via injection, heating, or of course light absorption). This is in contrast to metallic conductors where a high density of charge carriers is always present. The arrangement of energy levels and the photoelectrochemical behavior of our pigments are consistent with the definition of semiconductors. While rigorously our pigments might be better classified as photoconductors, the same consideration would have to be applied to TiO_2 and many other inorganic photoelectrode materials."

Dr. Linkous indicated that the main difference is between light absorption and conductivity. The pigments will absorb light efficiently with a much thinner surface deposition. However, since the pigment particles are vander Waal's solids rather than crystals they lack the conductivity levels of the inorganic semiconductors. It is important to keep the pigment particles small so as to minimize conductivity losses.

As to why FSEC is moving away from inorganic semiconductors, there are simply not that many materials out there, according to Dr. Linkous. They were already using what they considered to be the best. Nevertheless, TiO_2 (anode, oxygen evolution) will always have a limited efficiency due to its narrow bandwith. InP (cathode, hydrogen evolution) has a good bandwidth (1.1 ev), but is not very stable in iodate. The phosphide decomposes in the presence of an electron acceptor. The other high bandwidth inorganic semiconductor, GaAs (1.3 ev) is very unstable in aqueous systems. On the other hand, there are many more organic pigments that can be synthesized and explored.

This may be the crux of the entire matter: there's nowhere new to go with inorganic systems, and the ones used to date are chemically unsatisfactory.

4. **In your FY 2000 paper, you presented a plot (*Exhibit 1*) for experimental vs. calculated ionization potential. You plan to use this as a correction mechanism to determine IP for a series of pigments by a simpler method, thereby screening the pigments. How accurate/reproducible is the plot? (For example, it appears that one data point lies halfway between the least squares line and a line that could be drawn for y=x, that is, for IP(exp) = IP(calc).)**

"Within an analogous series of compounds, the correlation is quite good. An R^2 value of 92% was achieved in this case. The analogous series that we are most interested in consists of those organic pigments that have at least three fused rings and contain oxygen, nitrogen, or both. That may sound restrictive, but actually most of the compounds worth considering fit this description. If somebody suggests a pigment to us, we can run a 25 minute calculation on our p.c. and determine whether it will be good for water-splitting."

Dr. Linkous said that if they went to a different class of compounds, they would have to generate a new correlation curve.

Despite the 0.92 correlation, I was concerned that there were few points and a nontrivial amount of scattering. If we look at Exhibit 1, one of the five points shown is as close to a hypothetical y=x line as it is to the fitted line. It sheds a little doubt on the screening process. (*Perhaps a small point.*)

5. **In the FY 2000 paper, you include in your oxygen evolution table (*Exhibit 2*), an entry for "acrylic blank". You indicate that this may represent background noise and must be subtracted out. Does this mean that only your top four pigments (Perylene Diimide through Perylene TCDA) outperform TiO_2?**

"It turns out we were wrong about the acrylic blank. The acrylic blank value had nothing to do with the acrylic itself. We tested several other polymer substrates and got the same result. We ultimately discovered that the O_2 was coming from a direct photolytic reaction between the deep UV part of the Xe lamp spectral distribution and the IO_3^- redox mediator. Inserting a UV filter in the beam eliminated the effect. It hurt us badly to present that result to the review panel. Now they are speculating that we can't even make H_2 using visible wavelength light. They are plainly wrong, and we now have the data to prove it, but it's too late to have any impact on their harsh evaluation.

"We have gone back and tested some, but not all, of the pigments. Certainly the four that we identified the first time through still outperform TiO_2 and will provide plenty of work for us to do."

Given the fact that most of the oxygen evolution was due to IO_3^- *photolysis, it appears that all of the numbers in Exhibit 2 are incorrect. New oxygen evolution rates (or* *amounts) need to be determined with a UV filter in place for screening purposes. Oxygen evolution is further addressed in the comments to the next question.*

6. **There appears to be an abundance of data for oxygen evolving pigments, and only a small amount of data for hydrogen-evolving pigments. In addition, the amount of hydrogen formed appears to be less than 1/10 the amount of oxygen on a molar basis. Theoretically, we should be getting twice as much hydrogen as oxygen. Are the differences in the results simply due to different sized reactors, or is there an actual disparity? Are there plans to screen more pigments for hydrogen?**

"The UV effect described in the previous question accounts for the disparity. Actually, the rate constants for both reactions appear to be in the same ballpark. From a design and performance standpoint, it is desirable to have similar rate constants for both O_2 and H_2 evolution. This is especially true for future configurations of the dual bed design, since the photocatalytic layers will be stacked upon one another in a tandem arrangement.

"Yes, we will be screening more pigments for H_2. The reason we have emphasized O_2 evolution over H_2 evolution is that it is the more challenging problem. You need to be able to generate a rather large, positive potential to electrolytically evolve O_2 from water. We determined that for any semiconductor substance to oxidatively split water, it should have an ionization potential of at least 7.5 eV. As it turned out, most pigments do not have a sufficiently large IP. To look at it another way, it is easy to find other organics that have a large enough IP, but they are poor absorbers of solar radiation. Relatively few of the endless array of organic compounds fulfill the conditions of large IP, visible wavelength absorption, and photochemical stability that we were looking for. Indeed, we deserve some credit for quickly coming up with a short list of pigments on our modest resources.

"In contrast, there are a good many pigments whose electron affinity would indicate they are capable of water reduction to H_2. Admittedly, we had spent comparatively little time looking at H_2-evolvers going into the annual review meeting. We will certainly spend more time looking at H_2 evolution in the next project period."

The answers to the last two questions can be summed up with one comment: The oxygen-evolution data were incorrect. Unfortunately it was "wrong the wrong way" – the oxygen evolution numbers were incorrectly too high as opposed to the hydrogen evolution numbers being incorrectly too low. The comments raised by the Review Panel last spring that FSEC was not making enough hydrogen still stand.

7. **Your Annual Review presentation indicated that you planned to look at new membrane impregnation techniques. This task is not evident in your AOP write-up. Has it been abandoned? Do you feel that these techniques would not effect the degree of hydrogen formation?**

"The impregnation technique effort is hidden in the task 3a, "Module Construction-photocatalyst and co-catalyst distribution." We are always looking for better ways of immobilizing the photocatalyst without reducing its activity. The same goes for the co-catalyst. The use of co-catalysts has been quite effective in improving gas evolution rates in both photocatalytic modules. Despite the need to work on better distribution techniques, we think one of great advantages of the dual bed approach in comparison to other photoelectrochemical methods is that when we finally develop an active system, it should be relatively easy to scale things up. "

8. Your results for hydrogen evolution in your FY 2000 paper does not show a comparison to InP. What is the comparison?

"We did not present data on InP because it is fundamentally unstable in the redox electrolyte that we are using. The initial rates of H_2 evolution look impressive, but over the course of a few hours, gas evolution grinds to a halt. At first we thought it was just a photostationary state effect (equalization of forward and reverse reaction rates), but X-ray photoelectron analysis showed convincingly that the phosphide was being oxidized to the oxide ($InP \rightarrow In_2O_3$) and becoming inactive. Our first inclination was to call it photocorrosion, since many photoelectrodes are plagued with that problem, but ultimately we found that the alkaline iodate solution itself could decompose InP without even turning the light on."

Again we see a potential problem with the iodate – the redox mediator. It produced oxygen in one bed under ultraviolet radiation, and also could have been decomposing the photocatalyst InP in the other bed resulting in a falsely high hydrogen evolution reading. It would appear that stability of the photocatalyst (pigment or inorganic) in the presence of the mediator is a necessary screening procedure.

Dr. Linkous indicated that the InP/iodate reaction only happens in basic solution, and that InP might work in an acidic medium. One possibility might be to use WO_3 as the oxygen generator. This could be done in an acidic environment, which would in turn inhibit InP oxidation, thus increasing the value of InP as the hydrogen producing photocatalyst. A group in Switzerland has been looking at WO_3 systems. However, Dr. Linkous prefers to stick with the pigment system in an alkaline environment at this time. He says that he believes he can maximize efficiency by stacking the two beds, "one red, one blue." Dr. Linkous said that his goal was to demonstrate the proof of concept of evolving both gases using the same redox electrolyte; they were not focusing on hydrogen.

There may be many scenarios by which one of these systems may work. However, to date, they are not working. There has been no pigment system that has been demonstrated to produce encouraging amounts of hydrogen – or oxygen, for that matter.

9. You give results for oxygen and hydrogen evolution in units of volume. How large a system is used, and how long must it run to produce these volumes?

"The samples were 3.0 cm in diameter, so that the total surface area was ~7.1 cm^2. The actual illuminated area was somewhat less; 6 cm^2 is probably a good value. Photolysis time is 6 hours. The gas evolution rates from these sample were considerably less than when we use the same photocatalysts as free powders. The thing that really hurt us was the primitive way of admixing the co-catalyst powder. For the inorganic photocatalysts, we distribute the co-catalyst by performing a chemical reduction of a metal salt, a sort of electrodeless plating, but with the organics we had early on encountered some problems with this approach, and had gone away from it. In other photocatalytic research projects, we have been fairly successful at making photoactive formulations via direct admixture of powders, but for these experiments, it did not work out as well."

So, the best reported value for hydrogen evolution in Exhibit 3, 113 micro liters for copper phthalocyanine, is based on 6 cm^2 of photolysis area over 6 hours. This is not satisfactory, as Dr. Linkous admits. (He says, that it should be in the 3-5 milliliter range.

This is discussed after the next question.) Note that FSEC is now looking at triaryl methines. Oxygen evolution levels, as we have discussed, are undetermined.

Dr. Linkous attributes the low hydrogen evolution rate to the poor method of distributing the photocatalyst. It is necessary to immobilize the powder; if you do not, the two beds would mix. Otherwise they would go with a free powder. There are several things that FSEC can try; they just need time.

This would mean that it could be the distribution process rather than the phthalocyanine – or maybe it's both. I would perhaps try a few distribution experiments first before moving to new materials.

10. Please conceptualize a system where a dual bed photoelectrolytic system is providing hydrogen for, say, a vehicle refueling station. How large would the electrolytic system have to be? How often would you have to replace pigments, mediators, etc.?

"Let's make the following assumptions:

Solar conversion efficiency: 8%
Solar irradiance: 1.0 kW/m^2
Daily insolation: 6 hours at maximum solar irradiance (6 kWh/m^2)
Tandem cell (stacked) configuration
Station open from 7:00 AM to 9:00 PM
Steady flow of customers (no down time)
Single pumping station (we're not ready for self-serve)
Vehicle refilling time: 5 minutes
Capacity of vehicle fuel tank: four cylinders, 43.8 liters each, 2200 psi.

"As for lifetime performance or replacement costs, all we know at this point is that most of our pigments have shown no degradation after 6 hours.

V = the volume output of H_2 at 1.0 atm and room temperature per unit area per day.

$$= (0.08)(1.0\ \mathrm{kW/m^2})(10^3\ \mathrm{W/kW})(1\ \mathrm{J/W\text{-}s})(1\ \mathrm{cal}/4.184\ \mathrm{J})(10^{-3}\ \mathrm{kcal/cal})$$

$$(1\mathrm{mol}/56.6\ \mathrm{kcal})(24.5\ \mathrm{L/mol})(3600\ \mathrm{s/hr})(6\ \mathrm{hr/day})$$

$$= 178\ \mathrm{L}\ H_2/\mathrm{m}^2\text{-day}$$

C = fuel capacity of each vehicle at same pressure and temperature as stated above

$$= (4\ \mathrm{tanks})(43.8\ \mathrm{L/tank})(2200/14.7)$$

= 26,220 L (about enough to cruise at highway speeds for 2 hours)

A = area required to supply the entire daily station demand for fuel H_2.

$$= \frac{(14\ \mathrm{hr/day})(12\ \mathrm{cars/hr}) \times C}{V}$$

= 24,746 m^2, or ~ 6 acres

"That's a lot of real estate, but the numbers have little to do with the dual bed technology itself. Rather, it's a reflection of the intensity of sunlight versus the energy consumption of an automobile."

Dr. Slattery added that they are uncertain as to how long a pigment will last. She felt that doing a life test on a material that is just making microliter quantities of hydrogen would be premature. Her "gut feel", however is that the pigments will hold up quite well; these pigments have been used for a number of applications. If holding up means a month or a year, she's not sure.

By way of comparison, let's first use Dr. Linkous' estimate of a potential 8% efficiency for a 1 kW/m^2 *solar irradiance for 6 hours per day. He calculates the production of 178 liters of hydrogen per* m^2 *per day under these conditions. Coincidentally, his bench-scale (6* cm^2 *active surface area) reactor is also run for six hours. If it also were 8% efficient and were exposed to 1 kW/*m^2 *irradiance, it would evolve:*

$6\ cm^2 \times (1\ m^2 / 1 \times 10^4\ cm^2) \times 178$ *liters = 0.107 liters (or 107 ml) hydrogen.*

The best data in Exhibit 3 show about three orders-of-magnitude less hydrogen evolution, which could be attributed to less than maximum simulated solar irradiance, less than perfect photocatalyst distribution, and/or perhaps an inferior photocatalyst. Testing the system using the aforementioned solar simulator might be in order to best approximate irradiance. Addressing distribution is something that FSEC proposes as part of the FY 2001 work. As mentioned earlier, FSEC is already looking at methines for hydrogen evolution.

Dr. Linkous assumed four 2200 psi, 43.8 liter hydrogen tanks aboard an automobile. That works out to 2.34 kg of hydrogen. (Capacities in the 3-5 kg range are generally used.) His refueling station services 12 cars an hour for a 14 hour day, or 168 cars/day. This requires a field of dual bed arrays totaling about six acres of surface. (If we use a 4-kg figure, it comes to a little over 10 acres.)

VI Additional Discussion:

The pigments that are being evaluated are not uncommon, and are in fact, used in the photography industry.

Dr. Linkous indicated that the difference between a "pigment" and a "dye" is similar to the difference between a paint and a stain. Pigments (and paints) contain particles that are insoluble in their carrier, while dyes are soluble.

Exhibit 1. Plot of Experimental vs Calculated Ionization Potentials from FSEC Report with a y=x Line Added.

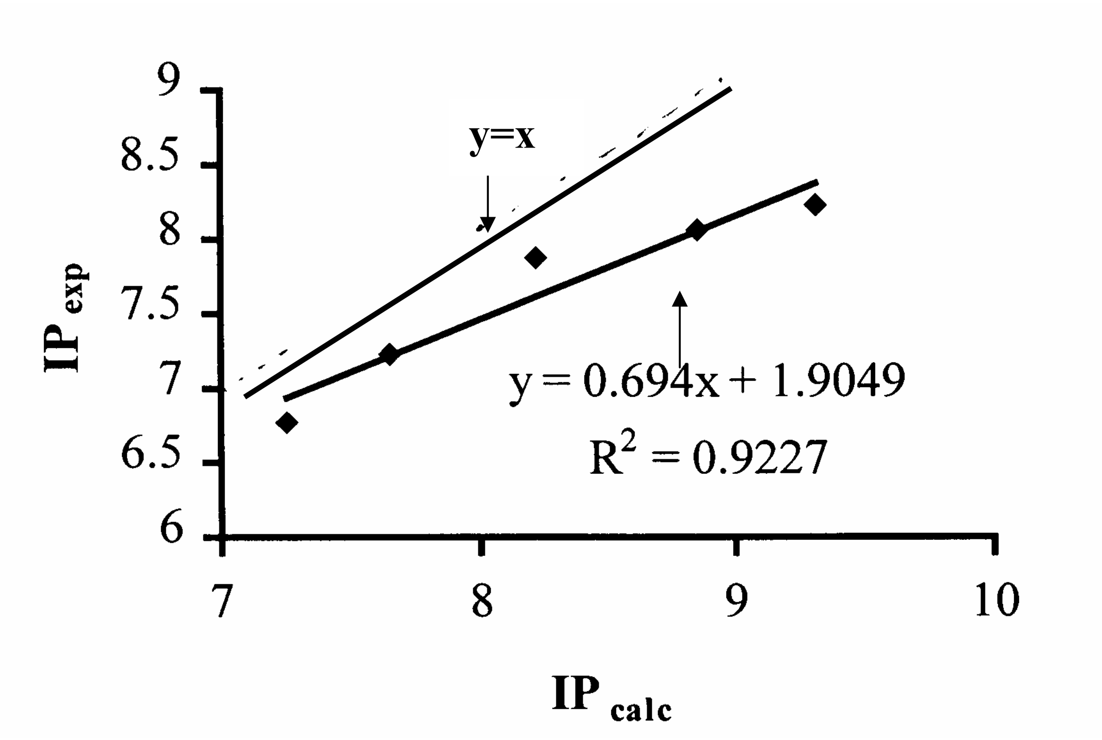
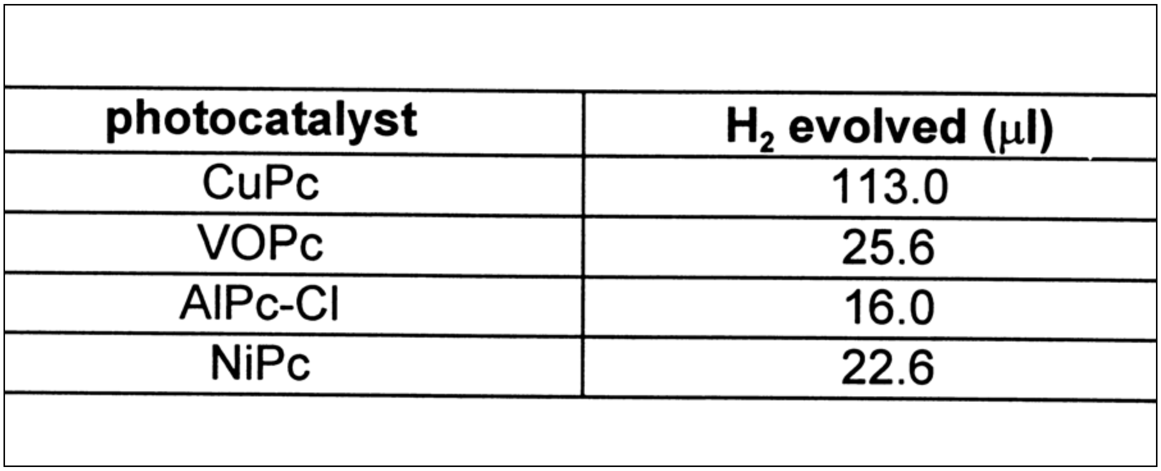


Exhibit 2. Oxygen Evolution with Various Organic Pigments (from FSEC FY 2000 Report)

Photocatalyst	O_2 Evolved (ml)
Perylene Diimide	4.4
bis(p-chlorophenyl) DPP	3.6
Indanthrone	3.3
Perylene TCDA	3.2
Pigment Red 177	2.6
Indanthrene Yellow	2.0
Quinacridone	1.8
Isoviolanthrone	1.5
Acrylic blank	1.5
Indigo	1.4
Dimethoxyviolanthrone	1.3
TiO_2	1.3
Indanthrene gold orange	0.9
Indanthrene Black	0.7

Exhibit 3. Hydrogen Evolution with Phthalocyanine-based Organic Pigments (from FSEC FY 2000 Report)



photocatalyst	H_2 evolved (μl)
CuPc	113.0
VOPc	25.6
AlPc-Cl	16.0
NiPc	22.6

This page intentionally left blank.

Technical Evaluation Report
Project: Production of Hydrogen Through Electrolysis
Company: Proton Energy Systems, Rocky Hill, CT
P.I.: Rob Friedland
Date of Visit: December 7, 2000
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

Proton Energy Systems is a small company (about 40 people) located in Rocky Hill, CT, who, in the words of Rob Friedland, Vice President of Operations "exist to make PEMs." They have two major types of products – stand-alone electrolyzers (HOGEN® series) and regenerative fuel cells (UNIGEN® series). There are two concepts for UNIGEN – a box containing one stack that will serve as both an electrolyzer and a fuel cell (unitized system), and a box that will contain two discrete stacks – an electrolyzer stack and a fuel cell stack (discrete system). Presently, Proton is mainly involved with cost reduction of their products and is pursuing this with both DOE and internal funds.

The DOE Hydrogen Program is currently funding only the electrolyzer work. This includes cost-reduction-based improvements on Proton's small HOGEN 40 (6 kW electricity intake; produces 40 standard cubic feet per hour (scf/h) of hydrogen) and larger HOGEN 380 (60 kW of electricity in; 380 scf/h hydrogen). Proton uses a "holistic" approach to cost reduction and is thus addressing cell stack, power conditioning and interfaces, and system costs.

Project Strengths:

- Proton personnel come from a long history of dealing with PEM technology, both electrolyzer and fuel cell. As such, they are well qualified for the present endeavor.
- The cost-reduction-based development that Proton is currently involved in appears to be a sound way to approach the project at this stage.
- The UNIGEN options provide a good potential alternative to battery storage for renewable-based remote power.

Issues that should be Addressed:

- The cost targets for the electrolyzer seem to be a little higher than others I have seen. Proton has indicated that the reason for this is that cost estimates by others may be too low. If public monies are being used for development of the electrolyzer, it is in the public's interest to see how the potential market is being impacted by these higher costs.

- While the emphasis on cost reduction is justified, and the approach (discussed in the report) of picking off "the low hanging fruit" is fine, we get very little feeling for how big an effort is needed for each of the various electrolyzer parts. We do recognize, however, that some of these data are proprietary.

II Introduction and Background:

I met with four members of the Proton team. They included **Rob Friedland**, Vice President of Operations, who acted as my host; **Trent Molter**, Vice President of Engineering and Technology; **John Speranza**, Systems Engineer; and **Fred Mitlitsky** (formerly of Lawrence Livermore National Laboratory), Director of Advanced Engineering.

Proton was founded in 1996 by former employees of Hamilton Standard looking to develop commercial products derived from the military-based products of their former employer. Proton's products are currently aimed at the industrial gas market and backup power market. Later, as alternative and renewable energy opportunities increase, they plan to include the fuel cell refueling market as well as the renewable and distributed power markets.

The HOGEN 40 is a "real commercial system" now. In the industrial gas market, it replaces cylinders and tube trailers.

We spent several hours discussing the Proton electrolyzer project, reviewing the questions that I had sent to Mr. Friedland, and taking a tour of the facility.

III Tour:

The tour consisted of being shown a series of HOGEN and UNIGEN systems in various states of completion as well as being shown components of both. A HOGEN 380 was pointed out as being the same type as what was used at the Arizona Public Service demonstration. While the system ran very well in Arizona, Proton did point out that it was "babied" – it never got too cold in Tempe, for one thing.

Units that were run under more difficult conditions did have some technical issues – mainly life cycle and cell stack problems brought about by large temperature and humidity gradients. These problems caused Proton to step back to smaller units.

Two items were pointed out while looking at an opened HOGEN 380 box: Proton pressurizes the electrical side of the box to keep hydrogen out of it and avoid a potential ignition. Proton is replacing many of their electrical components with a single circuit board. This will result in a reduction in cost from about $2000 to about $250.

Other systems that I was shown included:

- A test HOGEN 40 that they use to run parametric studies on cell materials, water flow, current density, and load – there is more "balancing" to be done in an electrolyzer than in a fuel cell.

- Separately, Proton is testing an electrolyzer that will produce hydrogen at 2,100 psi.

  This may be one of the most important pieces of equipment that Proton is developing.

- A "Chrysalis" electrolyzer, a small 300cc hydrogen generator for gas chromatographs

- Components of a prototype 1kW hydrogen/air regenerative fuel cell with discrete electrolyzer and fuel cell stacks

- A 250 W unitized regenerative hydrogen/oxygen system for EPRI

- A 50 W unitized regenerative system for NASA – This is meant for zero gravity operation. It uses no pumps, under the premise that fewer components result in higher reliability. Proton has a Phase II Small Business contract with NASA for a 1kW follow-on project.

- Several other 4-cell unitized fuel cells

IV Questions and Answers:

I sent Mr. Friedland a set of questions that then became the basis for a major part of our discussion. These are shown, and discussed, below:

General Issues:

1. **In Proton's current focus on electrolyzer technology, what efforts are being made to ensure that the new technology will be consistent with regenerative fuel cell technology? How necessary is it for there to be a consistency?**

"Proton defines regenerative fuel cells two different ways. We consider a system with a unitized cell architecture as well as a system with discrete electrolyzer and fuel cell components both to be UNIGEN systems. This is done because the system (i.e. the box) will still make gas and deliver electricity, but the architecture will be determined by the application the box is serving. To this end, the fundamental technology advancements made on the electrolyzer carry over well to the regenerative fuel cell. In the discrete component system, the transfer is direct and obvious. In the unitized cell, the basic cell support features, fluids distribution, pressure capability and materials choices all are valuable and consistent.

"Proton's business strategy relies on the fact that much of our technology carries forward into our other products and technologies. That is the essence of PEM technology and a large part of the outside attraction to our story. As for this program specifically, we will not be tracking or forecasting how the technology will work in our regenerative systems."

Technologies that are consistent with electrolyzers and regenerative fuel cells include electrodes and flow field assemblies. High pressure is important for both electrolyzers and regenerative systems, but there is not necessarily a consistency here.

Proton has shown that they can be as efficient with the unitized regenerative system as with the discrete type. They claim performance has been as high with the unitized system as with a discrete electrolyzer or a discrete fuel cell.

It is all an applications issue. In some cases, a unitized system makes sense; in others, it does not. Mr. Friedland cited backup and uninterruptable power needs as scenarios in which a unitized system would not be applicable. You would want a small electrolyzer, one that could run off of a trickle charge of electricity, but you would need a large fuel cell; when the main power goes off, you need electricity quickly.

The consistency would obviously be greater between electrolyzers and the discrete UNIGEN system, where there is a separate electrolyzer stack.

The question was based on the fact that despite the interest that has been generated about regenerative fuel cells over the past several years, the focus seemed to be moving away from this important area. Seeing some UNIGEN systems, however, and hearing the Proton philosophy on them reassures me that this is not the case.

The UNIGEN discrete system in particular makes a lot of sense; it allows for single non-stack components and for more efficient sizing of stacks.

2. Why is electrolyzer technology considered the “most difficult and critical link?”

“As we look at storing energy from renewable sources and having that energy available on demand to meet a varying load requirement, a device is required that can handle input from an intermittent source like renewables, store that energy, and respond like a battery to create that energy on demand. The electrolyzer is one of the only ways to enable that reaction, especially in off-grid applications where alternative fuels are either not available or not easily transported for use.

“The ‘difficult’ part comes in the fact that the electrolysis reaction is a more difficult reaction to enable, at pressure, than the fuel cell reaction. Few companies have historically been able to manufacture reliable electrolyzers especially at elevated pressures. Much of this can be attributed to the fact that the cell architecture is dramatically different in a PEM electrolyzer than that of a fuel cell, including the type and thickness of membrane and the formulation of the catalysts for the electrodes.

“The ‘critical’ part comes from the fact that the key to sustainability in an energy system is for it to work without the need for logistical fuels and constant external involvement and support. The only way we know of to harness solar or wind power and convert it into an alternative form of energy is through electrolysis.”

There are not many people working on electrolyzers today. During the ‘70s and ‘80s there was very little work done at all. Very few, according to Proton, have been able to get their “arms around the electrolyzer” since the ‘50s.

Mr. Friedland added two more facts that result in electrolyzers being more difficult to deal with than fuel cells: 1) seal technology needs to be more sophisticated because you are "making pressure" and 2) the higher voltage makes for a harsher electrochemical environment.

These are reasonable arguments for continuing to push the electrolyzer side.

3. **You indicate that cost-reduction work will be (is being) performed on the cell stack, power conditioning and the renewable interface, and on the overall system. What level of cost reductions is being targeted in each area?**

In the next few years, power conditioning and system costs will be targeted. That is where there is much "low hanging fruit" to be addressed. One key early target area will be circuit board improvements. Stack cost reductions will come later. After 2005, Proton feels that they will be going into mass production (10,000-20,000 units per year). This will lower the costs as well. Of course, costs would be lower still with a million units produced per year, but Proton recognizes that goal as "unrealistic."

Progress to date for cost reduction was presented, but the data are proprietary. Suffice it to say that Proton believes that they are currently beating their goals.

No actual numbers were presented for the cost, or cost reduction, of the major system areas (i.e., stack, power conditioning, etc.). Some numbers were presented for individual materials and components, and these appear in various areas in this report.

4. **In your FY2000 Annual Review report you cite an overall short term cost target of \$1000/kW and ten-year cost target of \$500/kW for hydrogen production using your HOGEN® electrolyzers. Figures 2 and 3 in that paper** (*reproduced as Exhibit 1*) **appear to show the projections in terms of cost per system, that is, cost per 6kW for HOGEN 40, and cost per 60kW for HOGEN 380 (assuming I am interpreting it correctly). If this is the case, it appears that you only get to about \$750/kW by 2010 with the smaller unit, and you may be hitting an asymptote. Do you see small units as viable at this cost of hydrogen?**

"In general, it is our belief that the value of being able to scale well to small power levels will allow for some higher pricing, up to \$1000/kW. While we feel that other technical advancements could bring our costs into line with our larger system projections, we are confident that the differences are acceptable, especially in our early entry markets like telecommunications applications. On the DOE program, we have contracted with a consulting group to ascertain price levels and offer third party projections of acceptable pricing and competitive analysis with other technologies and have also acquired the latest information from Frost & Sullivan with regard to the renewable markets."

Proton (*perhaps chiding others in the industry*), claims that it's cost figures are built on actual and projected numbers. They are not based on a "dream." Therefore, their numbers might be higher than those of others who project costs off of a laboratory system.

Proton agrees that the HOGEN® 40 probably will be about $750/kW in 2010, but believes that to be acceptable.

I wonder as to how acceptable the electrolyzer costs actually will be for both the 6 kW and the 60kW system. I have seen numbers more in the $300-400/kW range. Perhaps Proton's numbers (as they have stated) are more realistic. If so, the question becomes: how do these higher (or more realistic) numbers affect the potential market?

Cell Stack Questions:

This area was discussed in detail during my visit, although no written answers were supplied. Trent Molter led the discussion for Proton.

I sent Dr. Wilson a set of questions that then became the basis for a major part of our discussion. These are shown, and discussed, below:

5. **What methodology will be used for down-selecting components?**

To get started, Proton used a "brute force" approach. This included big tie-rods, machined end plates and spring washers, as well as stainless steel for one (the negative) endplate and aluminum for the other. The important thing was to get it to work. (In the near-term, they will continue to use stainless steel and aluminum plates.) Now, their goal is to reduce materials and labor costs. They are therefore using a modeling effort (using Pro Engineer software) with cost a critical parameter. There is very little trial and error. However, they do expect to use a "bake off" for the final down-selection.

6. **Is the plan to look only at metal endplates, or will you be considering composites as well?**

Yes, Proton is considering composites for the positive (currently aluminum) endplate, but the key driver is not weight, but cost, so they would need an inexpensive composite. They are also considering two component endplates.

We were not referring to weight. Composites would likely be significantly less expensive than machined metal endplates. They also would not suffer from the same corrosion problems that affect metal endplates.

7. **Will cast or metal powder materials use the same or similar metal composition as the machined endplates, or will they be different? How will corrosion be addressed?**

For the aluminum side, Proton would like to go with cast material eventually. They envision a spider web design – a thin plate with webs of thicker material. Proton plans on working with people who have casting experience.

Proton recognizes corrosion to be a problem, as are hydrogen embrittlement and material suitability.

In their plans, it seems that Proton will look at anything that will lower costs. Since embrittlement and corrosion issues will eventually affect cost, they will likely address these issues.

8. What level of cost savings do you anticipate by going away from machined endplates?

They are looking to cut the cost from about $900/set of endplates down to about $200-250/set. This includes all parts of the endplates.

9. Are any modifications planned for the hydrogen electrode?

Proton wants to modify both electrodes. The plan is to reduce the catalyst loading to increase the potential market by reducing cost. They are looking for a ten-fold decrease in catalyst, from 5-10 mg/cm^2 to 0.5-1 mg/cm^2. They feel the bigger challenge will be on the oxygen side.

Interface Questions:

John Speranza led the discussion for Proton for the interface and system questions.

10. What types of renewable resources will be considered?

"5kW Photovoltaics and Wind Turbines will be considered as the base renewables to interface with a HOGEN 40 hydrogen generator."

11. What is the interface? An AC/DC converter?

"The interface is a combination of power conversion devices optimized as a fully integrated system to function as the sole power interface to the hydrogen generator. The interface will have the capability to supply DC power to the electrolytic cell stack by converting AC power from the grid, conditioning DC power from a renewable source, or augmenting AC power from the grid with DC power from a renewable source. The diagrams [see Exhibits 2 and 3] illustrate two possible applications of such a device."

These applications are for remote, off-grid power, and for back-up power.

Proton considers off-the-shelf converters to be very inefficient. They want to develop a single integrated component that will work for both grid and non-grid scenarios. The power conditioners need to have the capability to do several things. For instance, the conditioner could have a component that would control PV power tracking and another component that would monitor several different inputs (*e.g., PV, hydrogen storage system, grid power if applicable, perhaps even a backup generator for the off-grid system)* and switch them on and off as appropriate.

PEM scales down quite well, says Mr. Speranza, and could work well for a small system.

I believe that the off-grid potential for this type of system is quite great. Even a remote, far-removed from "civilization" scenario would work. Some remote villages are looking at using a renewable intermittent resource such as PV or wind to provide power, with a battery or bank of batteries providing storage. A regenerative fuel cell (unitized or discrete) with hydrogen storage similar to the set-up presented by Proton and shown in the first figure above could be a very viable alternative, especially for longer term storage.

An investigation of load profile requirements and/or data for remote locations would be of value in determining how Proton's various HOGENs and UNIGENs would fit.

System Questions:

12. Please explain your manifold-mounting concept.

"The HOGEN 40 hydrogen generator currently utilizes a considerable amount of stainless steel compression fittings and tubing in the hydrogen fluid management section of the system. While this concept works well and adds flexibility during the prototype and evaluation stages of product development, the materials used are expensive and assembly is labor intensive. The approach of combining multiple fluid junctions into one common manifold needs to be considered as the product enters the production and commercialization phase in order to drive out cost. Machined manifolds will be looked at in both the high-pressure hydrogen side and the low-pressure water side of the generator. Casting those manifolds will be investigated also in order to determine if any cost benefits can be realized through powdered metal fabrication techniques. Welded tube assemblies will also be considered as a possible cost reduction method for these assemblies and may provide an interim solution for present low volume manufacturing."

A manifold is much more cost effective than a series of separate fittings. Mr. Friedland indicated that using a manifold will result in a cost reduction of 30-40% on materials alone. Labor cost reduction would add to this.

Proton will also be looking at injection molding of plastics as a potential manifold for the low-pressure (water) side of the generator.

V Additional Discussion:

- Proton has recently completed a demonstration (partially funded by the Hydrogen Program) of a HOGEN 380 generator as part of a sustainable energy generation project at the Ocotillo Power Plant (Tempe, AZ) owned by Arizona Public Service. Solar energy from a concentrating dish (SunDish™) is fed to a Stirling external heat engine to provide electricity. Additional solar energy is fed to the HOGEN 380 to make hydrogen. This is stored and used to power the Stirling engine during nights and cloudy days. The demonstration is finished, but Proton is still talking to the Dish/Stirling people about further work. Proton also is trying to see if there is any more interest in this at DOE.

- Proton has recently become a member of the California Fuel Cell Partnership. They will be supplying the Partnership with a refueler.

- Proton is currently seeking out several partners.

- Proton is currently supporting a remote (off grid) power project where hydrogen will be used for both electricity and fuel. The location and details of this project are currently confidential.

- Among the cost-saving strategies that Proton is employing is the attempt to identify lower cost membranes and catalysts. The current membrane being used is DuPont's Nafion®, which costs between $650-850/square meter. *Not much lower than it was five years ago!* Proton is looking at some non-fluorinated materials. Since electrolysis is more aggressive to a PEM membrane than is fuel cell usage, Proton is looking toward materials that can withstand higher pressure-induced mechanical stresses and a more oxidative condition. The methodology involves starting with the best fuel cell material and then trying to improve it.

  This may be one of the more important areas that Proton is addressing. Membrane costs unfortunately continue to be a cost driver.

- Proton is also examining techniques for putting catalysts on the membrane.

- Proton will also be minimizing the number of mechanical springs to reduce costs. They will use one or two big springs rather than hundreds of small ones.

Exhibit 1. Cost Projections from Proton's FY 2000 Annual Review Report

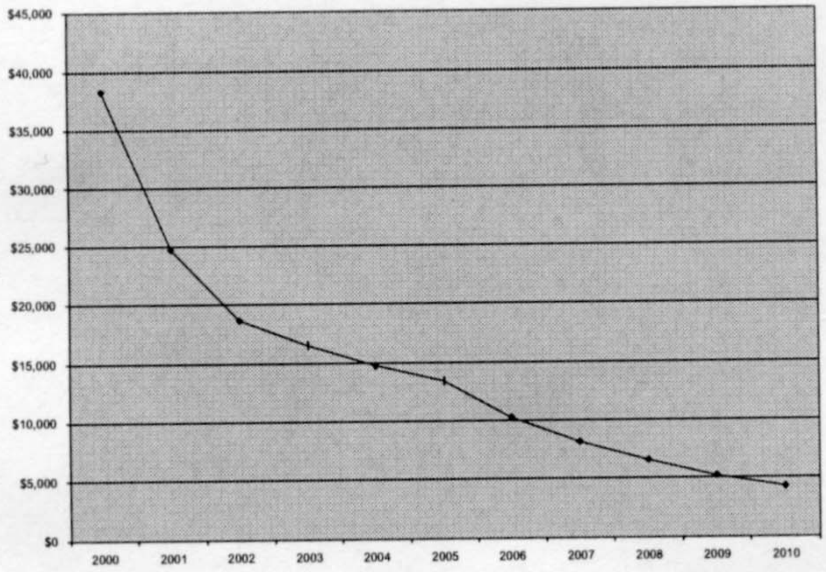


Figure 2 –HOGEN 40 (6kW) Ten Year Cost Projection

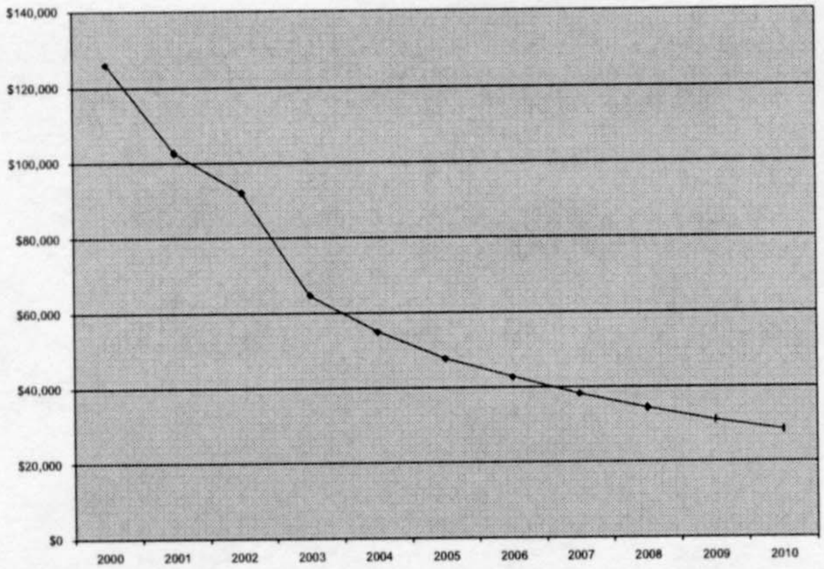


Figure 3 –HOGEN 380 (60kW) Ten Year Cost Projection

Exhibit 2. Off-Grid Village Power Application

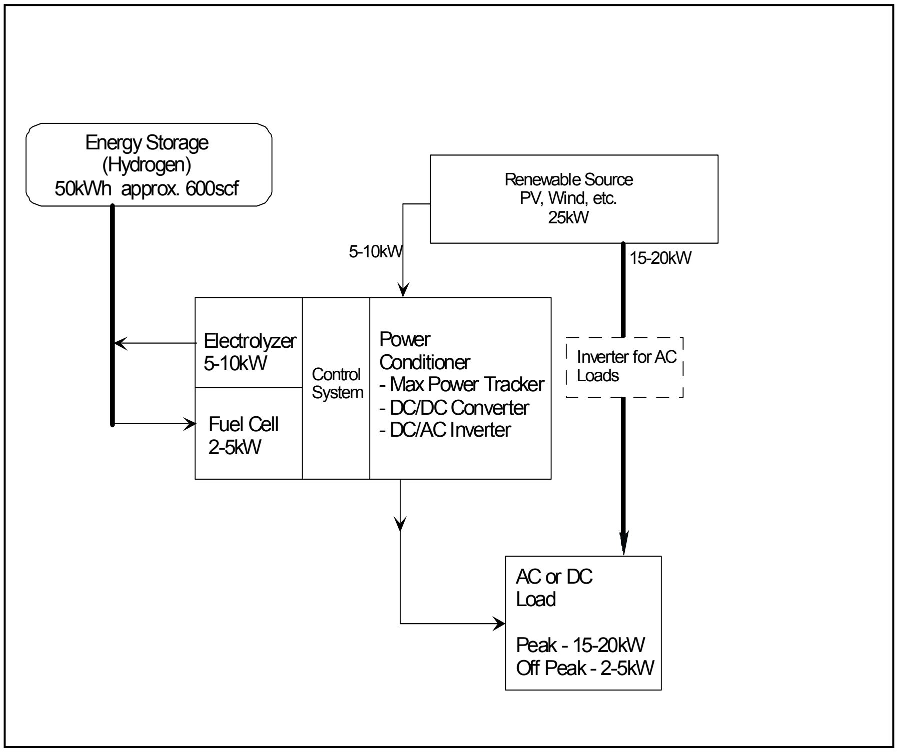
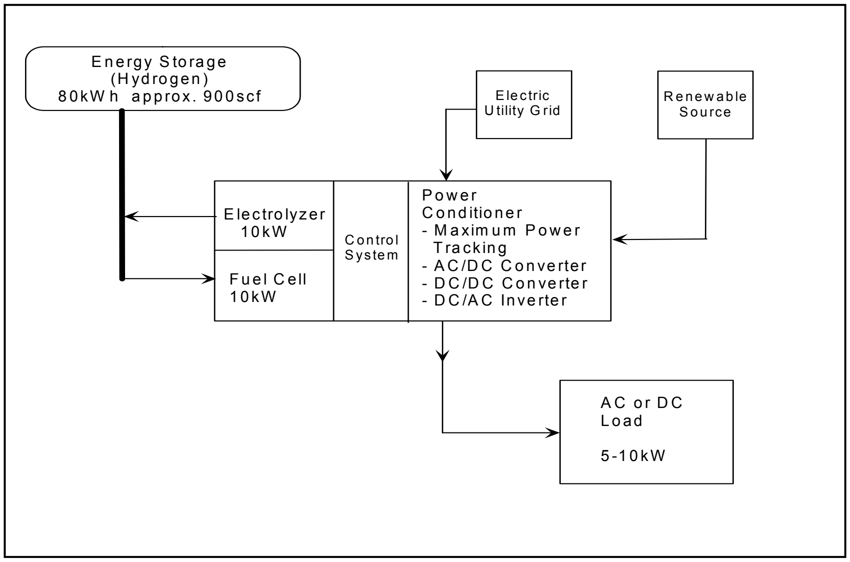


Exhibit 3. Back Up Power System



This page intentionally left blank.

Technical Evaluation Report
Project: Maximizing Photosynthetic Efficiencies for Hydrogen Production
Company: University of California, Berkeley, CA
P.I.: Dr. Tasios Melis
Date of Visit: February 27-28, 2001
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

The University of California, Berkeley, Department of Plant and Microbial Biology are part of the DOE Hydrogen Program's multi-lab project to produce hydrogen from sunlight and water by using engineered algae to photobiologically split the water. Specifically, Berkeley is involved in genetically altering the algae to reduce the size of their chlorophyll-based photoreceptors or antennae. Smaller antenna size will lead to more efficient use of incident photons, and therefore an increase in hydrogen production potential.

Project Strengths:

- Dr. Melis is a recognized expert in chlorophyll antenna size control. His self-built measuring system for antenna size is a marvel of 20-30 year old technology doing the job accurately today. His several methodologies for controlling the antenna size appear to be extremely sound and well thought out.

- Limiting the "footprint" (i.e., increasing the efficiency) of photoreceptors, be they PV panels, photoelectrochemical semiconductors, or algae is a top necessity for making hydrogen from sunlight and water. Antenna size reduction appears to be the way to do it for algae.

- Good progress has been made in identifying/isolating/developing several mutations and transformations of *Chlamydomonas reinhardtii* that show significant reduction in antenna size. While some of the chl *a* vs. *b* work was done earlier, the tlh-1 and lutein work is new. The PS I antenna reduction results for tlh-1 is a step forward.

Issues that should be Addressed:

- There is no data that show how much of an increase in hydrogen per unit area of solar irradiation will occur if the antenna size is reduced by a particular amount – or even to the theoretical limit.

- If *Chlamydomonas* is not going to be the commercial hydrogen producer, than a transfer to whatever will should be made. (Dr. Melis believes it will be *Dunaliella*.) We have to be sure that whatever we learn from *Chlamydomonas* is representative of what will happen in the real world.

II Introduction and Background:

I visited the laboratory of **Dr. Tasios Melis** at the UC Berkeley, Department of Plant and Microbial Biology to discuss the antenna reduction project. I was accompanied by **Dr. Tony San Pietro**, Professor Emeritus of Biology, Indiana University. Dr. San Pietro has been associated with the Hydrogen Program's photobiological efforts for several years. Aside from discussions with Dr. Melis (including our usual question and answer sessions) and a tour of the facilities, our roughly day-and-a-half meeting included talking with two of Dr. Melis' associates, Postdoctoral Associate **Dr. Sarada Kanakagiri**, a molecular geneticist, and Visiting Professor **Dr. Tatsuru Masuda**, a Molecular Biologist.

The chlorophyll receptors in green algae (and other plant) cells that capture sunlight for photosynthesis are quite large. They have evolved this way so that they can capture as many available photons as possible under low-light conditions. Consequently, when they are exposed to bright light, they absorb much more than they can use. Only about 10% of the photons that are absorbed under bright-light conditions are typically used for photosynthesis; the rest are wasted. For plants that are using light, carbon dioxide, and water to make more plant matter, this is not a problem. Plants "don't mind" being inefficient in this way.

Being able to survive by efficiently capturing all available photons under low-light conditions is more important. For photobiologists, however, who are trying to grow algae that will photolyze water to make hydrogen, using as many of the available photons as possible under bright-light conditions is more important. It is more likely that these algae will be growing in places with plentiful light. If the excess photons are not absorbed by the large receptors (antennae) on a particular alga cell, they can penetrate the alga matter down to another cell and be absorbed by <u>its</u> antennae, etc. Thus, instead of being wasted, more photons are being used for photosynthesis. That is, sunlight is being used more efficiently. If the photosynthesis is being used to make hydrogen, a larger volume of hydrogen will be produced per plant (note: <u>not</u> per cell).

In order to make the algae more efficient, their antennae must be smaller. With smaller antennae, fewer photons (ideally, only the amount that is needed for photosynthesis) will be absorbed by a single cell, but more cells will become involved as the light can travel deeper into the culture and access other targets. Transforming algae by reducing their antennae size is the research that is being carried out by Dr. Melis and his group. This antenna size-reduction work is meant to be a part of a collaborative effort between Berkeley, the National Renewable Energy Laboratory (NREL), and Oak Ridge National Laboratory (ORNL) to try to develop algae that will efficiently produce hydrogen from sunlight and water.

Dr. Melis' project is now in its fourth year as part of the DOE Hydrogen Program. Even before Dr. Melis was part of the Hydrogen Program, he was involved with Program photobiological workshops. The subject matter for these workshops at the time was that photobiological methodologies were not producing any more than minute quantities of hydrogen. *(It was originally recommended by the Photobiology Peer Review panel in 1997 that Dr. Melis should be invited to bid an antenna reduction project and become part of the photobiology effort.)*

During these workshops, Dr. Melis hypothesized that if the organism were deprived of sulfur, "visible" amounts of hydrogen would be produced. Thus, until recently, the Berkeley group was working on two photobiological hydrogen tasks: antenna size reduction, and sulfur deprivation. Currently, the work involves only the antenna size reduction project.

Dr. Melis has over 20 years of experience in manipulating and measuring antenna size, and has over 50 publications on the subject. His work is also supported by the Department of Agriculture, the National Science Foundation (NSF) and by Novartis, a Swiss biological company. The NSF work is being performed in cooperation with the University of Hawaii, and involves the use of biotechnology to pull the State of Hawaii out of its economic slump. The concept of reducing antenna size is almost 30 years old, and the methodology was developed at Berkeley.

III Initial Discussion:

The algae's photosensitive antennae are made up of several components; the main ones are two forms of chlorophyll, chlorophyll *a* and chlorophyll *b* (chl *a* and chl *b*). Other important components include carotene-derived "xanthophylls" (luteins and/or violaxanthins). The antennae structurally are made up of core and peripheral portions. The core is almost entirely made up of chl *a*, while the trimeric peripheral parts each contain 21 chl *a,* 18 chl *b*, and 9 xanthophylls. Dr. Melis mentioned that his laboratory at Berkeley is the only place where chlorophyll type can be measured. A schematic of what an antenna may look like is seen in Exhibit 1. Representations of antennae maximized for low, medium, and high light conditions are shown. The goal of this project is to reduce the antennae to their high light representation. This can be done by removing chl *b* (as Dr. Melis has done via genetic replacement) and/or lutein (as Dr. Melis is also working on.)

Dr. Melis has also isolated a regulatory mutant (see Question 8) that possesses truncated light harvesting (*tlh-1*) chlorophyll antennae. He is also considering controlling antenna size by slowing down chl *a* by inhibiting a magnesium chelatase gene (the mechanism for the formation of chl *a* involves a step in which a precursor is chelated with magnesium) or perhaps another gene.

Dr. Melis discussed the strengths of his laboratory at Berkeley:

- Berkeley is the only place where antenna size can be measured. The reason for this is the presence of the differential spectrophotometer that Dr. Melis developed. (See description in the "Tour" section.) Dr. Melis says that Berkeley is the "sole-source provider" in this regard.

- The laboratory also has a strength in the molecular genetic methods that they use to "transform" any green alga (not only *Chlamydomonas*). Transformation refers to the process by which a new piece of DNA is put into an organism's genetic structure. This is a genetic transformation – not just a mutation.

IV Tour:

Dr. Melis took Dr. San Pietro and me on a tour of his laboratories.

The centerpiece of the laboratories, at least as far as the DOE work is concerned, is an instrument that was designed and built by Dr. Melis to measure antenna size. He calls it a "sensitive, split-beam, differential kinetic spectrophotometer." *This is certainly not a piece of equipment that comes in a box from a science supply store. It is put together piece by piece, and includes some components that look very similar to some I remember from my days in graduate school in the early '70s. This is not to say that the system is outdated (although I wonder what he could do with today's equipment!). As Dr. Melis presented it to me, it appears to be right on target.*

The main components are:

- A stable white light beam for source radiation,
- a monochrometer with a manual crank for setting the wavelength you wish to use for studying a particular site,
- a split-mirror that will divert 5% of the light to a photomultiplier (as reference beam) detector,
- a sample holder
- an actinic (*reaction-causing*) light source, perpendicular to the main beam path to cause photosynthesis
- a second photomultiplier detector
- Enabling electronics.

The existence of the reference photomultiplier allows differential data to be accumulated. The amount of light absorbance as well as the rate of absorbance can then be measured. Since the monochromatic light can be set to observe the change in any species (e.g., chl *b*, lutein, etc.) it can be used to determine amount of this species present, and from this, antenna size.

Dr. Melis also has a second, less sensitive, but scanning-capable (over wavelengths of light) spectrophotometer.

Other equipment/facilities in the laboratories included laminar-flow hoods for sterile transfers, freezers to store biological samples at –80°C, incubation chambers utilizing light and 233°C heat, a second totally separate growth room (with a multitude of cultures present), and preparation rooms with centrifuges, incubators and bacterial growth chambers. They use the bacteria to produce DNA, which is then transferred into the *Chlamydomonas* alga for transformation.

Physically, insertion of DNA into a cell is done in one of two ways. In the first, the cells and DNA are shaken together in the presence of glass beads. The beads break the cell wall, allowing admission of the DNA. In the second method, an electric field and a very short pulse of high voltage is used. The DNA is negatively charged, and tries to jump to a positive electrode, but the cells are in the way, so the DNA penetrates the cell wall.

V Questions and Answers:

I sent Dr. Melis a set of discussion questions prior to my arrival. These were covered thoroughly during my discussion with Dr. Melis and Dr. San Pietro. In addition, I was given a written set of answers. All of this is reproduced below.

1. **How does a truncated chlorophyll antenna size lead to increased hydrogen production? (I had heard/thought that the chlorophyll antennae were sites that promoted photosynthetic conversion of CO_2 into plant matter and oxygen. And that smaller antennae reduced this tendency allowing light-induced water splitting to be the preferred reaction. But what I'm reading in your reports is that the smaller antennae lead to more *efficient* photosynthesis. How does this all tie together?)**

"Green algae (and other photosynthetic organisms) synthesize and assemble large arrays of chlorophyll, placed within protein (large Chl antennae), in order to capture as much sunlight as they can. Absorbed sunlight is channeled to a specialized Chl *a* molecule (reaction center Chl), where the energy of sunlight is converted into chemical energy. The evolutionary trait of "large Chl antennae" helps the organism to compete for sunlight under weak light-intensity conditions. Thus, when the light intensity in the environment is low, large arrays of Chl-proteins confer a competitive advantage for the survival of the organism.

"When the light intensity is strong, large Chl antennae absorb sunlight in excess of what photosynthesis can utilize and wastefully dissipate up to 90% of it.

"In a commercial biomass/hydrogen production process, based on the conversion of solar energy, such wasteful loss is not acceptable. The solution: genetically truncate the size of the Chl antennae in the green algae to limit their ability to absorb sunlight. Such mutant strains would lose their competitive advantage in the wild. However, in mass culture for biomass/hydrogen production, they will be prevented from wastefully absorbing and dissipating valuable solar energy. Thus, a mass culture of "truncated Chl antenna" strains will show significantly greater solar conversion efficiencies and, therefore, biomass/hydrogen productivities."

Basically, what I'd heard before was wrong. You don't want to interfere with making plant matter; you want the light to be used efficiently. You have about 2000 photons striking a cell's antenna each second, but you only have about 200 reactions per second, so you are wasting about 90% of the photons. Therefore, you want to shrink the antenna size so that (ideally) only about 200 photons will strike the antenna. The other 1800 photons can strike other cells. This is a more efficient use of light.

Why do the cells have large antennae, then? One would think that nature would try to be efficient. But in nature, the algae need large antennae to absorb as many photons as possible under dim light conditions. Being able to survive under dim light conditions is much more important than using all the bright light photons. However, in a hypothetical hydrogen producing pond, the system would likely be sited in an intense bright light region. The large antennae will not be needed for survival. Furthermore, in this bright light environment, the large antennae could absorb too many photons resulting in a phenomenon known as “destructive photo-oxidation”.

So having small antennae does not inhibit plant growth. Water splitting is part of photosynthesis. You want the chloroplast to use as much light as possible; it’s not a plant matter vs. hydrogen situation.

Dr. San Pietro mentioned a very useful way of visualizing the way the antenna work. If we look at the antennae as funnels, and we see large funnels with wide flutes, they would capture a large amount of whatever they were collecting, and send it all to one concentrated spot. What we want instead are more, smaller fluted funnels, so the matter they are collecting gets distributed to more spots.

2. **What is chlorophyll *b* as opposed to chlorophyll *a*, and why does this research concentrate on Chl *b*?**

“They are slightly different tetrapyrroles. Chl *b* is biosynthetically derived from Chl *a*. They have slightly different spectroscopic properties and help one-another in the capture of sunlight.”

Basically, Chl *a* contains a methyl group, which can be oxidized (via an oxygenase) in a two-step oxidation to an aldehyde. The aldehyde-containing species is Chl *b*. The difference between the *a* and *b* configurations is enough so that they can be distinguished spectroscopically.

“Chl *a* antennae are placed closer to the reaction center of the photosystems and are essential for photochemistry. Chl *a* as a photosynthetic pigment cannot be dispensed with. Chl *b* occupies a more peripheral position in the Chl antennae and can be dispensed without affecting photochemistry. Thus, in the absence of Chl *b,* one would expect smaller Chl antenna sizes. This is the reason why, in efforts to generate a truncated Chl antenna size, Chl *b* was designated as one of the mutagenesis targets.”

Chl *b* is a component of the peripheral area of the antenna – a “building ingredient” of the trimer that makes up this antenna portion. Chl *b* basically only operates in dim light conditions.

When you interfere with the gene – the chlorophyll *a* oxygenase (CAO) gene – that oxidizes chl *a* to chl *b*, you shrink the antennae. Dr. Melis’ laboratory reported on this effect with *Chlamydomonas reinhardtii* and has confirmed it with the *Dunaliella salina* algae. They are confident that they can use the same process on other green algae as well. Dr. Melis believes that the alga *Dunaliella salina* will be the one that eventually will go to commercialization due to its ability to survive in a salt-water environment. Dr. Melis also believes that they can identify similar genes that will affect other components of the antenna periphery region:

“Similarly, “xanthophylls” are peripherally localized carotenoids. They are part of the light-harvesting antennae and contribute to the stability of assembly of the Chl-protein arrays.

Insertional mutagenesis to knock out xanthophyll biosynthesis is another approach by which to minimize the Chl antenna size in green algae."

3. Both standard photosynthesis and water splitting *(both are part of 'normal photosynthesis')* result in the evolution of oxygen. How does oxygen evolution measurement serve as a monitor of standard photosynthesis decrease?

"Oxygen evolution is a convenient method by which to measure the performance of *'normal photosynthesis'* in the algae."

4. At what point do you foresee actual hydrogen production-based testing of reduced-antennae algae? What level of increased hydrogen production do you predict as a result of the antenna reduction?

"Hydrogen or biomass production could be attempted with any of the "truncated Chl antenna size" strains. The positive effect would be manifested under mass culture conditions, i.e., conditions where the geometry of the reactor and/or the density of cells in the mass culture would result in a 100% absorption of the incident irradiance.

"Integrated over the course of the day and through the depth of the culture, the prediction is for a 5-fold increase in productivity (maximally truncated Chl antennae vs. normally pigmented cells)."

Dr. Melis mentioned that this success would be manifested as a 5-fold increase in either biomass or hydrogen production. (A "normal" cell at noon, only uses 5% of the available light)

A 5-fold increase (which, I suppose reflects an increase of efficiency to 25-50% -- depending on whether you are talking about 5% normal efficiency at noon, or the 200 of 2000 photons used per cell) is substantial. One key reminder, however: Dr. Melis speaks of increase in biomass or hydrogen. His goal is to reduce the antenna size. It is the responsibility of others to turn that into hydrogen. Cooperation between the laboratories is necessary, and it must be reciprocal cooperation.

5. Will the reduced antennae in any way play in the tendency of hydrogen production to be inhibited by the presence of oxygen?

"Based on current knowledge, there is no reason to believe that genetic interference with the Chl antenna size would have a direct effect on the activity of the hydrogen producing enzymes. Nevertheless, a drastically smaller Chl antenna size for photosystem-II would lower the rate of oxygen evolution in the chloroplast and, therefore, may diminish the tendency of hydrogen production to be inhibited by oxygen."

Dr. Melis also mentioned that under low light you might get less oxygen, and therefore, more hydrogen. However, with less activity, you'd get fewer electrons, and therefore, less hydrogen. But the reduced antenna size will not affect the hydrogenase. *(In other words, there are a lot of potentially conflicting phenomena, but it does not at this time appear to be a matter of concern.)*

6. **Much of your FY 2000 Annual Review report compares wild and mutant (Chl *b* –less) algae that are grown in either TAP** *(Tris-Acetate-Phosphate)***, TABP** *(TAP supplemented with Tris-HCl) and with sodium bicarbonate),* **or TBP** *(Tris-HCl-phosphate supplemented with sodium bicarbonate)***. If the mutant algae were to be used in the "real world" to split water for hydrogen, is it to be expected that one of these media would be used to grow the algae? Would this be a reasonable thing to expect in large scale?**

"Yes, exactly! Experimentation with different growth media in my lab is a way by which to prepare for a "real world" scenario. It is a prelude to defining conditions suitable for scale-up. We were also testing the different growth media to find out whether they exert any effect on the Chl antenna size in wild type and mutant."

Dr. Melis added that although TBP will grow cells, you need the acetate component to get hydrogen. You would likely add acetate for that purpose, perhaps using just enough bicarbonate to grow cells, and then when it runs out, you would replace it with acetate. In small scale, you could filter and replace.

The question is what would you do in large scale?

7. **In the same report, please explain Table 3.**

"Table 3 is the cornerstone of our analytical approach and a unique Berkeley capability. It provides measurements of the number of Chl molecules that are specifically associated with each of the photosystems (i.e., it measures the Chl antenna size of the photosystems). This type of measurement and experimental analysis is **absolutely essential** in this project. Such technological know-how (the measurement of the Chl antenna size of the photosystems) is an exclusive know-how of the Melis Laboratory (**sole source provider**). The technology has not been duplicated in any other photosynthesis research lab worldwide. (We receive 2-3 requests for help with such direct Chl antenna size measurements from photosynthesis colleagues each year)." (*Emphasis provided by Dr. Melis*.)

Table 3 is reproduced in this report as Exhibit 2. The various "N"s refer to the number of available sites for photons. That is directly related to antenna size. The smaller values for N for PS II for the Chl *b*-less mutants indicate a decrease in antenna size for PS II. (Note that for Photosystem II, there are no α and β breakdowns for chl *b*-less mutants.) PS I antenna actually appear to be increasing. Dr. Melis believes that this is because chl *a* may be taking the place of chl *b* in the trimers, keeping the peripheral sites intact.

Dr. Melis also states that PS II photosynthesis is the rate limiting step, so that the size of the PS II antenna sizes are probably more important than the PS I sizes.

8. **What is a "regulatory mutant?"**

"Green algae have the ability to adjust the number of the Chl molecules that assemble in the Chl antennae of the photosystems. These adjustments are triggered by the prevailing environmental conditions. For example, persistent exposure of the algae to bright sunlight triggers the assembly of smaller size Chl antennae; a meaningful response by the cells designed to conserve resources.

"Conversely, persistent exposure of the algae to low-intensity illumination triggers the assembly of large size Chl antennae; again a meaningful response designed to enhance sunlight absorption. A "regulatory mutant" is one that has lost the ability to make such adjustments and either assembles the maximum possible or minimum possible Chl antenna size, irrespective of the prevailing conditions."

Ideally, you would like to have variable antennas that would get larger in low light and smaller in bright light. This sort of phenomenon could not happen quickly enough to follow the amount of sunlight.

The light-harvesting mutant (thl-1) that Dr. Melis' group has isolated shows smaller antennae for PS II sites – although not as small as the chl *b*-less algae. Encouraging, however, is the fact that the PS I antennae were somewhat smaller. Exhibit 3, taken from Dr. Melis' work over the last couple of years shows antenna sizes for wild, chl *b*-less, thl-1, and lutein-less versions of the algae, together with the minimum theoretical antenna size that could exist.

If we examine Exhibit 3, and use the antenna sizes for the wild algae as baseline we see that for PS II, chl b*-less transformants produce 60% smaller antennae, thl-1 produces 49% smaller antennae, and lutein-less transformants produce 42% smaller antennae. For PS I, thl-1 reduce antenna size by 22%. The other two species show an increase in PS I antenna size. A better measure, however, might include looking at the theoretical limits as the ideal. We can show roughly how far the group has gone toward reaching the "goal" – the theoretical values. For the PS II system this is: 72% of the way toward the theoretical value with chl* b*-less transformants, 58% for the thl-1 mutant, and 52% of the way for lutein-less transformants. For PS I only the thl-1 mutant produces a reduction in antenna size, and it goes 41% toward the theoretical.*

9. **Has there been general consensus among the photobiological hydrogen group that *Chlamydomonas reinhardtii* is and will be the alga of choice for water splitting? If this turns out not to be the case, will the data gathered here be easily transferable to the "new" alga?**

"My own feeling is that *Chlamydomonas reinhardtii* will not be the alga of choice for either hydrogen or biomass production. There are other better candidates. However, *Chlamydomonas* is an excellent model organism to collect the data, which then can be transferred to other microalgae. The approach in the Melis laboratory is to clone those genes that affect the size of the Chl antennae in this microalga. These can be later over-expressed or down-regulated in other algae that are more amenable to mass culture for biomass/hydrogen production. In this respect, the Melis laboratory is developing and applying transformation technologies in a number of green algae, including *Chlamydomonas reinhardtii* and *Dunaliella salina.* Transformation technologies will permit the delivery of plasmid constructs into the genome of novel green algae that are promising for mass culture. Such plasmids will be designed:

(a) to over-express a certain gene by selection of the gene's promoter region or,

(b) via the application of antisense technology, transformation will be used to silence genes of interest, thereby affecting the size of the Chl antennae."

In the DOE program, they are looking only at *Chlamydomonas*, but their USDA work, which will benefit DOE as well, involves *Dunaliella.* According to Dr. Melis, *Chlamydomonas* is not a very hardy organism. If the transformation can be performed on other algae such as *Dunaliella*, it will be able to be tested under a larger variety of different conditions.

The laboratories involved with photobiological hydrogen are all working with Chlamydomonas, but at least two of them have other "pet" algae that they think might be better suited toward their specific work. Care must be taken that either consciously or subconsciously the work does not individually migrate toward incompatible organisms. Equally important is the need to step back and ask (as a group): when do we move away from Chlamydomonas and toward the organism(s) that will be the mass hydrogen producer?

VI Additional Discussion:

Collaborations:

We spoke to some degree about the functions of the various laboratories that make up the hydrogen photobiological group – meaning the people who are trying to get algae to use sunlight to split water and make hydrogen. Dr. Melis summarized the original intention of the collaborative effort to include:

- Dr. Eli Greenbaum's group at ORNL: produce hydrogen and oxygen simultaneously from a single organism and use a mechanical method of removing the oxygen.
- Drs. Mike Seibert and Maria Ghirardi at NREL: use chemical mutagenesis to find hydrogenase mutants that were not sensitive to oxygen.
- Dr. Melis: Tackle the chlorophyll antenna problem.

Dr. Melis states that he also teamed with NREL to promote his idea that sulfur deprivation of green algae might facilitate hydrogen production. However, Berkeley is no longer part of this latter project, and now does only antenna reduction work. *I am not quite clear on how the roles have all played out – or will play out.*

Discussions with others:

Dr. San Pietro and I also spent some time talking to Drs. Kanakagiri and Masuda. Dr. Kanakagiri, a geneticist, is performing genetic insertion for antenna size reduction. She has made over 6,500 transformants. These were screened by fluorescence – a transformant with small antennae will not fluoresce strongly due to its low chlorophyll concentration. Dr. Kanakagiri found 60 of the 6,500 transformants exhibiting low fluorescence. Not all low fluorescing transformants, however, have small antennae; they could just be inefficient photosynthesizers.

Dr. Kanakagiri then tested the chl *a*/chl *b* ratio of the 60 remaining candidates, and attempted to grow the transformants under high light (recall that under high light, chl *b* presence leads to inefficient use of light.) She found that 4 transformants showed good growth under high light conditions. A DNA analysis on the four transformants indicated that one (*out of 6,500!)* appeared suitable.

Dr. Kanakagiri mentioned that the plan is now to clone the gene so that they can introduce it into different algae if desired.

Dr. Masuda, a molecular biologist, is working with *Dunaliella salina*, using high (2000 W/m^2 and low 50 W/m^2 light conditions and looking for low total chlorophyll and high chl *a*/chl *b* ratios. He is looking for these conditions in two projects. In one, he is trying to inhibit the overall production of chlorophyll by inhibiting one of the reaction steps that leads to a chlorophyll precursor using gabaculene as the inhibitor. He found that although chlorophyll production was down, the chl *a*/ chl *b* ratio was actually decreasing. He believes that the *a* variety was changing to *b*.

In his second project, Dr. Masuda is looking specifically at chl *a* to chl *b* conversion. He is trying to inhibit this by working with the CAO gene. (*See Question 2).*

A third research associate, Dr. Juergen Polle, a spectroscopist/biochemist, also works on the hydrogen program, but he was out of the country. Dr. Melis briefly described his work to us. Dr. Polle is basically responsible for the measurements. He compares data on wild type, chl *b*-less type, thl-1 type and lutein-less type of algae. Comparisons are done both spectroscopically and by Western blot measurements for chlorophyll proteins. These two totally separate tests serve as a check against one another.

VII Final Thoughts:

I think it's of value to try to determine how far Dr. Melis has come in the antenna reduction process, and if he is still making progress. So we turn again to Exhibit 3. The first point is that there is significant reduction demonstrated for all three types of altered algae (chl b-less, tlh-1 and lutein-less) for PS II. In addition, we are seeing a reduction in PS I antenna size for tlh-1. Progress is being made; the tlh-1 and lutein-less results represent this year's work.

Next, I think it's only fair to bring up the point that other researchers do indeed look at antenna size reduction as a means of increasing photosynthesis efficiency. I'll mention one: a paper by Y. Nakajima and R. Ueda, J. Appl. Phycology ***12,*** *285-290 (2000), discuss the effect of reducing "light-harvesting pigment" in Chlamydomonas perigranulata algae. Light harvesting pigment and antenna size are basically synonymous. The reduction reported by Nakajima and Ueda comes after UV mutagenesis* *on the algae. They report a decrease in PS I antenna size by 50%, and an increase in PS II size. Thus, (putting aside the fact that it's a different Chlamydomonas,) it appears that these researchers are more adept at reducing PS I antennae and Dr. Melis' group is far more successful with PS II.*

What may be troublesome, however, is the report in the same paper that photosynthetic activity improvement does not keep pace with antenna size reduction. In other words, the question is the same one that we continue to ask ourselves in all hydrogen production projects: ***How much hydrogen does it make??*** *The answer may not be part of Dr. Melis' particular task, but it's the leading question of the overall photobiological hydrogen program.*

Exhibit 1. Schematic of Photosystem II light receptor antennae.

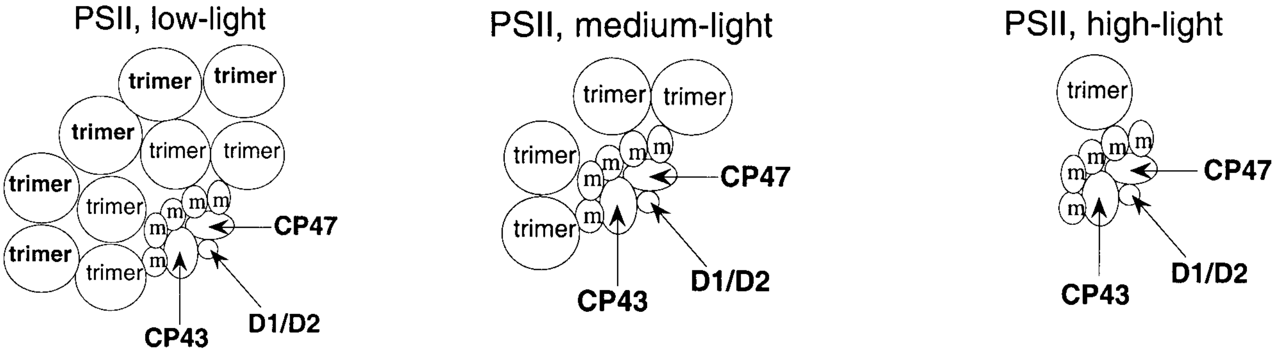


Exhibit 2. Dr. Melis' FY 2000 Annual Review Report, "Table 3" showing chlorophyll antenna sizes for various wild type and chlorophyll *b*-less mutants.

	wild type			Chl *b*-less		
Parameter	TAP	TABP	TBP	TAP	TABP	TBP
$PSII_\alpha$	42±7.4 %	53±10.5 %	29±9.5 %	-	-	-
$PSII_\beta$	58±7.4 %	47±10.5%	72±9.5%	-	-	-
$N_{(PSII\alpha)}$	322 ±7	284 ±49	474 ±49 (325)	-	-	-
$N_{(PSII\beta)}$	127 ±3	141 ±3	119 ±3	-	-	-
$N_{(PSII)}$				93 ±3	107 ±9	88 ±7
$N_{(PSI)}$	291 ±17	217 ±8	204 ±4	245 ±14	284 ±6	289 ±12

Exhibit 3. Summary of latest results on antenna sizes for different mutants or transformants.

Parameter	Wild type	Chl *b*-less	tlh-1	lutein-less	Theoretical Limit
N (PS II) Average of α and β	222	88	114	125	37
N (PS I)	204	289	159	294	95

This page intentionally left blank.

Technical Evaluation Report
Project: Thermal Dissociation of Methane Using Solar Coupled Reactor
Company: University of Colorado, Boulder, CO & NREL, Golden, CO
P.I.: Dr. Al Weimer (CU) [with Dr. Al Lewandowski (NREL)]
Date of Visit: June 13, 2001
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

The hydrogen production R&D project being carried out by the University of Colorado (CU) with a subcontract to the National Renewable Energy Laboratory (NREL) involves the use of a solar reactor to provide the heat necessary to dissociate natural gas into hydrogen and carbon black. The solar reactor project is an intriguing one. It allows for non-catalytic thermal dissociation of methane by providing very high temperatures (~2000°C) where the dissociation reaction kinetics are orders of magnitude faster than at more commonly used temperatures for hydrogen production from hydrocarbons (700-1000°C). It provides a means of producing no greenhouse gases, and offers a saleable byproduct (carbon black) that could offset the cost of producing hydrogen. Alternately, the carbon black could be burned, perhaps supplying energy to a steam turbine. This would negate the CO_2 benefit, but it would increase the energy output from the natural gas and still leave a renewable approach to producing hydrogen.

In general, projects of this type suffer from two major criticisms: i) Solar thermal energy is generally viewed as being economically viable in too few locations to have a strong impact on the overall energy mix, and ii) converting methane to hydrogen and carbon fails to release all of the energy from the methane; if you discard the carbon, you are discarding energy.

Project Strengths:

- The process produces hydrogen from fossil fuel without releasing CO_2. Whether they sell the byproduct carbon black (assuming it doesn't eventually become a combustion resource) or bury it, it seems a better solution than sequestering CO_2. Thus, (energy efficiency and economics aside) it is an environmentally attractive process.

- The dry reforming option (this is not part of the DOE Hydrogen Program) seems like an attractive method for reactivating CO_2-contaminated natural gas wells.

- Much of the experimental work has been built on solid scientific and engineering models.

Issues that should be Addressed:

- The range of applicability for such a system appears limited. Death Valley is a rather unique location. How many other locations will provide sufficient insolation for acceptable efficiencies? These other locations would also have to be fairly sizeable. Heliostats take up a lot of room.

- Because of this apparent location limitation, it is even more important to have a good plan for where and how the hydrogen will be used. Scenarios such as the ones discussed in Question 1, below, need to be developed and justified.

- The direction that this project appears to be headed is towards the development of a non-stand-alone system. With a quoted solar capacity factor of 0.28, either the heliostats will have to be upsized and storage added, or large capacity backup (or more accurately a different primary system with the solar thermal system as backup) will be needed. If the backup is to use fossil, the contribution to CO_2 reduction will be small.

- Sensitivity analysis shows the cost of hydrogen is heavily based on the cost of natural gas and the cost of heliostats, two items out of the projects control.

II Introduction and Background:

I visited both CU and NREL to meet with the researchers and to view the system that is meant to produce hydrogen by thermally dissociating natural gas using concentrated solar-thermal as the heat source. **Dr. Al Weimer**, Professor of Chemical Engineering at CU, heads the project, which is in its second year of funding. A subcontract to NREL to run the solar furnace is led by **Dr. Al Lewandowski**, Senior Engineer. I met with both of these people as well as with Dr. Weimer's postdoctoral associate, **Dr. Karen Buechler**, and his graduate student, **Ms. Jaimee Dahl**. I saw the UC laboratory where the first generation reactor (Exhibit 1) was present but disassembled, and the second-generation reactor (Exhibit 2) was being built. We also went to the Solar Furnace Facility at NREL where a 10 kW heliostat provides the heat to decompose methane. Drs. Weimer (Overview), Lewandowski (Economics), and Buechler (new reactor design) and Ms. Dahl (results and modeling) all made presentations. I had provided Dr. Weimer with a list of questions in advance of my visit, and he responded in writing. These were discussed in detail during our meeting as well.

III Initial Discussion:

Chemistry:

The dissociation reaction in question is simply:

CH_4 (+ heat) $\rightarrow$ $2H_2 + C$; ($\Delta H = 75$ kJ/mole)

The group is also looking at the potential for "dry reforming" of methane as a means of recovering natural gas from wells that have been capped because they have become contaminated with CO_2. The product is a syngas:

$CH_4 + CO_2$ (+ heat) $\rightarrow 2H_2 + 2CO$; (ΔH = 250 kJ/mole)

The concept of solar-based thermal dissociation is of interest because the system can easily reach temperatures of the order of 2000°C, where the dissociation kinetics are orders of magnitude faster than at more "conventional" temperatures, where one would need a catalyst to drive the reaction.

Carbon Black:

As stated earlier, byproduct carbon black can either be combusted, buried, or sold. *From an energy standpoint burning is favored, but it negates the* CO_2 *elimination "hook." Burying is attractive in that it is easier to sequester carbon than* CO_2*, but it puts the entire economic onus on the cost of hydrogen (unless carbon credits exist). Selling provides the best of both worlds — providing the market does not get flooded with carbon black from this process, and provided a reasonable price target can be reached.*

Dr. Weimer states that bulk carbon black costs about 20 cents per pound. This is the impure material that is used in the tire industry for rubber reinforcement and strengthening. Better grades of carbon black, made from natural gas range in cost from 35 to 60 cents per pound. High purity "acetylene black" costs about $1.40 per pound. *Carbon black is also used in paints, plastics, inks, brake liners, and many specialty products. It is used for its thermal conductivity and electrical conductivity as well as a filler, pigment, and viscosity control.* Dr. Weimer's group is currently using 35 cents per pound as a reasonable estimate of for how much they believe they could sell their byproduct. The group is also trying to get Cabot Corp., a large carbon black manufacturer, on their team. Cabot could assess "the real value" of carbon black.

Commercial Location:

The research group is targeting Death Valley, CA as a potential site for a commercial system. The area possesses the highest solar intensity in the country and is the home of the Barstow 10MW Solar Thermal Facility. CU is looking at a 30 MW facility. A 30 MW solar facility translates to about 5 million standard cubic feet per day (scfd) hydrogen (based on 0.28 solar capacity and a 50% thermal efficiency). (Dr. Weimer mentioned that in conversations with the DOE Hydrogen Program's Dr. Sig Gronich, Dr. Gronich indicated that perhaps 10 MW would be a more attractive size.)

Dr. Weimer also uses the approximation of a 30 MW unit making about 5 million kg of hydrogen per year, using the following calculation and justification:

30 MW x 1000kW/MW x 0.28 x 0.5 x 1000W/kW x (1 J/s)/W x 3600 s/hr x 8760 hr/yr

x 1 kJ/1000 J x 1 mol CH_4 reacted / 74.9 kJ x 2 mol H_2 produced/1 mol CH_4 reacted

x 2 grams H_2/1 mol x 1 lb / 454 g x 0.454 kg / 1 lb = 7.1 million kg H_2 per year.

Some sensible energy (enthalpy) goes to heat up the CH_4 to reaction temperature and some leaves with the produced H_2. This is accounted for in other calculations to conservatively give 5 million kg/yr H_2.

Because there are 365 days/year, and for hydrogen 424 scf/kg, then:
7.1 million kg/y x 424 (scf/kg)/ 365 (d/y) = 8.25 million scfd, which I guess can also be conservatively approximated as 5 million scfd.

Dr. Weimer recognizes the potential problems that could arise at the desert site. They would either have to run a fuel cell on site or would need a compressor to prepare the hydrogen to be pipelined away. Hydrogen comes out of the reactor at one atmosphere; compressor costs could be high.

<u>Status and Plans</u>:

CU is currently building the second-generation reactor. The major improvement is that the graphite reactor will run the full length of the outer quartz tube, and the annular space between the quartz and graphite will be completely separate from the reaction zone inside the graphite tube. (The old design had the graphite reactor run for only about ½ the length of the quartz tube. Deposition on the quartz was a big problem.) CU plans to use the new reactor "extensively" during the next year.

They plan to/are starting to use a secondary concentrator. They need to concentrate more of the heat on the tube, but spread it out over the entire tube. The secondary concentrator is mounted right on the reactor; it further concentrates the solar radiation that had been gathered by the primary concentrator and reflected toward the tube. Work on the reactor has slowed due to a funding hiatus for the first six months of FY 2001.

The group is currently doing a mass and energy balance closure for the system.

CU/NREL is at various states of agreements or negotiations with five companies that they hope to get to partner with them on this project. These are the aforementioned Cabot Corp., BP Amoco (natural gas supply), Harper International (solar furnace design), Foster-Wheeler (carbon black boiler), and Plug Power (fuel cell integration).

The group is also thinking of building a 100 kW solar furnace facility at NREL (the current facility is 10 kW) that would be dedicated to thermal dissociation.

There is no plan to try to make the system continuous, nor has CU addressed hydrogen storage. *We discussed the various scenarios for how a real system would work in Question 1 below. Because the sun isn't out all the time, and there is no plan for storage (any plan would likely need a compressor as well) this is certainly not a stand-alone system.*

Dr. Weimer stated that the project "looks promising" but more research is needed to determine if it will really work.

Modeling and results from first generation reactor:

Ms. Dahl presented the results of the modeling effort she has undertaken. The model for the reactor was taken from an electrically heated reactor developed and patented by Thagard Technology Company (Irvine, CA) in 1977. The reactor also used hydrogen added through the porous reactor walls. A key finding of the Thagard work was that residence time in the reactor is a non-factor if the temperature is above 1900°K (2173°C) (Exhibit 3).

Using the Thagard results, Ms. Dahl also performed mathematical modeling to back out the reaction kinetics at 2000°C. These kinetics are used to design the solar reactor. *There is no doubt that there is a lot of benefit to the high-temperature kinetics (short residence time, high conversion, no catalyst). The question is how does it balance against capital cost, intermittent periods of production, and limited high insolation regions.*

With the first reactor, CU/NREL was using only about 10% of the solar thermal energy, that is, 10% of the 10kW being delivered by the heliostat. With the single concentrator (see description of the NREL Solar Furnace below) much of the energy was not focused on the reactor. The new reactor will incorporate a second concentrator wrapped around the reaction zone. The concentrator has an octagonal opening with a diameter of 23 cm. It concentrates down to 9.4 cm in the area wrapped around the reactor. This will further focus the solar radiation, the group believes, and result in about 74% of the energy going to the reactor. (The rest of the energy is lost either by being absorbed before it gets to the reactor, reflected back through the entrance, or leaked out of the ends. CU believes that with the second concentrator they will get 100% conversion to hydrogen at 2000°C. Should the secondary concentrator not be sufficient, it is conceivable that there could be several smaller secondary concentrators used instead, each wrapped around and focusing the energy on a different section of the reactor.

Results from the first generation reactor showed 90% conversion of methane to hydrogen from a feed of 0.45% methane in Argon. (The gas chromatograph showed about 0.81% hydrogen after the reaction, corresponding to nearly 90% conversion.) Residual methane was measured at less than 0.02%; an equal amount of acetylene was also measured. The same set of results showed a CO concentration of 0.06% and a CO_2 concentration of 0.05%. Ms. Dahl and the rest of the team attributed these two readings to a sampling anomaly. *We really need to see numbers for pure methane dissociation, not highly diluted methane; Dr. Weimer recognizes this. Hopefully, the second-generation reactor, which will use a pure methane stream, will lead to accurate numbers.*

Results with the first reactor indicated that better conversion efficiency was obtained when carbon black particles were added to the feed. The carbon black aids in heat transfer. (See Questions 3 and 4 below.) Dr. Weimer, however, believes that eventually, with the right design, they may not require the added carbon black, and that the generated black may be sufficient.

Dry reforming in the first reactor at 1500°C produced about 70% conversion to hydrogen, but again this was obtained from a diluted feed stream of CO_2 and methane in argon.

The Second Generation Reactor:

Dr. Buechler presented the new reactor design. They recognized that they needed to improve the feeder system and to keep the particles off the quartz tube. In the new design (see Exhibit 2) the graphite tube actually extends beyond the quartz tube, but it should be relatively cool at the edges, probably under 500°C.

Models are showing that the quartz tube will not get above about 1000°C (Exhibit 4) even if there is not a cooling system with concurrently flowing water. CU is a little concerned about the quartz nevertheless. Quartz melts at 1200°C. If the second concentrator heats the reactor to well over 2000°C, it would likely overheat and melt the quartz.

Economics:

Dr. Lewandowski presented an economic analysis. The analysis started from a standard carbon black process, added solar components, and developed a cost/performance spreadsheet.

In their base case, Dr. Lewandowski used a heliostat cost of $200/m^2. This assumes a scenario where heliostats are being mass-produced; today's cost is closer to $500/m^2. They assume hydrogen production at 5 million scfd, and carbon black production at 15 million kg per year. They allow for 20% hydrogen recycling (*for the commercial reactor, they plan for hydrogen to be the annular gas*), a residence time of 0.1 seconds, and a reaction temperature of 2000°C. The cost of natural gas was set at $3/MMBtu (see Question 13) and a 0.28 solar capacity was used. They assume that there is very little methane loss.

A sensitivity analysis was developed, and the results are shown in Exhibit 5. It shows that if carbon black could be sold for $0.48/ lb, hydrogen would be free. Conversely, if you had to throw away the carbon black, hydrogen would cost $23/MMBtu, under base-case conditions. The analysis is very sensitive to the cost of the heliostat, but Dr. Lewandowski believes that the lower costs are achievable. The biggest sensitivity issue, however, is the reactor efficiency.

The capital requirement for a 30 MW plant is about $25 million, about 2/3 of that being the cost of the heliostats.

IV Tour:

CU Reactor:

There was really not much to see here. Phase I was completed in FY 2000, and the old reactor was disassembled. The FY 2001 money didn't arrive until March. They are still building the Phase II reactor.

What I did see was a vertical screw feeder with a gas port on the side to disperse particles (*i.e., added carbon black*). The old system used a spinning brush to disperse the particles. The system tended to clog, however, and they couldn't get a good carbon mass balance.

The dissembled graphite reactor is one inch in diameter, and four inches long.

NREL Solar Furnace:

The solar furnace facility at NREL is located on a hill overlooking the major portion of the overall laboratory. The furnace facility includes a 10 kW flat-plate heliostat, 33 square meters in area, which has the ability to track the sun across the sky. Solar energy is reflected down to a 12.5 square meter primary solar concentrator from which it is reflected again into the laboratory building through a set of slits that can be controlled much like Venetian blinds.

The hydrogen reactor was not in place at the time of my visit, but its former and future position was pointed out to be at the focal point of the reflected sunlight. A 3-axis moveable track and gas-handling system was in place to be used with the reactor.

V Questions and Answers:

I sent Dr. Weimer a set of discussion questions prior to my arrival. He responded in writing and we also discussed the questions and answers in detail.

1. **Please discuss how a "real" system would work – one where the sun isn't always shining. How would start-up and shutdown conditions affect the overall output and efficiency?**

"Specifically, as far as the solar-thermal aerosol reactor is concerned, there is no insulation in the reactor and the required residence time at 2000°C for complete reaction is on the order of 0.01 seconds. Hence, the start-up and shut-down times would be associated with heating the graphite tube, which will be extremely fast using concentrated sunlight (probably at most, minutes). At the NREL High Flux Solar Furnace (HFSF), the presence of clouds is continuously tracked and, hence, it is known if a cloud is going to pass by. In this case, it would be possible for the methane to be replaced by recycled hydrogen if need be (just to prevent unreacted methane from passing through the process and to keep air out; one would not use inert gas as it would need to be separated at the outlet).

"Different processes would be affected differently. We envision the following various process configurations: (i) a solar-thermal natural gas dissociation process feeding a hydrogen gas pipeline and collecting carbon black for sale; (ii) a solar-thermal natural gas dissociation process feeding tube trailers and collecting carbon black; (3) a solar-thermal natural gas dissociation process feeding a fuel cell on demand (operating only when the sun is out) and stockpiling carbon black for sale; (4) same as 3, but with carbon black not only being sold into the carbon black market, but also being used to feed a carbon black boiler to supply steam to drive or to have off-gas directly drive a turbine to generate electricity.

“Configuration 1 (hydrogen pipeline/carbon storage): For this case, the intermittent operation would be an issue for the pipeline. Most likely, some hydrogen surge tank with a compressor would be needed where the surge tank pressure would vary (increasing when the sun is out as hydrogen is fed to it; decreasing at night when hydrogen is not being made). Hence, a pipeline would always be fed at constant pressure, but the upstream surge tank pressure would vary. We would expect both the compressor and surge tank to be expensive. Carbon storage would be unaffected

“Configuration 2 (tube trailers/carbon storage): For this case, the compressor would be needed, but there would be no need for a surge tank (use the tube trailers). Carbon would be unaffected.

“Configuration 3 (fuel cell/carbon storage): For this case, the hydrogen would supply a fuel cell and generated electricity would supply a grid. There would be no major storage or transportation issues.

“Configuration 4 (fuel cell/carbon burning boiler/carbon storage): For this case, the hydrogen would be the same as in (3) without storage issues. Also, instead of trying to sell all of the carbon black into the carbon black market, it is possible to operate a carbon black boiler burning clean and fine carbon black (probably < 20 ppm sulfur and no ash; fine micron sized particles). The boiler could be sized so that it operates continuously on the basis of the solar-thermal operating time (stockpiled carbon black). This scenario takes advantage of the fact that the heating value of the produced carbon black and hydrogen is approximately 10% higher than that of natural gas and that the carbon black is high purity and fine. Coal could be left in the ground and minimal environmental pollution control equipment would be needed. In addition, some of the carbon black could be sold into the carbon black market. This scenario may make the most overall sense.”

Dr. Weimer stated that an economic analysis would be needed to evaluate the four configurations.

I am concerned with some of these configurations. The system only runs when the sun is out, so additional energy must come from somewhere. For Configurations 1 and 2, surge tanks, compressors, and tube trailers provide hydrogen storage, so in theory, at least, sufficient hydrogen can be made during daylight hours to supply hydrogen (to a fuel cell, I presume) at night. Configuration 3, which provides no hydrogen storage, requires either some alternative source of hydrogen for the fuel cell when the sun is not shining (perhaps a steam reformer) or an entirely separate electricity generating system. (I am assuming a local grid rather than simply providing electricity to the national supply.) It also assumes that the alternative supply is running constantly (i.e., that the solar reactor is undersized for the amount of required electricity). Otherwise you would have to either make exactly the amount of hydrogen you need, or you would have to flare some hydrogen. Configuration 4 is a double-edged sword. It allows you to get all of the energy out of the methane rather than storing, burying or selling carbon black, but it removes one of the real “hooks” that I believe this project has: not making CO_2.

It's true that you have a nearly 10% higher heating value in carbon black and hydrogen than you do in methane:

$$CH_4 + O_2 \rightarrow 2H_2 + CO_2 \quad (\Delta H = -802.5\ kJ)$$

Vs.

$$2H_2 + O_2 \rightarrow 2H_2O \quad (\Delta H = -483.7\ kJ)$$

$$C + O_2 \rightarrow CO_2 \quad (\Delta H = -393.7\ kJ)$$

$$\text{Total: } \Delta H = -877.4\ kJ$$

Perhaps you can argue that you can keep the coal "in the ground" as a first approximation, but a lot more detail is needed.

2. What is an HEPA filter? Does the presence of a downstream filter alter the gas flow rate?

"HEPA (High Efficiency Particulate Filter) is used only to collect all of the carbon black for research material balance purposes. HEPA is required for asbestos, but is overkill for our process. I expect that typical baghouse filters used in the fine chemical industry would be suitable in this process. At most, maybe Gortex™ bags are used. The filters would be back-pulsed to control pressure drop and maintain operations continuously. Any alteration of the gas flow rate should not be an issue."

3. When you use carbon black particles for heat transfer, what is their concentration compared to the amount of carbon black you are generating by methane decomposition?

"The voidage in the aerosol reactor is around 0.9999, hence, the amount of carbon black is minimal. The amount generated by natural gas decomposition will be much more and most likely the carbon black feeding can be stopped once the reaction is initiated (the Thagard Patent using an electrically heated graphite aerosol tube describes this). This is not a big issue since carbon black is generated in-situ."

Dr. Weimer did mention, however, that as they scale up in reactor size, the surface to volume ratio would decrease. Thus, more carbon black feed may be necessary to optimize heat transfer. Carbon deposition may be the more important problem, however.

4. You state in your FY 2001 Review report that in one set of experiments feeding carbon black to the system resulted in a 30% conversion of methane to hydrogen and carbon; when carbon black was not fed, the conversion was down to 18%. Yet shortly thereafter you make a statement that the formation of carbon black itself "provides an in-situ method of generating carbon black radiation absorbers in the reactor without having to feed it." It would seem that if you do not add carbon black your efficiency decreases considerably. Please comment on this. Also, have you looked at all at the effect of using different carbon blacks with different surface areas?

"Again, we don't think carbon black will be a big issue. The data given in the report are taken out of the examples used in the U.S. Patent filing. We also claim in the patent filing that the carbon black can be generated in-situ. The intention was to show that carbon black feeding was desirable and so a most extreme case was reported. We believe that the carbon black requirement is reactor size dependent. We will see much less need in the lab reactor where the wall surface area to reactor volume is large. As we scale-up, the reactor wall surface area to reactor volume decreases and the need for carbon black particles to be co-fed to initiate the reaction will be greater. This is an area of significant investigation. Our math modeling sensitivity studies are taking to take a hard look at this. This is not a big issue. Carbon black particle are fed commercially through graphite aerosol reactors (heated electrically) today for processes to make ultra-fine tungsten carbide."

In addition, particle size is not an issue. The blackness of the particles is more important for absorbing sunlight.

I would think that if heat transfer is surface-dependent, the particle size of the carbon black would be quite important as well.

I also question why, if the decreased surface to volume ratio in the scaled up reactor is "not a big issue," is it "an area of significant investigation."

5. You mentioned that your apparatus was also used to study "dry reforming" of methane. Are there plans to look at this further? What are the advantages/disadvantages of dry reforming as opposed to thermal decomposition?

"We submitted a proposal ("Dry Reforming of Methane Using a Solar-thermal Aerosol flow Reactor") last August, 2000 to the DOE Sequestration RFP that was issued (Applied Research and Development of Technologies for the Management of Greenhouse Gases," FE-PS26-99FT40613. The proposal was not funded (too bad – great project).

"For hydrogen production solely, we believe that thermal dissociation is advantageous since carbon black can be easily stored and sequestered. Any gas separation – if required for dissociation – will be minimal compared to separating CO from H_2. However, if syngas is desired to produce methanol or other hydrocarbon chain building processes (via Fischer-Tropsch syntheses, etc.), dry reforming is an excellent alternative since it uses CO_2. Also, there are a number of CO_2 contaminated gas wells (BP says their largest producers in the Four Corners area are capped due to high CO_2 content) containing approximately 15 % CO_2. Currently, this gas is not being utilized because of the cost of separating CO_2 from CH_4 and then having to deal with it. A solar-thermal process carried out on this gas stream would allow combined dry reforming and thermal dissociation to occur. Such a process would make use of such gases to produce a product consisting of a high H_2 content syngas and some carbon black.

"A key consideration in dry reforming is to look at the relative reaction rate for dry reforming at 2000°C vs. 700°C (where many catalyst researchers are trying to make incremental changes in process improvement). The bulk of dry reforming research today is directed at reducing the temperature in order to reduce the amount of energy needed to carry out the endothermic reaction and to prevent (or at least try to minimize) carbon deposition that kills the catalyst. Hence, conventional dry reforming is being directed at 700°C temperatures (carbon is still depositing out) operating continuously vs. solar-thermal at 2000°C with carbon deposition not being an issue. If one looks at the relative reaction rate ratio of solar-thermal (2000°C) vs. conventional (700°C) dry reforming, assuming similar order of magnitude pre-exponential factors and activation energies, $\text{Rate (2273 K)/Rate (973 K)} = \exp(0.00059 * E/R)$. For typical E/R, the relative reaction rate is two to four orders of magnitude faster at 2000°C relative to reaction at 700°C. Hence, it should be possible to design a solar-thermal process for massive throughput when the sun is out (2000°C) – say 28% of the time - and that this throughput will be significantly higher than that for a process operating at conventional temperatures (700°C). To make equivalent amounts of product, the solar-thermal would need to be about 4 times faster. The 100 to 10,000 times faster is truly significant. A brute force high temperature process such as dissociation or dry reforming takes advantage of this significant relative reaction rate. The challenge comes with designing a process for massive throughput (when the sun is out) to operate semi-continuously."

The dry reforming portion of the project is not funded by the hydrogen program. However, says Dr. Weimer, perhaps you can shift the syngas. (The syngas was said to be composed of 6 hydrogen molecules to one CO.) *The reaction shown earlier in the paper says it's a one-to-one mix.* To switch from thermal decomposition to dry reforming is a simple process – you just change your feed bottle.

If you shift the syngas, you of course get CO_2 back, but what you've accomplished is that you've recovered the previously unusable natural gas. It's not a hydrogen technology, but I think it has some real merit.

6. In the new reactor you are building (built?) will your graphite reactor tube extend throughout the quartz tube? (In other words, is this how you will prevent deposition on the quartz tube?)

"Yes, the new graphite reactor tube extends throughout the quartz tube. For the lab, inert gas will flow in the annular region between the two concentric tubes. For the commercial process, we envision that this annular gas could be hydrogen (of course, inert gas would be safer). The gas will prevent air from attacking the graphite tube on the outside. Also, the process gas stream and resulting carbon black will never contact the inside quartz wall or mix with the annular gas."

Deposition is an issue, but may be less of one in a commercial system where the reactor and the annular region will be larger.

In the redesigned system, the annular gas can be kept entirely separate from the reactants. If hydrogen is used, it can simply be recycled from product hydrogen. It appears that the new reactor was designed with lessons learned from the first system incorporated well. I will be very interested in hydrogen production efficiency in the new system.

7. Figure 16 in your report seems to show that you are switching from argon to nitrogen as a carrier/purge gas. Is this due to cost, thermal considerations, or some other reason?

"In the lab reactor, we will have 99% methane flowing through the reactor tube (actual flow will be down and not up as shown) with a 1% of argon as an internal standard. We will either flow N_2 or Ar in the annular region between the two concentric tubes. Argon is preferred because of higher heat transfer, however, nitrogen may be used. With no experience yet in the processing, argon is a more conservative gas to use. In practice, hydrogen will most likely be used. In practice, pure NG will feed the reactor tube. The 1% standard is only to close atomic material balances in the lab unit for research purposes."

8. **I am confused by the annular cooling gas. Aren't you operating at cross-purposes, heating and cooling the same material?**

"The annular "cooling gas" is to both prevent oxidation of the graphite reactor tube and to cool the outside quartz tube. The graphite tube will be heated by concentrated solar radiation. Although the sunlight will pass through the quartz tube, the quartz tube will be heated by the hot graphite tube (heated by radiation). We have done and will be doing additional modeling calculations to determine the temperature of the quartz tube. So, the "cooling gas" is to cool the quartz tube and not the graphite."

9. **Could this system be used as a heat source for steam reforming?**

"Yes, except that we would be concerned with reaction of the graphite tube with water. Fine co-fed carbon black would be much more reactive than the graphite wall, however, wall attack would be inevitable. If, however, lower temperatures were desired, we could use an oxide or metallic alloy tube that is not reactive with water. However, the real advantage of the solar-thermal process is to operate at extreme temperatures (> 2000^{o}C) that cannot be easily or cheaply achieved using conventional heating. The ultra-high temperature to carry out "brute force" dissociation or dry reforming reactions is a unique niche of the solar-thermal aerosol process."

Their patent includes the thermal dissociation and dry reforming processes, and also includes a process to react the carbon black with water to make syngas.

10. **How will the hydrogen be separated from the carrier gas, unreacted methane, etc.? Will the methane be recycled?**

"There is no carrier gas. If gas is used to sweep carbon black into the process, it will be methane or hydrogen. The annular gas will be kept separate from the process gas. At the temperatures we hope to operate at (2000 + ^{o}C), dissociation should be nearly complete. Experimental results from Thagard Research, contained in their US Patent, indicate complete conversion at these temperatures. Our results of nearly 90% conversion at 1600^{o}C are consistent with what Thagard reported. We expect there to be some acetylene, etc., but at < 100 ppm levels. Any separation system should not be big and may not be required. We do not expect any significant amount of unreacted methane, if any. Please note that those processes carrying out dissociation at 1300 to 1800^{o}C (like the Florida Solar Energy Fluid Bed NG Decomposition Process) will have significant separation issues and recycling of methane. This is a big advantage for the 2000^{o}C solar-thermal process. The degree of conversion achievable will be a key consideration in our experiments. This is why we are building the new reactor system – to achieve the 2000^{o}C needed. We don't believe separation and recycle will be an issue. It is possible that there might be some selective adsorption process, etc. to eliminate trace impurities, but we have not yet considered any details."

Dr. Weimer believes that they can get essentially 100% conversion to hydrogen at 2000^{o}C. They'll know later this year.

11. **On a commercial scale, this process would be run using natural gas rather than methane. This will presumably increase the types of and amounts of impurities present in the mix, both reactant and product. How do you intend to deal with this?**

"Any hydrocarbon should "crack" to carbon black and hydrogen. Other impurities, like H_2S, will crack to H_2 and elemental S. Typical natural gas carbon blacks (like Cancarb Thermax) have sulfur contents less than 20 ppm. Any residual CO_2 will reform to CO and may be an issue for a fuel cell. We need to eventually look at this. We intend to run natural gas in this reactor as part of the program."

They'll also likely get some higher hydrocarbon reaction products, acetylene, for example.

12. In your new process design you indicate that some of the hydrogen is recycled to prevent deposition of carbon black on the reactor window. I assume this isn't a chemical process. Why are you using hydrogen recycle? Why not just use purge gas?

"Carbon deposition on the quartz tube will not be an issue for the graphite tube going all the way through. What you are referring to is the early reactor. We don't want any inert gas in the methane feed stream (or mixed with it) because it would require separation downstream. We are concerned with carbon deposition on the inside of the graphite tube. If we swept any gas along the inside wall to prevent deposition, it would be hydrogen. One advantage of no insulation and a reactor system shut down at night is that operators can clean out the tube if any buildup occurs."

Dr. Weimer stated that it would be easy to remove carbon black buildup from the graphite reactor wall. Deposition on the quartz outer tube will not be an issue with the modified reactor as long as nothing comes off of the outer wall of the reactor. CU is using a high quality graphite for the reactor, and don't expect it to volatilize.

13. Please comment on your use of $3/1000 scf of natural gas as a base price in light of current costs being double that.

"We worked with Maggie Mann of NREL on this one. We used the $3/1000 scf as the base case as most people are familiar with this value and most economics involving NG have used it in the past. We did use it as a low value base and then investigated higher cost NG. Each additional $3/1000 scf in NG cost adds about $4.40/MBtu to the cost of hydrogen. This is independent of the selling price of carbon black, therefore, the relative impact on hydrogen selling price is higher when carbon black sells for reasonable amounts."

It's really probably not a bad number to use. The number of analyses is rising that says that the high natural gas price will not last very long.

14. During the annual review, I heard a comment from one of the reviewers about the concern that by dissociating methane rather than combusting it, you fail to recover all of the energy. Obviously you can rebut that by indicating that 1) you have a saleable product in carbon black, and 2) that you do not contribute to global warming. Although I am in agreement with what I would think is your position, I think it makes a good discussion topic.

"You can't have your cake and eat it to! We know of no other process (other than nuclear) that can produce H_2 without generating greenhouse gases if that is the purpose. In addition, solid carbon black is much easier to sequester and store than CO_2. However, if one wants to take advantage of the heating value, the solar-thermal process actually increases the heating value of the feed by almost 10% (the heating value of the $2\ H_2 + C$ is 10% greater than the CH_4). One could leave coal in the ground, and have a fine high purity carbon black to burn and end up with almost a 10% increase in energy. The pollution considerations would be minimized due to low S and ash (none) in the NG produced carbon black. In addition, no CO_2 would be generated mining coal or grinding or transporting it, etc.

One other very important aspect is that we can make use of CO_2 contaminated NG that is currently capped and not used! We can carry out ultra-high temperature dry reforming using the 15% CO_2, and methane dissociation using the excess CH_4 (see our experiments that used a 2/1 ratio of CH_4 / CO_2). The product is a H_2/CO ~ 6/1 syngas and some carbon black."

The carbon black sell or burn issue can be debated back and forth. Hopefully the talks with Cabot will help answer the question. Personally, at this point I'm not sure whether burning the carbon black is preferable to just combusting the methane. Sequestering CO_2 as carbon black, however, seems to be of some interest.

VI Additional Discussion:

Dr. Weimer believes that the carbon black they are producing might be unique, or at least of high quality. It is a small diameter (20-40 micrometers), high surface area material. In fact, Dr. Weimer wonders if the process could produce carbon nanotubes as a byproduct; it hasn't happened yet. *You make hydrogen and the material in which to store it at the same time! Interesting. Nevertheless, I would concentrate on the basic process for now and not worry about nanotubes.*

Dr. Lewandowski pointed to a strong educational component to this project. Groups of undergraduates are performing design and life cycle studies.

VII Final Thoughts:

This project presents an interesting dichotomy, which, perhaps, is true for many renewable energy concepts. It is based on sound science and on what appears to be evolving into a good engineering design for the reactor: The kinetics at 2000°C are a lot faster than at 700°C; thermal dissociation produces no CO_2; there is a reasonably good chance that the final reactor design will efficiently recover close to all the hydrogen in methane. Furthermore, the ability to sell carbon black could favorably impact the cost of hydrogen. However, the overall usefulness of the project as a means to result in a large-scale commercial project needs to be considered. The locations where the process could be run efficiently appear significantly limited to very high insolation areas. Uses of hydrogen would either be limited to installations on site or close to the high insolation area, or transport costs (which would likely include compression) would have to be added. Also, the system, as it's currently envisioned, does not go beyond hours when the sun is shining. Either the system will need to be used in conjunction with another energy source or it will need to be built large enough to make enough hydrogen for nighttime use as well. This again would necessitate compression and storage components.

The economic analysis shows the system to be quite sensitive to at least two items out of its control: the cost of natural gas, and the cost of heliostats. These are areas of concern as well.

I believe that the researchers, need to address location (how efficiently does the system perform outside of Death Valley?), application (where will you use the hydrogen, and how will you get it there?), and systems considerations (what percentage of the load will be supported by hydrogen; if it is to be stand alone, how will storage be addressed; if a backup (or more likely a second primary system) is to be used what is it, and how will it be integrated?)

Exhibit 1. Schematic of First Generation CU Reactor (Figure supplied by CU)

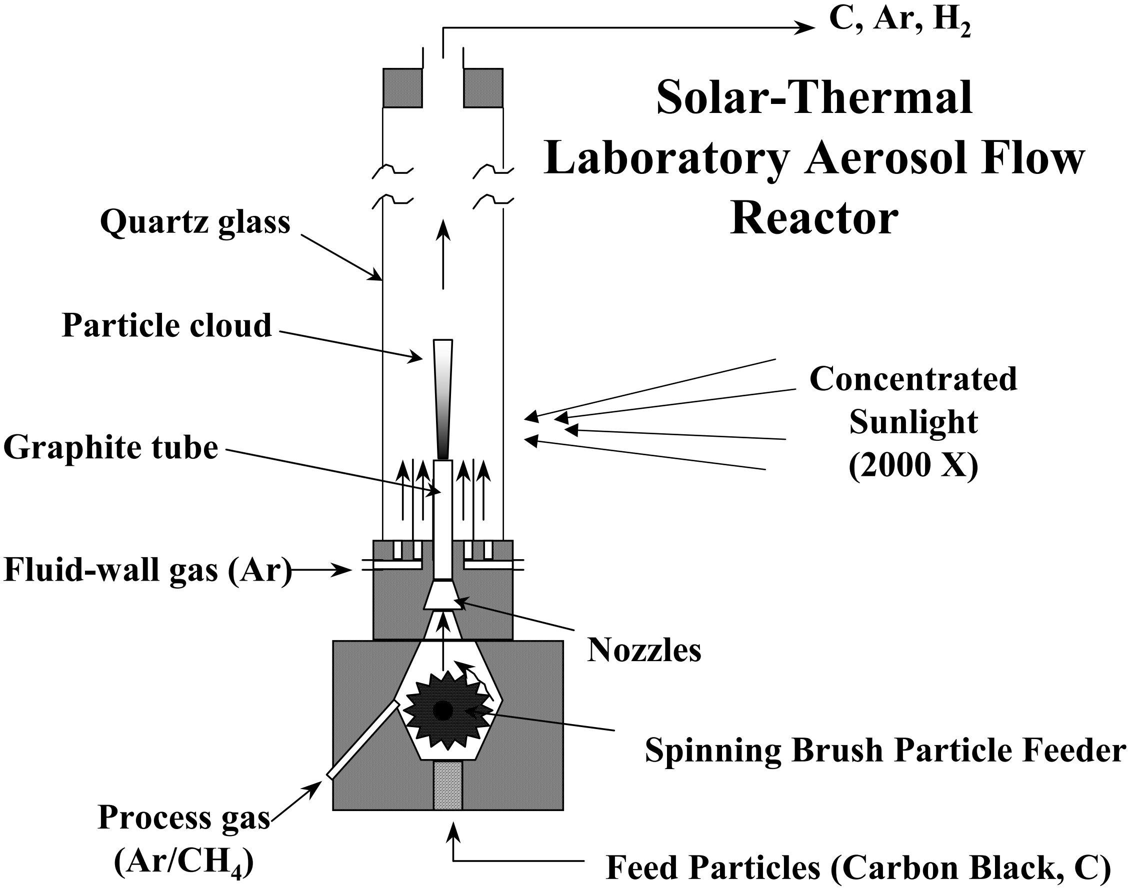


Exhibit 2. Schematic of Second Generation CU Reactor. Figure supplied by CU

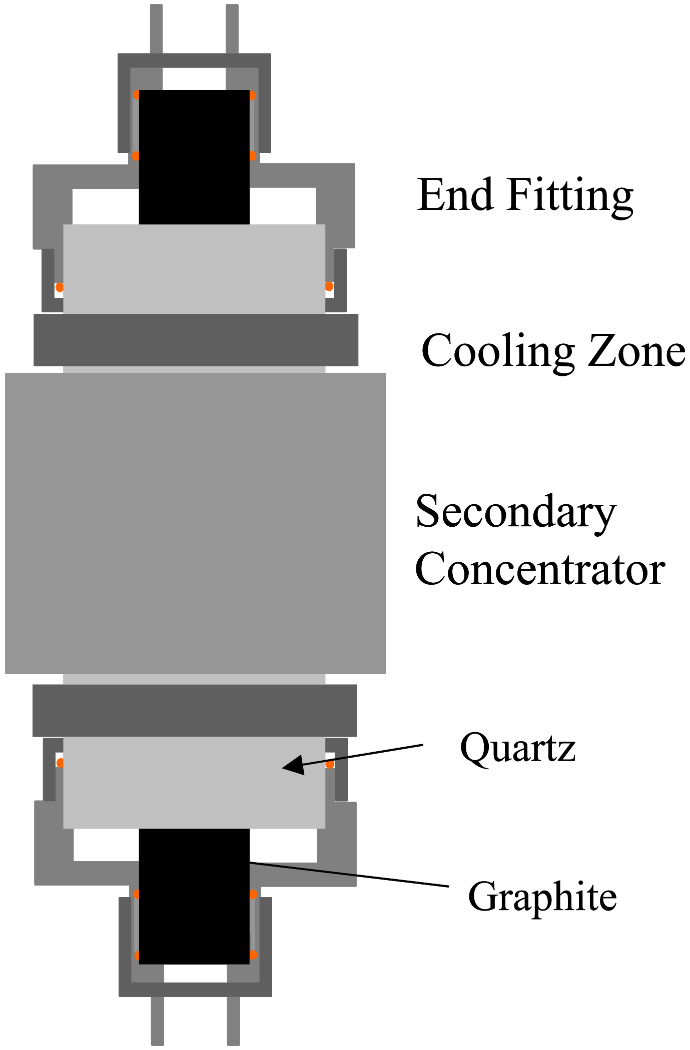


Exhibit 3. Data Derived from Thagard Patent (U.S. Patent # 4,056,602 (1977)) that Demonstrates Increased Methane Dissociation with Temperature. Figure supplied by CU

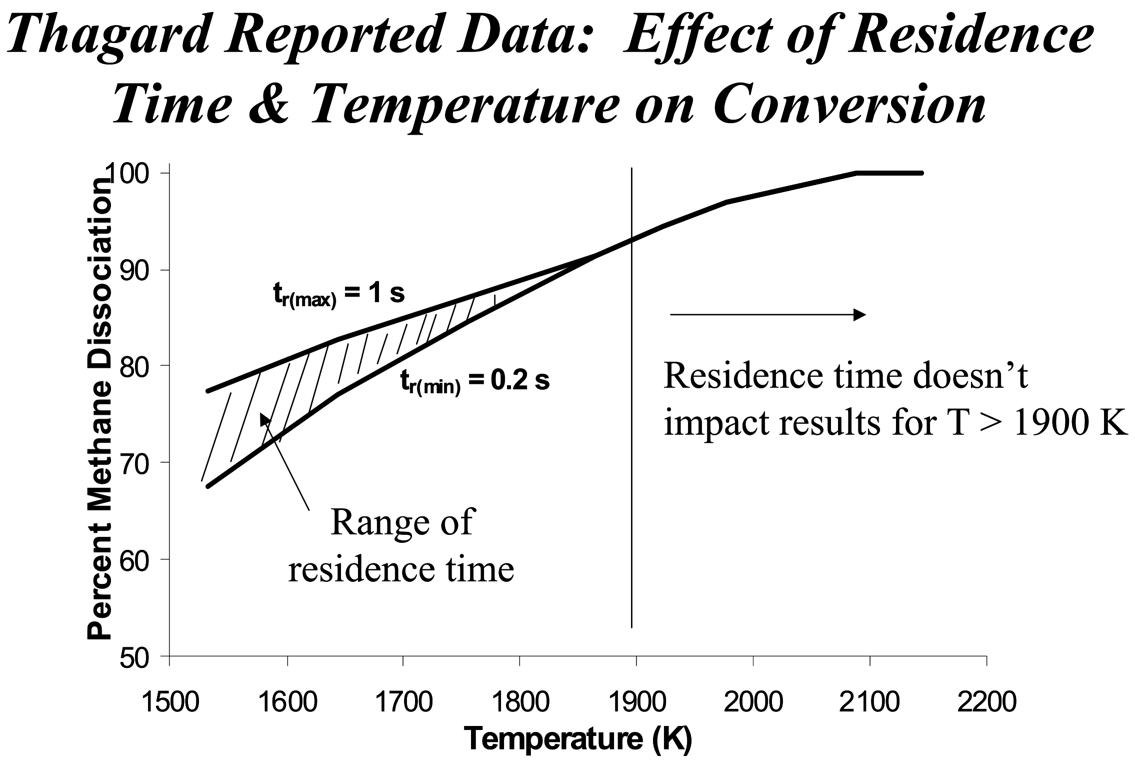


Exhibit 4. Heat Transfer Model for Second Generation Reactor. Figure supplied by CU

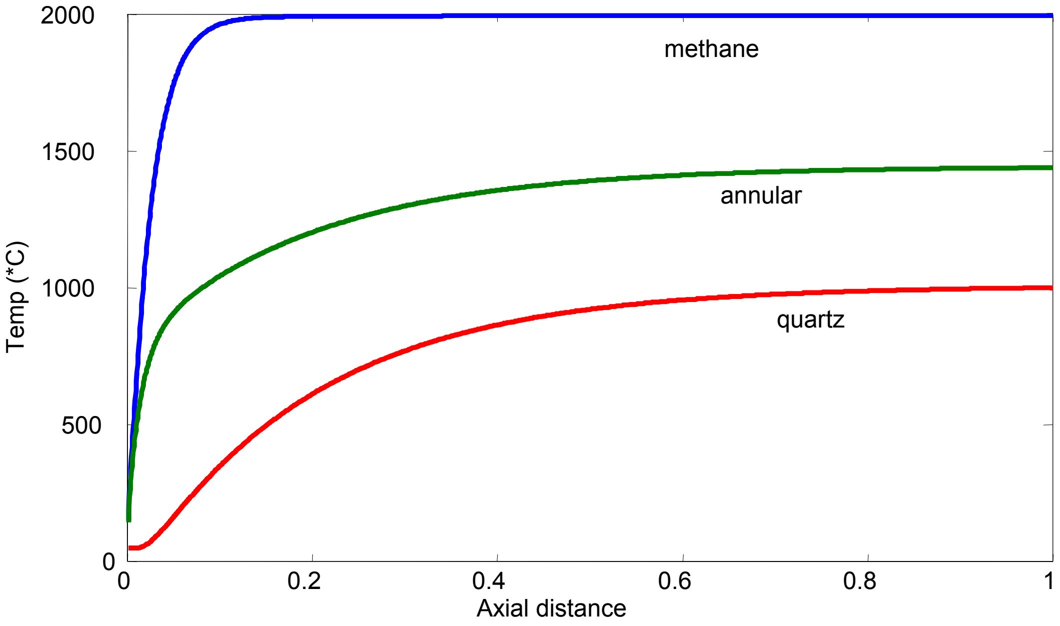
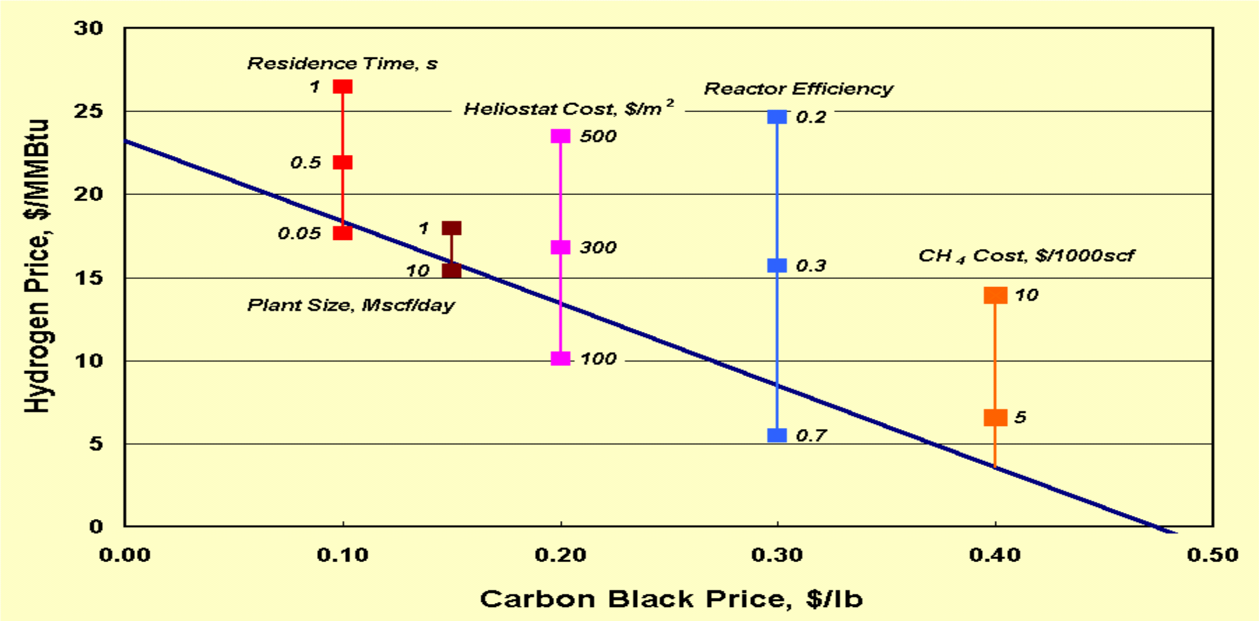


Exhibit 5. Sensitivity Analysis for the Price of Solar Thermal Dissociation-Price of Solar Thermal Dissociation-Produced Hydrogen. Figure supplied by NREL



Technical Evaluation Report
Project: Biological H2 From Fuel Gases and Water
Company: National Renewable Energy Laboratory, Golden, CO
P.I.: Dr. Pin Ching Maness
Date of Visit: July 2-3, 2001
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

Among the photobiological projects that are part of the hydrogen production effort, the subject project is somewhat unique. First of all, its primary component is not directed at water splitting (although this goal was previously part of the project), but at the water shift reaction. Secondly, the primary process is not photobiological at all. The bacteria perform the activity in the dark.

The researchers at the National Renewable Energy Laboratory (NREL) are looking to optimize an organism that can perform the shift reaction biologically at room temperature. (The reaction,

$$CO + H_2O \rightarrow H_2 + CO_2,$$

is conventionally run in the presence of catalysts in two operations at 800°C and then at 400°C.) In a separate project that is not being reviewed in this report (although we will discuss it briefly), NREL is designing and building a reactor that will allow the biological water shift reaction to be performed at a larger scale, and ultimately, for commercial use.

Project Strengths:

If the bacterial water shift proves to be economically sound, it presents an opportunity for an important component to the overall hydrogen/PEM fuel cell system – a single step shift and purification (CO removal) process.

- Even if hydrogen production via bacterial water shift does not prove to be a cost-effective process, if the bacteria can reduce CO to PEM fuel cell levels it's a very valuable contribution.
- The process appears to be quite robust, and would apparently work with any syngas regardless of source.
- The fact that the bacteria work in the dark will allow for a more compact system and one that can be located more widely.

Issues that should be Addressed:

- Focus. NREL recognizes that the Peer Reviewers had recommended that the project focus on water-gas shifting – not water splitting. There is still a lot of water splitting data being reported, especially oxygen tolerance issues. Also, if the work is supposed to center on the CBS bacteria, care must be taken not to go overboard with the mutant species.

- The robustness of the species needs to be demonstrated.

- Favorable economics need to be proven.

II Introduction and Background:

The development of bacteria for both shifting CO and water to hydrogen and CO_2, and for splitting water to hydrogen and oxygen has been an ongoing project at NREL for the past several years. Until recently, the project was led by **Dr. Paul Weaver**. Unfortunately, ill health has forced Dr. Weaver to reduce his workload. The Principal Investigator (PI) role for the biotechnology development work has been therefore taken over by **Dr. Pin-Ching Maness**, who has been working on the DOE Hydrogen Program project with Dr. Weaver since its inception. The accompanying work, building the bioreactor, is now led by **Dr. Ed Wolfrum**. Since my goal was the evaluation of the bacteria development project, I spent most of my time (the afternoon of one day, and the morning of the next) with Dr. Maness, although I did get the opportunity to talk with Dr. Weaver for a few minutes, and did visit Dr. Wolfrum in his laboratory. The laboratories are located in NREL's Field Test Laboratory Building.

Dr. Maness and I spent many hours in discussion of the project including in-depth analysis of several questions that I had sent to her prior to the meeting and for which she had prepared answers in writing. Dr. Maness also took me on a tour of her laboratories, and I was also shown Dr. Wolfrum's bioreactor systems.

Aside from the personnel changes, the key development over the past year is the allocation in focus entirely to the water shift process. This was done at the recommendation of the Peer Reviewers who felt that the transfer of the bacterial vector into a cyanobacteria or an alga was complex and unlikely to succeed. Thus, the water splitting component of the research has (at least temporarily) been halted.

III Initial Discussion:

Dr. Maness compares the NREL project to the conventional water shift process and feels that they hold a two-fold advantage: CO removal capability and a bacteria that is easy to grow as opposed to having to use an expensive catalyst.

The bacteria that has been used by NREL to perform the water shift reaction is of the type *Rodocyclus gelatinosus*, and is known by the acronym "CBS". Dr. Maness, in looking to harvest the proper bacteria felt that for a bacterium to be able to use CO, it should come from a CO environment. Dr. Maness thus harvested material from areas containing vegetation around parking lots – vegetation that would come in contact with high concentrations of CO from automobile exhausts. The CBS bacteria were harvested from the shrubbery at the edge of a parking lot at a Denver area Mexican restaurant. The bacterium was thus named for where it was found: *Casa Bonita Shrubbery (*CBS*).* NREL has now been working with CBS for 7-8 years.

Dr. Maness' group have found many other organisms that are akin to CBS in that they have water-gas shift properties that are similar. Nevertheless, if CBS were to turn out to have widespread application, Dr. Maness suggests that the CBS itself be transported and grown in other areas rather than try to find/use a similar material. Another material may have the same tendency toward CO, but, for instance, reaction rates would likely be different. *Does this imply that there could be bacteria out there that would be even better than CBS*, *if we go hunting in parking lots?*

CO is a primordial gas as is CO_2, H_2 and N_2. Bacteria, such as CBS live on CO, or at least use it, getting energy out of it. So (*unlike other biological undertakings*) what the bacterium is doing is not against its nature. It does not have to be mutated.

The reaction to make hydrogen, which is actually a two-step process:

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \quad [1]$$

$$2H^+ + 2e^- \rightarrow H_2 \ [2]$$

and requires an electron mediator, takes place in the dark. The bacteria would produce cell mass in the light. Dr. Maness suggested alternatives of making hydrogen at night and growing cell mass during the day, or using two systems that would alternate between making cell mass and hydrogen, or perhaps making cell mass for a few days and then pumping the material into a dark reactor. Later, (*see Question 11*) she spoke of perhaps only needing cell growth every year or so, but also considered the possibility of admitting limited light to allow cell growth in situ. *It is obvious that this portion of the project has not yet been worked out. It's more of an engineering problem, but it could involve some manipulation of the bacteria if using multiple reactors or different reactors for mass growth and hydrogen production are not cost effective.* Dr. Maness refers to the bacteria as "a self-replicating catalyst for shift reactions."

A bright spot *(pardon the pun)* is that the hydrogen production process is not hindered (*unlike other biological undertakings*) by the efficiency of the photolytic reaction – except, of course, during cell mass growth. The bacterial cells are grown with CO as the only carbon source.

CO uptake is very rapid, only taking a few seconds, says Dr. Maness. The best method of exposing the bacteria to CO, however, is unclear. Dr. Maness suggested a sprinkler head. *I'm not quite clear on this. As will be seen later, reactor systems using high surface area reaction beds are being developed. I don't know how a sprinkler head would fit in, or* *why you'd want one.* These bacteria are quite hardy, and have no problem being pumped; they handle pressure well.

Dr. Maness emphasized that the bacterial water shift process both produces hydrogen and removes CO at the same time; an additional purification step would not be needed. *If the plan is to use the hydrogen in a PEM fuel cell, CO would have to be virtually eliminated (<10 ppm).* NREL has one piece of data that shows that the bacteria removed CO down to the 0.2 ppm level. Dr. Maness, however, was quick to caution that this was one "special experiment" that Dr. Weaver ran. It proves that the bacteria are capable of removing virtually all of the CO, not that they can do it efficiently, continuously, *and commercially. If they can, this is a major breakthrough!*

Now, the durability and the recycling capabilities of the system need to be shown.

IV Tour:

Dr. Maness took me on a tour of the laboratories where the bacterial strain is being developed, characterized, and tested. Later, we visited Dr. Wolfrum's laboratory where I saw the bioreactors.

The first stop was the Water-Gas-Shift Laboratory. Among the testing and analysis equipment in the lab were: an "old but reliable" gas chromatograph (GC) that samples the headspace of the sample bottles for hydrogen; a hydrogen/oxygen cell (electrode system) to measure hydrogen production in solution (this is a homemade device), and a high performance liquid chromatograph (HPLC) to determine intermediates.

Adjacent to the laboratory were a standard sterile transfer room and an anaerobic chamber where the oxygen is removed from the air to condition it for the enzymes, as the enzymes are anaerobic.

Dr. Maness' laboratory shares centrifuges and spectrophotometers with Dr. Mike Seibert's laboratory.

In another room many bacterial cultures were growing. These brownish-orange CBS species absorb in the orange, red, and infrared light regions, using the part of the solar spectrum that is "wasted" by blue-green algae.

An old "carpet reactor" developed by Dr. Weaver was also present in this room. Dr. Weaver's premise was that since CO take up is controlled (at least at the laboratory scale) by mass transfer, the piece of shag carpet provided the surface area on which bacteria could be immobilized and CO efficiently taken up.

An inclined bubble reactor is used by the group to condition fuel gases (that is, to try to remove all of the CO so that the hydrogen can be used in a PEM fuel cell.) This is Dr. Weaver's old reactor according to Dr. Maness. While the carpet reactor immobilizes bacteria, the bubble reactor allows free movement. Mass transfer is bubble related –

smaller bubbles equal more surface area. The tubes are long (a few feet in this instance) to allow a long contact time between the CO and the bacteria. *The reactor looks like a smaller version of the one at the University of Hawaii that I saw two years ago.* The tube can be sampled at various locations so that one can see how long it takes for the CO levels to be down to acceptable levels. A very sensitive near-infrared CO detector is used. It can measure down to “a few ppm.” *This, of course is necessary for PEM fuel cells. I’d like to see some data.*

The reactors in Dr. Wolfrum’s area were not running when I visited there, but I was able to see one- and five-liter tubular “trickle-bed” reactor systems (they are looking at scaling, and will go to 25 liters next) and components including transfer media. I was shown the reactors by Dr. Wolfrum and his associate **Andrew Watt**. They are looking at wood fiber and cellulose primarily, but glass as well. Porous materials such as these are about five times more effective at mass transfer than non-porous material, and to quote Dr. Wolfrum, in the real world it is “way mass-transfer limited.”

They plan to look at pressurized reactors also; this will aid the transfer process. In addition, they will be checking to see at what pressure hydrogen can be produced. They have already shown that the bacteria can operate at ten atmospheres of pressure.

Reactor flow rate is not very fast because you really need that contact time. Dr. Wolfram estimated residence times to be in the “tens of minutes”. There is a sensitive balance between contact time and reactor size. However, as they move into pressurized systems they believe they will be able to reduce contact time significantly. At 200 psi, Dr. Wolfrum estimates an order of magnitude drop in residence time. Then, as they identify the most efficient bed material, they should be able to reduce the residence time by another factor of 2 to 4. Eventually residence time will be under a minute, they predict.

One “rule” in Dr. Wolfrum’s laboratory: they don’t deal with sterile conditions here; they’d rather consider real world situations. *This is an excellent approach, and should definitely answer questions about the robustness of the CBS bacteria.*

The plan involves looking at the effects of toxicity. Generally, with biomass products you do a water scrub first. This leaves approximately 1/3 hydrogen, 1/3 CO and 1/3 CO_2. There are, however, small amounts of benzene and toluene present. NREL plans to determine how CBS reacts to these impurities. It’s more than just keeping the bacteria alive; they have to keep water-shifting. It would take less benzene or toluene to inhibit the shift reaction than it would take to kill the bacteria. Some initial indications show that the CBS bacteria remain viable, but they are not sure about shift yet.

Dr. Wolfrum mentioned that they had hooked a reactor up to the back end of a biomass pyrolysis system as a proof of concept study.

V Questions and Answers:

I sent Dr. Maness a set of discussion questions prior to my arrival. She responded in writing and we also discussed the questions and answers in detail.

1. **Your project is titled "Biological H_2 from Fuel Gases and from H_2O" which seems to imply that you are working with two microbes – one that produces hydrogen from fuel gases and another that produces hydrogen from water. I seem to remember in past years, there being two tasks, one devoted to fuel gases and another to water. Your recent reports indicate that you are concentrating on shifting CO and water to hydrogen and CO_2. How does the current work relate to the original work?**

"We use the same microbe to accomplish both subtasks. "H_2 from fuel gases" uses the microbe as is, and "H_2 from water" requires a mutant of bacterial-cyanobacterial hybrid. However, DOE review panel had suggested last year to discontinue the work of H_2 from water due to its level of difficulty. They recommended that we focus on the "H_2 from fuel gases" portion, as it has more potential and immediate success. "H_2 from water" requires cloning the hydrogenase gene, constructing a vector, and getting the hydrogenase and its cofactor incorporated and expressed in a cyanobacterium."

Bacteria do not use water as an electron source; algae and cyanobacteria do use water this way. So in order to split water they would need to construct an algae or cyanobacteria. This is now beyond the scope of the project. Dr. Maness is concentrating on the water shift reaction.

"Even though the focus is shifted, we are still working on cloning the hydrogenase gene, and if successful, it has applications beyond "H_2 from water". Elucidating the genetic system allows us to understand the components involved and the rate-limiting step of the overall system. With this knowledge, we can then enhance the rates and durability of H_2 production from CO shift via biochemical and genetic approaches."

They are not planning to go back to water splitting in the future; they are looking at the molecular biology of the shift reaction. However, the information they are obtaining could be used for the water splitting project as well – should funding ever come back in this area. (*See also, Question 9)*

2. **You say that the rate constant for the hydrogenase enzyme *Rhodocyclus gelatinosus* CBS-2 is greater than 60,000. Is this a first-order reaction (i.e., k= 60,000 s^{-1}), or are you indicating an equilibrium?**

"It is an equilibrium constant at 30° C temperature."

That's what I thought, but the report had called it a rate constant.

Dr. Maness provided a temperature/equilibrium constant curve, shown in Exhibit 1. Since the equilibrium favors hydrogen production at cooler temperatures, they would want to pull any heat out. Dr. Maness says that they could use the heat to power the reactor.

3. **Please discuss the three different hydrogenases in the system, describing what each one is (or is supposed to be) doing.**

"**Formate-linked hydrogenase**, or the fermentative hydrogenase: induced under fermentative condition with a proposed function to dissipate excess reducing equivalents during growth. This enzyme normally equilibrates at low H_2 partial pressure and is extremely sensitive to O_2.

"**Uptake Hydrogenase** – induced under low redox condition. Its main function is to oxidize H_2 as a source of energy to support CO_2 fixation, therefore, it is not suitable for H_2 production. Uptake hydrogenase is quite stable to O_2.

"**CO-linked hydrogenase** – induced under low redox condition with CO present as part of a water-gas shift pathway. Only a few organisms have this pathway. In our organism, its function is to capture the energy in CO, via the enzyme CO dehydrogenase, and convert the reducing equivalent into the form of H_2, which can then be oxidized by the uptake hydrogenase for CO_2 fixation. CO-linked hydrogenase is most robust and favors the H_2 production direction.

"An organism may contain one, two, or all three of the hydrogenase enzymes."

For the NREL system, the key hydrogenase is the CO-linked hydrogenase. It is much faster than the formate-linked. In fact, the CBS bacteria do not even contain the formate-linked hydrogenase.

The formate-linked hydrogenase is not even a good candidate for hydrogen production because the enzyme is not long-lived. The uptake hydrogenase works only in the light, while the CO-linked hydrogenase can work either in the light or darkness. In darkness it uses CO to make hydrogen, and in the light it uses CO to make cell mass.

The hydrogen producing aspect of the CO-linked hydrogenase is helped by the high equilibrium constant of the shift reaction at ambient temperature (see Exhibit 1) and by the high ratio of the hydrogen evolution to uptake ratio (about 43-50).

The basic goal is to obtain mutants that will chose the hydrogen-forming CO-linked hydrogenase over the mass-growing uptake hydrogenase. Most bacteria would rather use hydrogen as an electron donor – that is, the uptake hydrogenase function.

4. **In your FY 2000 Annual Review report you state that it is difficult to measure oxygen resistance for the CO-linked hydrogenase because of the presence of the uptake hydrogenase. Yet you state that the uptake hydrogenase is very tolerant of oxygen. How does the fact that one material is tolerant of oxygen affect the oxygen tolerance of another material?**

"The existing hydrogenase assays do not discriminate one hydrogenase activity from the others. One might mistakenly attribute the O_2 tolerance of uptake hydrogenase to the hydrogenase of interest. That is why the hydrogenase of interest has to be purified from the other to avoid confusion."

This answer needed some clarification. I had assumed that if you were producing hydrogen in the presence of oxygen, and if the CO-linked hydrogenase was the key factor for hydrogen production, then by inference, the CO-linked hydrogenase was oxygen tolerant. Dr. Maness assured me that this was indeed the case, but for accuracy you needed to prove it separately.

5. **In your FY 2001 report you indicate that the CO-linked hydrogenase is tolerant to 3% oxygen, and that this is sufficient for scale up. How did you determine that this was sufficient for scale-up? What final tolerance level do you feel will be necessary for a successful system?**

"To be real conservative, the hydrogenase would have to be functional in the presence of full air, that is, 21% O_2. However, it all depends on the activity of cellular respiration, which will scavenge O_2, and also how O_2 partial pressure is partitioned within cells. A hydrogenase functioned at 3% O_2 gives us a starting point to examine a hybrid system. Most evolving hydrogenase has a half-life of 1 min in full air. Our hydrogenase has a half-life of 21 hours in full air and is partially functional in 3% O_2. Comparing to other hydrogenase reported in literature, our hydrogenase is probably the best candidate to be transferred into a cyanobacterium.

To scale up H_2 production from CO shift reaction, O_2 tolerance is not an issue since syngas is O_2-free."

In fact, says Dr. Maness, in a real system, tolerance would have to exist at least at 21% oxygen. Oxygen levels could go above 21% in a closed system with the bacteria making more oxygen.

The methodology for testing oxygen tolerance that the laboratory was using involved stirring CBS in full air, taking a sample of about 0.5 ml, and injecting it into a new assay vial with methyl viologen and sodium dithionate (a mediator reductant). Hydrogen concentration is then measured at different time intervals. This gives the rate. The problem is that sodium dithionate scavenges oxygen itself.

NREL has therefore switched to the "HD" assay. You add deuterated water to the bacterial suspension allowing a deuterium atom to exchange with an atom from water shift-produced hydrogen, to form HD. This procedure requires neither an electron mediator nor a reducing agent. Oxygen cannot be scavenged, and you have a better system for measuring oxygen tolerance.

It is all somewhat moot, however. Oxygen tolerance is only an issue in the now defunct water splitting mode.

6. **In Figure 1 of your FY 2001 report** *(shown as Exhibit 2 in this Report)*, **is the ion current representative of HD concentration? I'd like to spend a little time on this Figure during our meeting. I'm especially interested in understanding what you mean by the hydrogenase being not only tolerant of O_2 but also partially functional.**

"Yes, the ion current corresponds to mass 3, presumed to be HD. We have not yet calibrated ion current of HD in relation to its absolute quantity such as moles.

"Referring to "tolerant and also functional": "tolerant" means that hydrogenase activity can be restored once O_2 is removed. This was determined by exposing cells to O_2, followed by the removal of O_2 and then assayed hydrogenase activity anaerobically. "Functional" means that we observed partial H-D exchange activity in the simultaneous presence of O_2 – activity was determined in O_2. Tolerance and functionality in O_2 were determined with two different assays."

7. **Still on the same Figure: You show decreased – but nevertheless measurable HD at 3% oxygen. At what oxygen concentration does HD cease to exist?**

"We have not titrated O_2 concentration versus H-D exchange activity yet. It's in the plan."

The key is that the hydrogenase will work at least up to 3% oxygen. The rate decreases, but the reaction still produces HD in a linear manner – only slower. I asked if the HD production rate here was directly proportional to the hydrogen concentration. Dr. Maness believes it is, but is not yet sure. The "H" in HD likely comes from hydrogen production, and both the HD exchange and hydrogen production work at the same active site on the enzyme. For now, however, the HD exchange only demonstrates that the hydrogenase is working in the presence of oxygen; it doesn't necessarily relate directly and proportionally to the amount of hydrogen being produced. They need to find out if it does relate directly, Dr. Maness stated.

Again, this is a water-splitting concern. Nevertheless, Dr. Maness stated that they would like to publish these data, and will therefore try to reproduce it using purified CO-linked hydrogenase.

I think the reader can see a bit of a trend here. Having read several reports written by the PI, including the yet-to-be released (as of this writing) FY 2001 Annual Review Report, I see a lot of attention paid to oxygen tolerance. That is why I asked several questions about it. But oxygen tolerance is not an issue for water shifting of CO, which is what the project should be concentrating on— and what they indeed now appear to be concentrating on. Care needs to be taken that the focus continues to be on the water shift reaction.

Dr. Maness discussed the methodology they will use to actually measure hydrogen production.

8. **You reported surprising results in which seven mutants were isolated that increased rather than decreased hydrogen production compared to the parent species. Were these particular mutants unique? That is, did other mutants show the expected decrease, or were these seven the only mutants isolated? Were the results reproducible?**

"The results are the average of four independent measurements. They are reproducible and most importantly, the mutants are stable. We are not sure on the uniqueness. These seven were the only mutants isolated. Had we obtained some mutants with reduced activity, I would then say yes, they are unique. We plan to repeat their rate measurements again this summer. If still reproducible, we will propose to DOE in the AOP to characterize these mutants further."

The key factor is stability. Variants are not always stable; they have a tendency to revert to the properties of the wild type. (Mutants are generally less competitive than the wild type of bacteria, and it is difficult to keep them under the right conditions.) They need to find a way of determining if the mutants are stable, and don't degrade over time. If the mutants are indeed stable, they will try to get funded for the characterization work, and then eventually do some bioreactor work with them. This is well in the future, however.

The key thing that Dr. Maness pointed out, however, is that they do not use mutants generally. Their bacteria of choice is the parent (wild type) CBS. The mutants do help them to understand the water gas shift pathway, however.

Care must be taken to stay focused on the CBS bacteria if this is the organism of choice.

9. What is the status/plan for putting the hydrogenase into cyanobacteria or algae?

"DOE review panel has recommended that we discontinue that portion of work and instead focus on H_2 production from the water-gas shift reaction using CO as the feedstock. Our current effort in cloning the hydrogenase gene will facilitate that portion of work in the future."

They are looking to hire a molecular biologist to clone the gene, not to pursue water-splitting activities. They believe this will help in determining the mechanism for bacterial water shift.

10. Where would CO come from in an overall system? If it is part of a syngas, there is the likelihood that there is some unreacted fossil fuel (natural gas, coal gas, etc.) present together with various impurities (sulfur-containing materials, for example). Have you looked at all at the effect of these substances on your bacterial system? Would you expect any poisoning?

"The source of CO is syngas, generated from the gasification of waste biomass. Methane is present in minute amounts, and it will simply pass through the system unchanged diluting other gases. Most photosynthetic bacteria prefer sulfur in the form of H_2S to up to 3.5 mM level, although some can tolerate more. Sulfide is routinely used in medium preparation to scavenge O_2 and could even serve as an electron donor for certain microbes. Even with the water-scrubbed pyrolysis gas, there are usually still traces of toluene, benzene and phenols. Preliminary testing reveals that our organisms are fairly tolerant of both toluene and benzene in terms of cell viability and growth. No data yet on effect of phenols on growth/viability and effects all three solvents on shift activity although work is in the plan."

Dr. Maness referred to a four-day run that they did with the bioreactor using biomass pyrolysis products. The bacteria appeared to be unaffected by the impurities in the pyrolysis products.

Coal gas would contain more sulfur. The CBS bacteria are a non-sulfur bacteria. Dr. Maness thinks that it may not be able to tolerate sulfur, but she is not sure. She said, however, that they have isolated bacteria from a coal pile that appeared capable of performing a water shift. These bacteria would be sulfur tolerant.

11. If you were to set up a "real world" shift reactor at, say, a size by which a hydrogen refueling station could be maintained (assume 200 cars per day – about 1000 kg H_2 per day), how large would you envision your reactor to be? How would it work within the overall system? What are the problems you foresee having to overcome?

"We don't have a number on how large the reactor should be. We underestimate the shift activity at this point due to the mass transfer limitation of CO into liquid phase. Ed Wolfrum, an engineer and PI of the "Bioreactor Development" task, is examining various microbial immobilization techniques and bioreactor design to overcome the mass transfer limitation. With proper design, both cell mass and shift rates can be increased significantly. Ed has provided reactor volume and reaction rate data to NREL analyst to conduct an economic analysis of the overall process.

"For the overall system, induced microbes with good CO shift rates are immobilized onto a bioreactor. The bioreactor will receive water-scrubbed syngas from a gasifier after the syngas is cooled down to 35°C. The bioreactor can serve two purposes; one is to produce additional H_2 from CO shift, the other is to condition the fuel gas to very low CO levels so that the resulted H_2 can be injected directly into a PEM fuel cell.

"Through biochemical and genetic analysis, we hope to understand mechanism of the underlying pathway in order to further improve the activity and durability of the shift reaction. Another research area is to examine various packing materials to immobilize microbes so that both activity and durability of the shift activity can be maintained. Through immobilization and reactor design, we hope to overcome the mass transfer limitation. To summarize, this project is to enhance H_2 production through biochemical, genetic, and engineering approaches."

The laboratory-scale system is in a liquid suspension. This will not be the case for a dynamic bioreactor. As they scale up they will know more. Dr. Maness feels that Dr. Wolfrum and analyst Wade Amos will be able to answer the questions "fairly soon".

The eventual size of the reactor will be a function of the bed packing material. The packing material must have a high surface area and a surface that will accept the bacteria. Close packing is not a problem as it may be for other bioreactor systems because the shift reaction does not require light. The only time that light is needed is when you are trying to grow (regenerate) the bacteria. Dr. Maness thinks that this may be on the order of once a year, and plans to look at bacteria durability during the next year. Nevertheless, Dr. Maness believes that the regeneration will likely be done in situ. Therefore it will be necessary to have a reactor that will admit some light.

The regeneration process will be important. It appears that it could determine the size of the reactor, if in situ regeneration is warranted.

VI Additional Discussion:

If the source of Dr. Maness' feedstock is to be waste biomass, it must go through some kind of reforming or gasification process prior to the biological water shift process. Currently, Dr. Maness is working with a refinery (that wishes its identity to be proprietary information) that does some reforming, but is interested in biological shifting. The refinery is also interested in high-pressure hydrogen.

Dr. Maness is also working with the University of Victoria (British Columbia) who does a lot of PEM fuel cell research, and is interested in a CO reduction method.

VII Final Thoughts:

This is a good project, with potentially a very significant contribution. There's a long way to go, but if NREL can show that the CBS bacteria can not only shift water, but more importantly, remove CO down to acceptable levels for PEM fuel cells efficiently and economically, it will further the case for on-board hydrogen fuel cells. I think that this is the most significant component of the research.

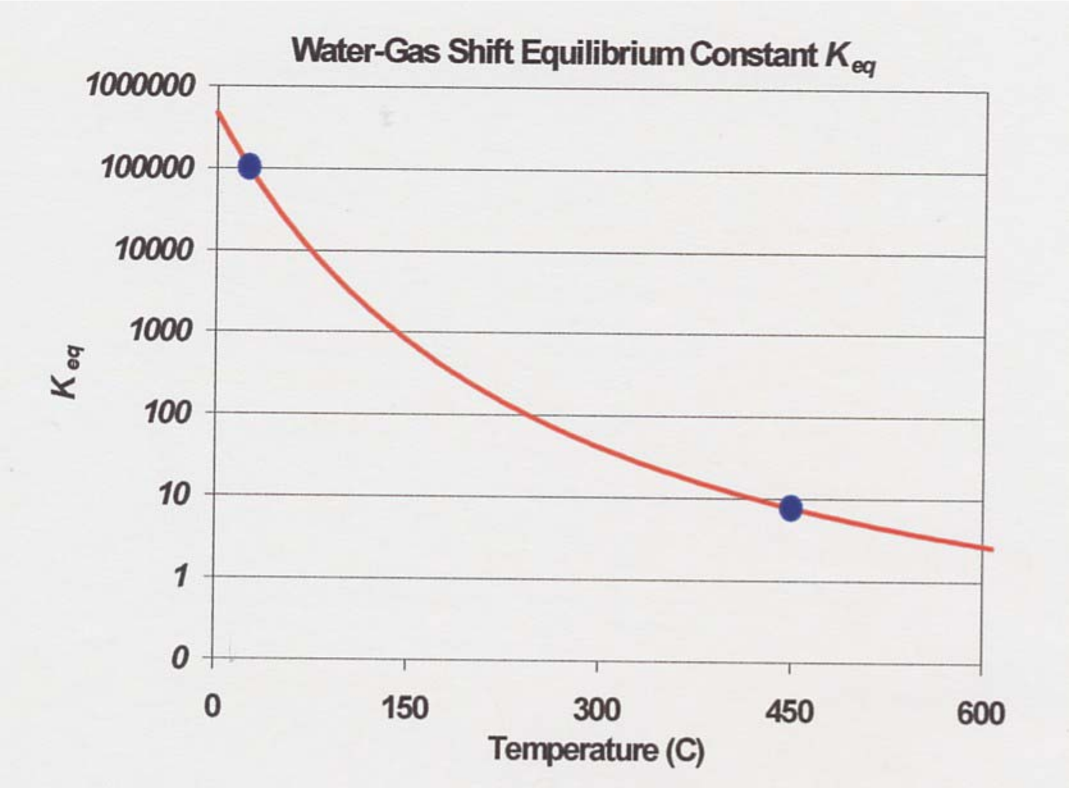
I realize that we are specifically evaluating the project using biomass as a feedstock, and a lot of my favorable comments do not focus specifically on biomass; the removal of CO from natural gas reformate or any fossil fuel gas is also attractive for the same reasons. Of course, biomass feedstocks provide the potential for a CO_2*-neutral process.*

I am not trying to minimize the role of this project as a potential hydrogen producer. It's just that the CO purification aspect can be decoupled from the hydrogen production if necessary, and still play an important role. As a shift reactor plus purifier it's even stronger.

On the other hand, it can't be a stand-alone hydrogen producer. You need a reformer, gasifier, pyrolyzer, or other syngas production system upstream.

I always say that the primary role of a hydrogen production project is to make hydrogen – lots of hydrogen. In this case, however, I say that the role of the project is to start with hydrogen (in syngas), and make it very pure.

Exhibit 1. Water Shift Equilibrium as a Function of Temperature

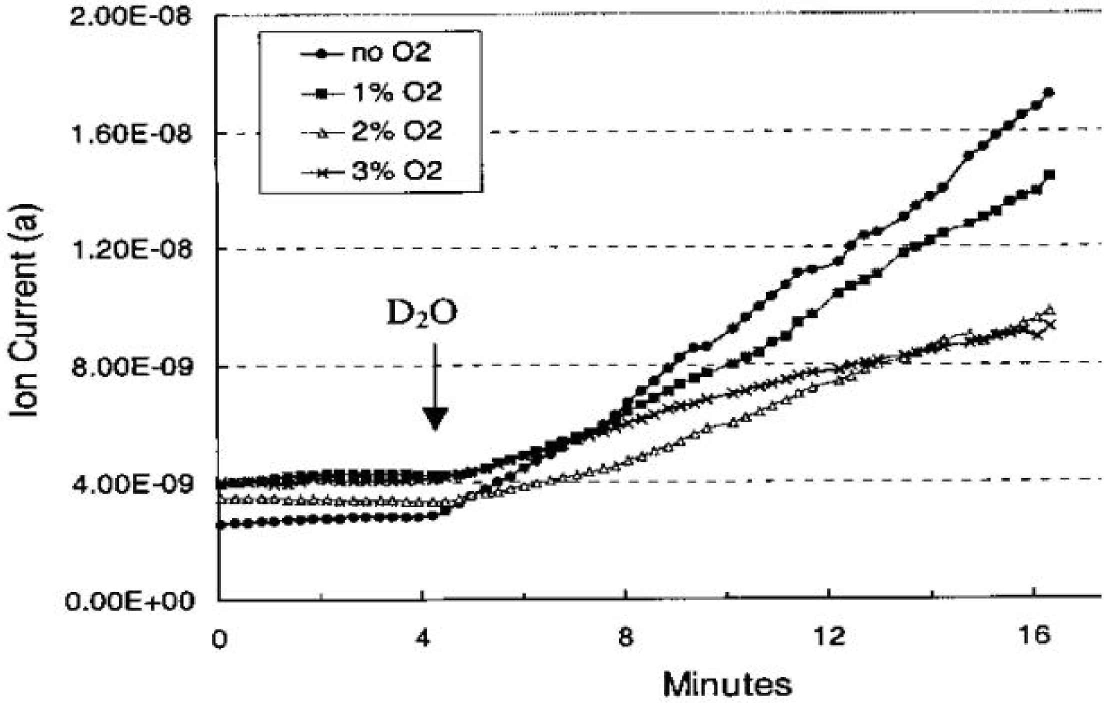


Note: An equilibrium constant is calculated from the concentrations of the reaction products divided by the concentration of the reactants. For the reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

a high number for K_{eq} would indicate that the concentration of the products (CO_2 and hydrogen) would be favored. In other words, hydrogen would be more easily produced.

Exhibit 2. Measure of Hydrogen Production in the Presence of Oxygen (From Maness FY 2001 Annual Review Report)



Technical Evaluation Report
Project: Hydrogen Storage in Carbon Nanofibers
Company: Northeastern University, Boston, MA
P.I: Dr. Terry Baker
Date of Visit: December 10, 1996
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

On December 10, 1996, I met with **Dr. Terry Baker** and **Dr. Nellie Rodriguez** at Northeastern University in Boston, MA. Dr. Baker and his group have a process that, if proven to work, could be the breakthrough that is needed in the area of on-board hydrogen storage. One of the biggest problems may be the fact that the results look so good that, even if they are real, they will be viewed with skepticism by many. The chemisorption value of 5.8 liters of hydrogen per gram of carbon that Dr. Baker claimed at the time of his proposal has now been surpassed many times. Dr. Baker has reported reproducible hydrogen take-up levels as high as 30 liters per gram, depending on fiber structure. The fibers are loaded with hydrogen at ambient temperature using a pressurized feed at levels of about 600-900 psi. The hydrogen will be retained at pressure, but can apparently be essentially totally recovered upon pressure release.

I believe that the Northeastern group should perform a proof-of-concept study. There is no need, at this time to optimize the nanofibers or catalyst past the point that has already been done. Reproducible results of 5 or 10 liters hydrogen per gram of carbon, would certainly be enough to work with at this point. What Dr. Baker could do is:

- Pick one of his "good" fiber configurations and characterize it as to cyclic sorbency and release of hydrogen. Demonstrate the reproducibility; show that the fibers are robust.
- Show that he can make fibers in reasonable quantity (say 100 grams) that exhibit the same ability to chemisorb hydrogen.
- Run a demonstration in which they can show a small prototype system (maybe a vessel 50-100 cc in volume.) The hydrogen would be loaded, the vessel disconnected from the source, a value for increased weight of the system obtained directly, the vessel stored off line for a predetermined time, maybe a day, and then the hydrogen is released. The purity and quantity of the hydrogen can then be measured independently.

If Dr. Baker is able to show that he has a viable system, then he can look at optimization at a later time. The important thing to see is, i) can he indeed store previously unheard of quantities of hydrogen in this manner?, and ii) are the fibers sufficiently robust for recycling without decay of capacity?

The rate of hydrogen take-up is slow at the present time and Dr. Baker plans to try some runs at elevated temperatures (maybe raising 100-200°C) to increase the diffusion rate. *This is not viewed as necessarily critical, however, if for instance the total hydrogen capacity can be made high enough to provide thousands of miles of range rather than hundreds. In such a case, the fuel tanks might be able to be made of a modular design with take-up rate not being a critical issue.*

II Introduction and Background:

Dr. Baker's team had recently relocated to Northeastern (from Penn State) and were working on the manufacture of graphitic carbon nanostructures and their subsequent use as a storage medium for large quantities of hydrogen. In an initial proposal to DOE, Dr. Baker's team claimed (while they were at Penn State) that theoretically, their platelet graphitic material was capable of chemisorbing a monolayer of hydrogen on all carbon surfaces. This, they claimed, [*apparently assuming planar graphite and hydrogen at the molecular level*] could result in a total monolayer presence of over ten liters of hydrogen per gram of carbon. At the time, however, they were able to show only the higher retentive abilities of the fibers as compared to active carbon at liquid nitrogen temperatures. The overall reported chemisorption by the fibers at that time was only about 20 cc per gram of carbon – almost two orders of magnitude lower than their theoretical claim. When they moved to Northeastern, they resubmitted their proposal and included some additional data. The most significant addition was their claim to have chemisorbed and retained 5.8 liters of hydrogen on one gram of carbon. This amounts to about 1/2 gram of hydrogen on every gram of carbon at STP, a truly remarkable claim!

During my meeting with Drs. Baker and Rodriguez, the two Northeastern researchers made a more-or-less formal slide presentation, ran a demonstration of a hydrogen chemisorption run, and spent several hours discussing their project. I had previously sent Dr. Baker a list of several questions, and these formed the basis for part of the discussion.

III Presentation and Initial Discussion:

Originally, the researchers, being catalysis experts, were trying to learn what they could about the mechanism for the formation of carbon structures, to prevent unwanted coking of catalysts. Thus, they learned how these structures grow, and from this, began to grow them intentionally. The hydrogen sorption properties were also found by accident, when during a calcining operation involving the nanofibers, the researchers found an unexpected rise in temperature, which they later determined was due to adsorbed hydrogen. The catalysts are proprietary, but are generally either nickel- or iron-based. They are structured to provide a large amount of "edge sites" for deposition of graphitic carbon. Another feature is the presence of an additional "add-an-atom", a proprietary modification to the catalytic surface that electronically enhances the adsorption surface for graphite deposition. The fibers are formed by passing a hydrocarbon such as ethylene, possibly with some hydrogen or some CO added, over the catalytic surface at a predetermined temperature (in the 600°C range). In this way, the catalyst acts more or less like a mold for the forming carbon material. The fibers take on a graphitic platelet-like structure with a spacing between the platelets of about 0.34 nanometers (nm). The spacing is thus selective for the insertion of hydrogen molecules (which have a kinetic diameter of 0.29 nm), while being too small for other molecules. The catalyst is then later removed by acid washing.

The fibers are generally somewhere between 10 and 100 microns in length and have an average diameter of about 5 nm, but the largest can have a diameter of about 100 nm. While the fiber packing density varies, being dependent on various preparation properties, a measurement on a sample was performed at the Morgantown Energy Technology Center (METC), and was found to be about 0.8 grams/cubic centimeter.

Dr. Baker feels the main advantage that his nanofibers have over nanotubes is that there are fewer access points for hydrogen to get into the nanotube when compared with the fibers, which have openings between platelets at each edge.

Two independent cost analyses have been performed, one by Exxon and one by Hyperion Catalysis. They both concluded that in mass-production, the nanofibers would cost about $1.50 per pound, and certainly less than $2 per pound.

IV Tour/Demonstration:

The demonstration, performed by a postdoctoral student, was very straightforward. About 0.1 grams of the nanofibers had been pre-placed into a small chamber attached to but valved off from a gas-handling system. The system, which could be monitored by a pressure transducer, had been evacuated. A tank of hydrogen was opened to the gas-handling system, resulting in a pressure of a little over 1500 psi. The hydrogen tank was shut off, and the pressure allowed to stabilize within the gas-handling system. The valve to the fiber chamber was opened, resulting in an instantaneous drop to about 1490 psi (due to the additional exposed volume). From this point on, the pressure in this closed-off, constant-volume system dropped steadily. At the end of about three hours, it was down to about 900 psi. The only place the hydrogen could go was into the fibers. The post doc indicated that based on the rate of pressure drop, this particular run would result in a hydrogen sorption of about 30 liters per gram of carbon fiber.

The research group has performed several other runs on various fiber structures as well as on some non-nanofiber material such as active carbon and alumina. A plot of some runs for various nanofiber structures as well as active carbon and alumina is attached as Exhibit 1. The two things that we need to see is that i) there is obvious hydrogen sorption with the nanofibers, but not with the other materials, and ii) the hydrogen take-up takes a long time. These items are addressed in the discussion.

It should be noted that at the time of my visit Drs. Baker and Rodriguez did not have the capabilities of definitively identifying the adsorbed gas as hydrogen nor could they demonstrate the regeneration of hydrogen.

V Questions and Answers:

Questions sent earlier to Dr. Baker are presented here with the answers we discussed. These questions were based on my reading of the technical portions of the two proposals to DOE.

1. **The claimed theoretical monolayer storage capacity for hydrogen of 10.368 liters per gram of carbon is based on a 100x100-ring model of graphite containing 44,100 carbon atoms. A diagram in the proposal shows hexagonal rings in which each carbon atom is shared by three rings. Thus, there are 6/3 = 2 carbon atoms per ring, and a 100x100 array of rings would only contain about 20,000 carbon atoms.**

Dr. Rodriguez indicated that her initial calculation shown in Exhibit 2 was incorrect, and the 100X100 array would contain close to 20,000 carbon atoms rather than 44,100. Therefore, the theoretical monolayer capacity for hydrogen would be closer to 6.5 liters per gram of carbon. *This was close to the number that I had calculated independently, assuming Dr. Baker's assertion of planar graphite and hydrogen at the molecular level.*

The 6.5 liters per gram is interesting in that it assumes that both carbon and hydrogen are planar on a molecular level, and that the coverage is total. Calculations using more likely packing densities for hydrogen under these conditions would result in much lower coverage – perhaps about 0.7 liters per gram of carbon. Of course, the fact that the researchers have apparently found far more than monolayer capabilities makes the point somewhat moot.

The researchers do not yet understand why their results are so good. They speculate that the hydrogen molecules must be reorienting into a more favorable form (and potentially condensing) within the platelet structure. Capillary action (similar to nanotubes) may also be a factor.

2. **If the inter layer spacing of 0.34 nm between platelets is ideal for selective hydrogen sorption, what is the rationale for developing larger spacings in multiples of 0.34 nm?**

Selectivity may not be as much as an issue as overall loading. The wider spacing may increase the hydrogen loading as well as the diffusion rate.

3. **How structurally sound are the nanofibers to begin with, and how much is their ability to sorb hydrogen bound to their structural integrity?**

The researchers believe their fibers to be "very sound" structurally. They have run at least two cycles with some fibers and found no breakdown in take-up properties or in structure.

4. **A figure was presented showing comparative sorption/desorption properties for the nanofibers and activated carbon at -196° C. While the percentage retention capabilities for the nanofibers are obviously superior, the curves also show that the activated carbon will sorb more hydrogen at high pressures, and that both materials appear to have the same absolute retention abilities at ambient pressure (about 20 cc/ g carbon). Is there any data similar to the sorption/desorption curves at the sorption levels now being obtained at room temperature (5.8 liters of hydrogen/ g carbon)?**

When active carbon was used, there was virtually no hydrogen take-up in the system at room temperature. This is shown in Exhibit 1.

5. **Why would spiral fiber structures produce higher hydrogen loadings?**

The researchers believe that the slightly irregular structure that one would get from a spiral fiber (different spacings at the edges and centers of the platelets) will lead to higher loadings. They have seen that non-uniform spacing of their standard fibers leads to higher loading.

While this may be true, it is probably a non-essential optimization process, and should not be a part of a near-term proof of concept study.

6. **What are the variables in fiber structure determination (temperature, catalyst, etc.)?**

Temperature, catalyst, the "add-an-atom" portion of the catalyst, and hydrocarbon gas mixture all are important variables.

7. **Do any volumetric packing data for the nanofibers exist?**

As mentioned above, METC data shows an average of about 0.8 grams of fiber per cc.

<u>VI Additional Discussion:</u>

- One of the keys to the high take-up levels is the fact that the carbon is graphitic. It's probably the π electron interaction on the graphitic structure that allows interaction with the hydrogen electron cloud. Dr. Baker referred to the unsuccessful Syracuse University carbon storage process as one that used amorphous carbon.

- The researchers have not yet identified the threshold pressure for sorption and desorption. They would like to build an apparatus to determine this.

- Dr. Baker raised another possibility: if they used a feed gas consisting of methane and CO_2, they may be able to simultaneously make nanofibers and hydrogen.

  This is an interesting thought, but probably not of short-term importance.

- When they make fibers, it's "100% fibers," and they have a homogeneous structure.

  This was said so as to compare it to the carbon nanotubes being researched at NREL. At the time of the visit to Northeastern, NREL was having trouble producing nanotubes in anything more than a fraction of a percent conversion.

- The highest hydrogen loading attained was 3.32 grams hydrogen (37.2 liters) per gram of carbon (76.9% by weight). They can "routinely" get 1.5 grams (17 liters) per gram of carbon (60%).

- Drs. Baker and Rodriguez have formed a small business, Catalytic Materials, Limited. They are looking for partners in this potential business venture, perhaps one company to produce the catalysts in mass quantity and another to make the fibers.

VII Final Thoughts (written at the time of the visit):

The levels of hydrogen loading being claimed here are almost too good to be true, and are therefore naturally looked at with understandable skepticism. As a first round "sanity check", the visit to Northeastern could provide no obvious answer as to the manner in which the researchers could have obtained erroneous results. There was nothing in the experimental work that looked either incorrectly performed or measured. It should be mentioned that we are talking only about the ability of the fibers to take-up hydrogen. No demonstration was provided at that time on fiber production, hydrogen desorption, or recycling capabilities. No leaks were observed, pressure decrease was readily monitored, and data was provided showing that these results were unique to nanofibers. Activated carbon demonstrated no take-up.

If these high loadings are indeed real, the possibility exists for a totally different route toward on-board storage, and refueling: modular "quick-connect" fuel tanks. Fibers are packed into a tank capable of withstanding, say 1000 psi pressure. Hydrogen is loaded into the system at a refueling depot. The driver picks up the filled tank, and drops off an empty one, much as one would a propane tank. Depending on how robust the fibers are, the tank can be filled and emptied several times. Depending on the hydrogen loading, the driving range may be measured in thousands of miles instead of hundreds.

To put these levels of hydrogen loading into perspective, let's take an "intermediate" case of 10 liters per gram (and one well below the 17 liters the researchers claim they can routinely obtain):

At STP, 10 liters of hydrogen is equivalent to 0.89 grams of hydrogen.

(10 liters) ÷ (22.4 moles/liter) x (2 gram H_2 *per mole) = 0.89 grams* H_2 *per gram of carbon. On a percentage basis, this is 0.89 ÷ (1 +0.89) = 47 percent by weight hydrogen. (The nanotube project researchers claim that they can get 6.5% hydrogen by weight in a system, and that is in a system where all the carbon is in nanotube form.)*

Independent measurements at METC performed on the nanofibers have shown average carbon packing densities to be about 0.8 grams/ cubic centimeter. Thus, the hydrogen concentration is:

$$(0.89 \text{ grams } H_2 \text{ per gram of carbon}) \times 0.8 \text{ grams carbon per cubic centimeter} = 0.72 \text{ gram } H_2 \text{ per cc}$$

If we use Gene Berry's number of a 300 mile range fuel-cell powered vehicle requiring a tank containing 3.75 kg of hydrogen, a tank of hydrogen stored in the Baker system, would only be 5.2 liters (1.37 gallons) in volume. A 10 gallon-sized tank of hydrogen would have a range of over 2100 miles!

Depending on hydrogen loading, fiber strength, and tank parameters, the options for the mode of fueling are numerous.

The important thing is to keep the project focused on a rapid proof-of concept. The researchers need to affirm their hydrogen loading, demonstrate the recycling parameters, show reproducibility, and if it still appears to be real, scale it up into a fuel cell vehicle demonstration.

VIII Additional Comments (added in 1997):

This project has become the subject of much disagreement and controversy over the past few months:

- The researchers were interviewed by the *New Scientist* in December 1996, and their claims were disputed by others in the same article.
- The Northeastern claims were featured as the lead article in an issue of *The Hydrogen and Fuel Cell Letter* in February 1997.
- During the 1997 National Hydrogen Association meeting, the Northeastern research was mentioned several times, including a presentation in which its authenticity was questioned.
- Representatives from industry have visited Northeastern, seen a demonstration, and have reportedly more-or-less mixed opinions.
- Drs. Baker and Rodriguez have reportedly been offered support from a "German Company."
- The project has recently received funding from the DOE Hydrogen Program.

Among some of the questions raised concerning the experimental procedure being used by the Northeastern group, were comments that hydrogen take-up was overestimated. This was due to the fact that the metal vessel was being pacified by hydrogen and/or that there was a leak in the system caused by a piece of filter paper protruding through a joint in the vessel. Pacification is an unlikely explanation, as it would have resulted in false take-up readings into activated carbon as well as into the nanofibers. Exhibit 1 shows that this did not happen. The filter paper issue is a harder one to rebut, as the paper was reportedly only present when the nanofibers were being used. It was apparently used in conjunction with the preparation of the nanofibers, but was not used in the case of activated carbon. *Nevertheless, I observed no filter paper protrusion during my visit.*

Regardless, a proof of concept study, at a somewhat larger scale would end the matter. If an error is present, it will be found. If the claims are valid, the overall way in which we view hydrogen on-board storage will change.

Exhibit 1. Hydrogen Pressure Drop Attributed to Adsorption in Nanofibers and Other Materials

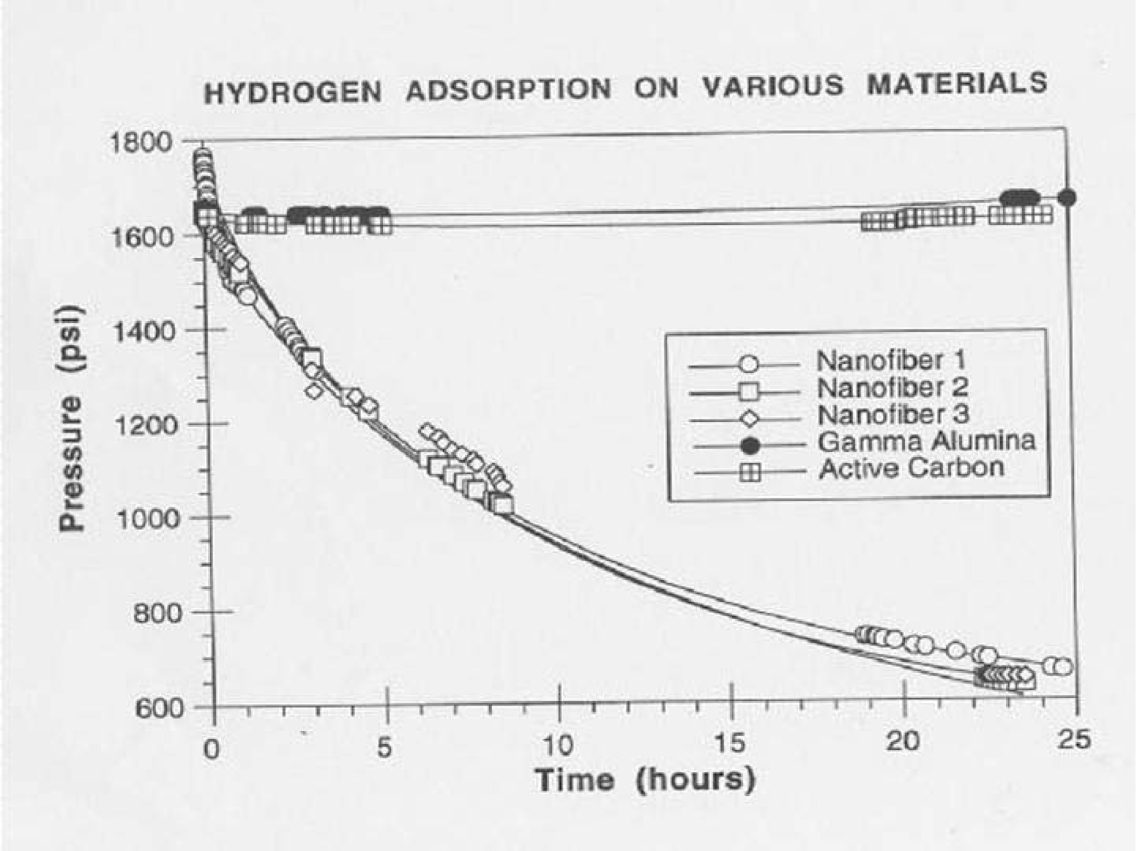
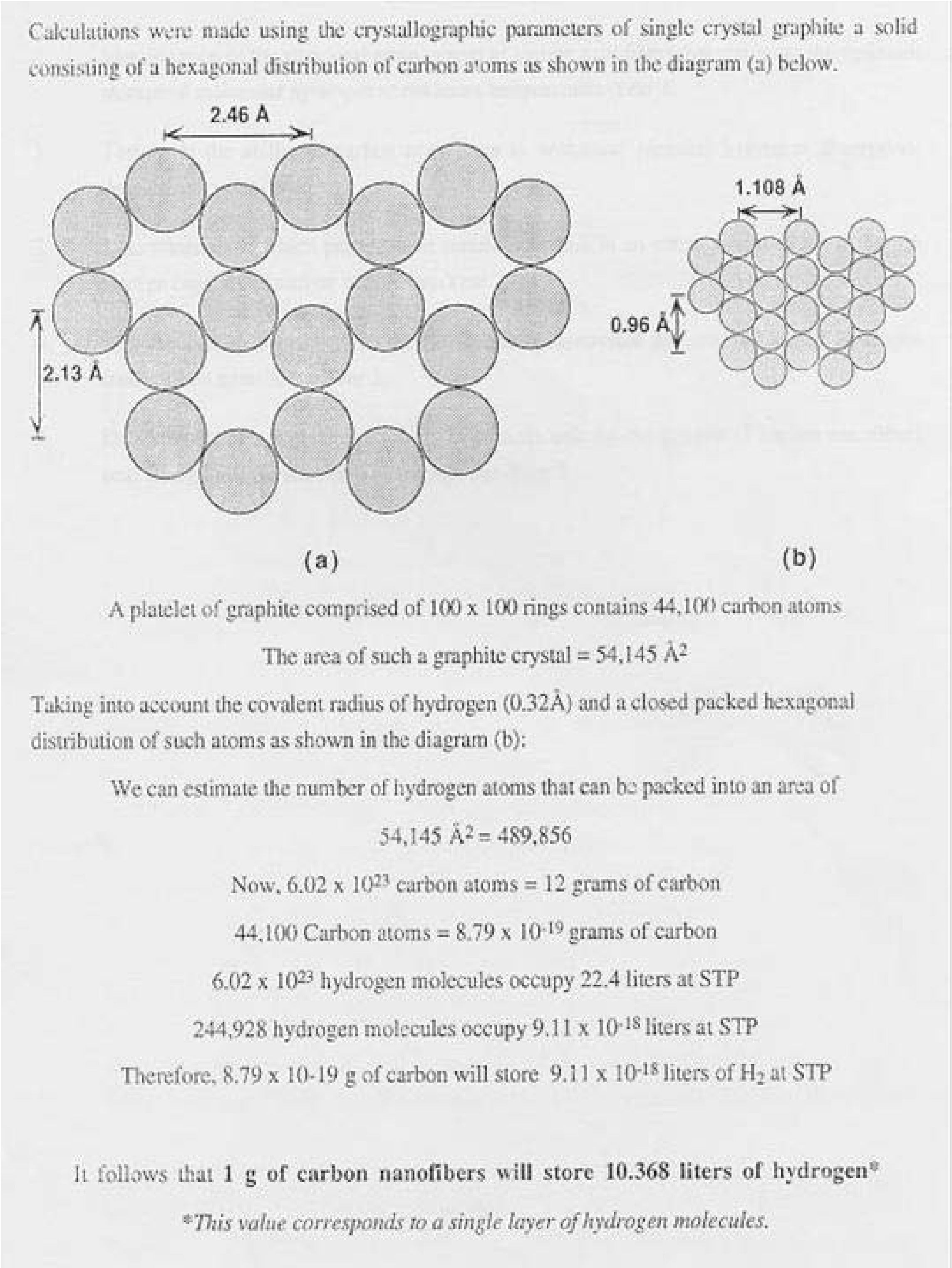


Exhibit 2. Theoretical Calculations for Hydrogen Storage in Nanotubes



Calculations were made using the crystallographic parameters of single crystal graphite a solid consisting of a hexagonal distribution of carbon atoms as shown in the diagram (a) below.

A platelet of graphite comprised of 100 x 100 rings contains 44,100 carbon atoms

The area of such a graphite crystal = 54,145 Å^2

Taking into account the covalent radius of hydrogen (0.32Å) and a closed packed hexagonal distribution of such atoms as shown in the diagram (b):

We can estimate the number of hydrogen atoms that can be packed into an area of

54,145 Å^2 = 489,856

Now, 6.02×10^{23} carbon atoms = 12 grams of carbon

44,100 Carbon atoms = 8.79×10^{-19} grams of carbon

6.02×10^{23} hydrogen molecules occupy 22.4 liters at STP

244,928 hydrogen molecules occupy 9.11×10^{-18} liters at STP

Therefore, 8.79 x 10-19 g of carbon will store 9.11×10^{-18} liters of H_2 at STP

It follows that **1 g of carbon nanofibers will store 10.368 liters of hydrogen***

**This value corresponds to a single layer of hydrogen molecules.*

This page intentionally left blank

Technical Evaluation Report
Project: Carbon Nanotubes for Hydrogen Storage
Company: National Renewable Energy Laboratory (NREL), Golden, CO
P.I.: Dr. Mike Heben
Date of Visit: June 17-18, 1997
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

This project has been the source of significant progress over the past year in generating nanotubes. The team at NREL, led by **Dr. Michael Heben,** has built on the work of Dr. Smalley's group at Rice University. Dr. Heben has been working for the past several years on a project that will develop single-walled nanotubes (SWNTs) composed of carbon for storage of hydrogen. They have developed a process by which their production capabilities for SWNT have increased by about three orders of magnitude! In contrast to the group's former arc-discharge production method, which produced a soot containing only about 0.05 percent SWNTs, their current laser vaporization process, modeled after Dr. Smalley's work, produces materials that are 60-90 percent SWNTs.

Aside from optimizing the parameters for this process, there is still much to be done. The most significant problem is that hydrogen adsorption in these nanotubes is essentially zero. The arc-discharge nanotubes exhibited 5-10 percent hydrogen adsorption on a nanotube basis. Dr. Heben suggested two explanations for the current problem. First, many of the tubes are still capped, thus blocking adsorption. Second, the tubes produced by the laser method are so long that hydrogen adsorption is limited by the tube length. It would seem that the first explanation is more likely. Since there is essentially no hydrogen being adsorbed, it would indicate that none of the tubes are open at all. Limitations on hydrogen adsorption due to tube length would likely provide yet another problem once the tubes are decapped. Much of Dr. Heben's current efforts involve methods that will both de-cap and shorten the tubes. Dr. Heben's theory about the difficulties of cap removal seems reasonable; that is, that the caps on the laser based nanotubes are harder to remove because they form stable, fullerene-like, C_{240} structures, while the arc-discharge nanotubes form with unstable caps.

The laser method produces tubes that, due to vander Waal's forces, are aligned parallel to one another, forming bundles. In an eventual commercial scenario, these unidirectional bundles could lend themselves for easy wrapping and incorporating into a fuel tank. Bundle formation appeared to be much more difficult using the arc-discharge method.

Carbon-based systems have the potential for being the lowest cost, lightweight, safe, practical approach to on-board hydrogen storage in automobiles. While Dr. Heben's claims do not approach that of the research group at Northeastern University (Northeastern claims have ranged up to 70% by weight hydrogen storage), he has demonstrated high nanotube production yields by the laser method, and reasonable hydrogen adsorption (on a nanotube basis) in nanotubes produced by arc-discharge.

These results are much better documented at this time, than the Northeastern results, and they do address the DOE program storage goals.

Following the meeting, Dr. Heben spent some time in France in discussions with Dr. Bernier at the Universite de Montpellier. He later informed me that the French have discovered a high nanotube yield method using an arc-discharge method. Dr. Heben believes that this method holds promise and plans to investigate it further.

Project Strengths:

- The nanotube yield has been dramatically increased.
- Dr. Heben and his staff are well versed in the multitude of disciplines needed to carry out this project.
- NREL has the proper production and diagnostic equipment to facilitate the project.
- Collaborations with other researchers, especially Dr. Smalley at Rice provides a large added value.
- Dr. Heben's projected 5 percent hydrogen of total storage-system weight with room temperature operation meets the DOE Hydrogen Program goals.
- Carbon nanotubes provide a lightweight, moderate pressure, room temperature method for storage of hydrogen in automobiles. It could be the best way to get there!

Issues that should be Addressed:

- I consider the biggest short-term priority for the project to be the ability to decap the tubes. Closely aligned with this is the affirmation of the fact that the lack of hydrogen take-up is in fact due to caps rather than, say, an activity problem based on the method of nanotube production or catalyst form.
- Once hydrogen take-up has been regained, a prime objective should be pressure, temperature, and importantly, recycling data gathering on the system.
- Tube length may limit hydrogen adsorption levels, but I don't think this has been shown experimentally yet. At any rate, tubes probably do need to be shorter to make them more commercially viable.
- The use of the solar furnace and other different methods of producing nanotubes may be of interest, but it should not be a primary focus. It could detract from what I believe to be the main objective (the ability to repeatedly adsorb and desorb hydrogen by laser-generated nanotubes).

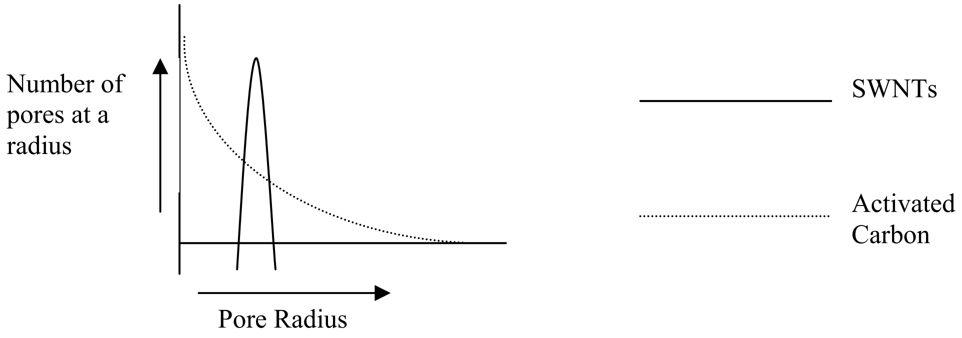
II Introduction and Background:

On June 17-18, I met with Dr. Heben in his laboratory at the Solar Energy Research Facility at NREL to discuss his research on the development of carbon nanotubes to be used for the storage of hydrogen on-board a vehicle. Dr. Heben has spent much time trying to develop a method by which he could produce SWNTs in sufficient quantity, and then demonstrate the adsorption and desorption of hydrogen from these nanotubes at room temperature. While Dr. Heben was earlier able to show hydrogen adsorption levels of up to 10 percent on a SWNT basis, generation of SWNTs from an arc-discharge was only about 0.05 percent of the total soot formation. Therefore, increasing SWNT concentration was a key consideration.

In addition to Dr. Heben, I met briefly with his associates **Dr. Anne Dillon** and **Mr. Phil Parilla**. Dr. Heben and I discussed his project at length. He also answered several specific questions that I had prepared for him, and gave me a tour of his laboratories. I was also fortunate to be present at the laser vaporization experiment on the evening of the 18th, where I witnessed actual nanotube production.

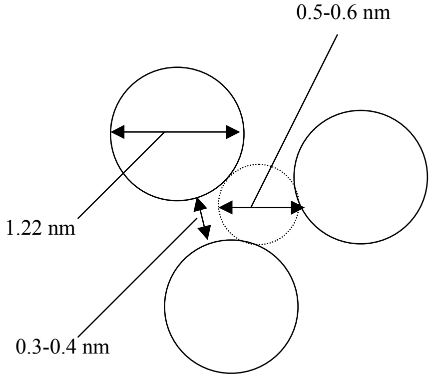
III Tour:

The SWNT project is based on some early work performed by A.D. Little, who demonstrated the superior adsorption potential of nanotubes over activated carbon. By using heat to prepare the SWNTs to begin with, the tubes can be constructed to adsorb and hold hydrogen at room temperature. As opposed to activated carbon particles, SWNTs prepared by a particular method (e.g., arc-discharge, laser-vaporization) are uniform in pore diameters:



Pore diameter will vary according to the production method, but all SWNTs produced by a particular method under the same set of conditions will produce a single size of pore. For the arc discharge method, the tubes have a diameter of 12.2 Å; for the laser method under the current conditions, the diameter is 13.8 Å. Different experiments produce different sizes of tube. Theoretically, the larger diameter, and therefore, larger pore-volume tubes can adsorb more hydrogen, but Dr. Heben is not finding this to be true as yet. In fact, his laser-produced nanotubes are not yet adsorbing any hydrogen. Dr. Heben is attributing this in part to the fact that the laser-produced nanotubes are very long (up to hundreds of microns in length) and may be unable to effectively adsorb hydrogen up to that full length. In addition, the cap on the laser-generated nanotube may be harder to remove than its smaller counterpart. This is because a cap fitting on a 13.8 Å tube is a C_{240} molecule – a “perfect” fullerene, and therefore a stable structure. The cap fitting a 12.2 Å molecule is not as stable. Finally, vander Waal’s energy between the hydrogen molecule and the nanotube will be smaller for the larger nanotubes, making them harder to fill. Dr. Heben believes that some over-pressurization during the fill step might help to overcome this third phenomenon. It will be necessary to remove the caps and shorten the tubes, however.

If one looks end-on at a nanotube bundle and considers the spacing between the tubes (being held in place by vander Waal's forces), the arrangement is somewhat like:



The laser vaporization system being used at NREL now, employs a Neodymium/ "YAG" (yttrium/aluminum/garnet) laser. The low-power (30-watt) laser produces a near-infrared (10640 Å) light beam that can operate either in pulsed or continuous mode. It impacts the target with a 50-micron spot that scans across the target. The target, a disc that is about one inch in diameter, is composed primarily of activated carbon impregnated with small amounts of nickel and cobalt catalytic material. (The activated carbon is supplied by Spectracorp, a potential partner in this activity). Another proprietary additive is used to control thermal conductivity within the target. The target is set on-end in a tube through which about 500 mm of argon gas is flowing. The laser generates a temperature of about 3500^{o}K at the point of impact. If the thermal conductivity of the target is too high, the heat will too readily disperse throughout the target rather than remain concentrated – the necessary scenario for SWNT formation. As I witnessed the experimental procedure, I could easily see carbon "streamers" coming off the target as it was being impacted by the laser beam. Dr. Heben has analyzed the streamers via transmission electron microscopy, and has seen them to be composed largely of bundles of nanotubes. He believes that tube growth (length) is enhanced by the presence of the metal catalyst at the tube edges attracting more carbon deposition at that site. If necessary, an acid wash could be applied to the tube to remove catalysts after fabrication.

Dr. Heben sees a heat treatment step as a potential to both decap and activate the tubes. He has found that heating SWNTs to, say, 800^{o}K (527^{o}C) will result in desorption of CO, CO_2, and water. He believes, plausibly, that this is due to the decomposition of surface oxides from the cap material. In other words, the caps are being removed. The process also activates the inner surface of the tubes, making them more attractive to hydrogen adsorption.

Dr. Heben sees pressure/temperature profiles of hydrogen ad- and desorption by SWNTs as being dependent primarily on their diameter. He thus envisions several different methods of making nanotubes, each providing a different diameter tube. The tubes could then be tailored to meet the pressure/temperature needs of a particular application.

IV Questions and Answers:

Prior to the meeting, I had prepared a series of questions for Dr. Heben. These were discussed in detail:

1. **What are the differences in the methods and products for the arc-discharge Rice University laser vaporization and NREL laser vaporization methods of SWNT preparation? Compare by yield, energy use, estimated cost, SWNT size (length, hole diameter, thickness), crush and breakage properties.**

Arc-discharge methods generally produce less than 1-2 percent SWNTs. A group in France (headed by Dr. Bernier at the Universite de Montpellier II) is reporting much higher yields (approaching laser values) using an arc-discharge approach. Dr. Heben was going to France the week after our meeting to meet with Dr. Bernier.

Dr. Smalley at Rice University is now routinely making 80-90 percent nanotubes using a laser discharge method under certain controlled conditions, and is approaching 100 percent yield in some cases. Dr. Smalley uses a pulsed laser, and preheats his target to about 1200°C to change its thermal conductivity properties. Even so, this process requires periodic down time so that amorphous carbon can be physically scraped off the target.

The NREL process, as previously mentioned, operates the laser in both pulsed and continuous mode. It controls thermal conductivity via a proprietary additive that creates porosity within the target. The system is at room temperature and is much less energy intensive. Yields are nominally at the 60 percent level, although yields as high as 90 percent have been reached.

NREL has also looked at tube preparation in their solar furnace, but they find that they have a problem with the thermal conductivity of the target with this approach.

All of the nanotubes discussed are single-walled tubes (that is, single molecule thickness) having the same thickness and nominally the same crush strength.

2. **What pressures are needed for the room temperature ad- and desorption of hydrogen?**

Currently, all hydrogen sorption work has been run at one atmosphere. The laser-generated tubes are not adsorbing hydrogen at the expected level yet. This is probably due to the tubes being too long, and/or not having had their caps adequately removed yet. Dr. Heben anticipates that the tube length problem might be overcome with pressure of a few hundred psi.

As pointed out earlier, the problem with hydrogen adsorption is more likely due to failure to remove caps rather than tube length. It is likely, however, that once the cap problem is solved, a tube length problem will manifest itself. Tube shortening may be a better solution than overpressurization.

3. **How are the problems of tube shortening, cap removal, and eventually packing the SWNTs into a tank being addressed?**

Decapping and shortening of the nanotubes is being addressed by two methods: high power sonification, and ultraviolet photooxidation. Early results are showing that both methods are "damaging" the tubes, especially the UV method. It is known that UV photons damage fullerenes, and the SWNT caps are fullerene-like. It is hoped that this damage can be converted to actual decapping and tube cutting. Some of the longer tubes are now hundreds of microns long. Dr. Heben would like to see much shorter tubes – perhaps one micron in length.

Dr. Heben envisions a bundle of nanotubes all lined up in a brick-like formation, held in place with a surfactant, and wrapped into a tank-like structure. He is also considering looking at an alternate technology in which a template material is created containing a system of holes. A metal catalyst film is placed on one side of the template, and carbon nanotube bundles are precipitated into the holes. The details of the concept of a macroscopic organization of nanotubes are considered proprietary.

4. **What are the proposed mechanism differences for hydrogen take-up and discharge between the arc-discharge SWNTs and the laser vaporization-formed nanotubes***?*

There is probably not a mechanistic difference; degree of hydrogenation apparently depends on both tube diameter and length. (This has already been discussed earlier in this report.)

5. **How do the size of the nanotube caps compare to the length, and are there any cases where a significant portion of the tube length is in the cap?**

As mentioned earlier, even the shortest tubes are about a micron (1000 nanometers) long. The caps are of fullerene dimensions, 2-3 orders of magnitude smaller.

6. **One of the reports from NREL on nanotubes described an attempt at cap removal by a hydrogen-based reduction method involving high temperature and pressure. It appeared that the tubes became hydrogenated during the process. Was the decapping attempt successful as well?**

No. It appeared that the hydrogenation occurred on the outside walls of the SWNTs only, and that the caps were not removed during this process.

This could indicate the possibility of increased hydrogen loading, if hydrogen can be adsorbed onto the outside of the tube as well.

7. **Is there any information yet available on the effect of repeated recycling of the ad- and desorption process?**

There have not been many attempts yet at this aspect of the process. The low (one atmosphere) pressure runs did not appear to cause degradation of the tubes. The attempt to remove caps via the reduction method discussed above in Question 6 did not appear to cause any damage to the tubes either.

8. **Two of the items proposed as future work for this project involve arc discharge in the NREL solar furnace and looking at polyacrylonitrile decomposition. What are the goals of these studies?**

Both the present arc-discharge and laser vaporization methods are energy intensive. If the solar furnace can be used it would be significantly cheaper.

Polyacrylonitrile decomposition is a precursor to the formation of the template material addressed in Question 3.

9. **If effort is placed on shortening of nanotubes, doesn't this actually result in decapping as well?**

Yes, but cutting itself is a problem. In fact, Dr. Heben hopes to use the knowledge gained in cap removal to develop cutting techniques. The cap is less stable than the tube walls, and it therefore should be easier to decap than to cut.

This may be fortuitous. Decapping seems to be the key.

10. **If the laser (or another) process were deemed to be most effective at less than a total conversion to SWNTs (for instance, the 60 percent conversion that is currently indicated for laser vaporization) would the non-nanotube fraction be removed? How would it be done?**

The amorphous carbon would be removed, most likely by a gentle oxidation process. Since the amorphous fraction is much less stable, this would be a low energy process. In addition, remnants of metal catalyst would be removed, if necessary, by a vapor transport method, or by acid washing.

11. **Are the reported hydrogen take-up percentages based on hydrogen-to-carbon values only, or is the weight of a container also taken into account?**

The estimates for hydrogen take-up are on an installed basis. Dr. Heben believes 5 percent hydrogen on an installed basis is possible. This works out to a density of about 50 kg hydrogen per cubic meter.

This works out to approximately a 16 gallon tank being able to hold about 3 kg of hydrogen – or about a 300 mile range for an advanced system. Not unreasonable.

12. A reviewer at the Annual Hydrogen Review suggested that cap removal might be possible by a ball milling process. Is this at all plausible?

It does not appear doable. The grinding medium is so much larger that the nanotubes, that it is unlikely that ball milling would have any effect. Dr. Heben feels that chemical methods such as cap oxidation are much more likely to succeed. He will make the attempt at ball milling, however.

Perhaps this may be doable after all. Grinding media are generally much larger than the material to be ground.

13. How would you envision a commercial product?

Dr. Heben sees bundles of aligned nanotubes of a pre-selected diameter being extruded into thin sheets. The sheets would then be stacked, forming a "box", maybe a cube. The stack would be enclosed in a lightweight material, maybe aluminum. The system would be installed on-board and filled with hydrogen from a pressurized source. Hydrogen would be removed using either a small electric heater, or simply its own head pressure. As hydrogen was removed, more would come out of the nanotubes to replace the head pressure. Nanotube diameters could be tailored for operation at or near ambient temperatures.

Once the nanotubes and their hydrogen take-up are perfected, this is going to be the next big challenge.

V Final Thoughts:

Following our visit to NREL, Dr. Heben was flying to France to meet with Dr. Bernier at the Universite de Montpellier. He has indicated that Dr. Bernier's group has developed a method of arc-discharge production that yields SWNTs in the same quantity as the laser vaporization method (60-90 percent). In addition, it produces them at a rate that is an order of magnitude more rapid. "Several grams per hour" was mentioned. Dr. Heben is planning to collaborate with Dr. Bernier.

The French arc-discharge method would, I presume, (although not confirmed) provide the smaller diameter (12.2 Å) nanotubes that would be easier to decap due to the caps' less stable, non-fullerene structure. This would probably lead to better hydrogen adsorption.

The near-term affirmation of SWNTs that can both be produced in high yields, and can adsorb 5+ percent (total system weight) of hydrogen is critical to this project. It would therefore appear that the French method is worth considering. Decapping the laser-produced SWNTs remains a top priority in my view.

VI Follow-up:

I had a conversation with Mike Heben (NREL) on August 4, 1998 on the progress made with nanotube storage.

Major points:

1. He is using a more powerful YAG laser that can now make “a couple of grams of material in about 20 minutes”

2. They are shooting for up to 99% yield using the laser vaporization method. This would mirror the type of yields that Smalley’s group is getting . (Concern: could it be that the high yield is tied to a diameter that is not very appropriate for hydrogen adsorption?)

3. Although they are becoming more formalized in their relationship with Bernier at U Montpelier, they are not going to use the Bernier arc discharge method at this time.

4. They (or “people”???) have developed methods to cut long nanotubes—sonification in mixtures of acids. They believe that cutting may be the only answer to decapping because the laser produced nanotubes (as opposed to the arc discharge types) have caps that are the same composition as the walls themselves. This makes the selective oxidation process (used to remove the old arc discharge caps) unusable here.

5. They have no control as yet as to the length of the tubes once cut; they do believe that they can do a fractionation by length (no word on how).

6. While the diameter of the nanotubes controls the thermodynamics of the hydrogenation process, the length controls the kinetics. Therefore, Heben feels they will have a good handle on both thermo and kinetics of the system.

7. Nanotubes was a top 100 R&D project according to Discover Magazine in January 1998

8. They are planning to start pressure adsorption experiments on hydrogen take-up by cut nanotubes.

Final Thoughts, August 1998:

1. *They have made some progress in quantity of nanotubes produced, but are still at the ~60 percent yield point. They had made the significant yield breakthrough a year ago using the laser vaporization method, but have not progressed from this point yet.*

2. *More worrisome is the fact that they have not as yet demonstrated any hydrogen take-up with laser-produced nanotubes. All of their data is based on the old arc discharge nanotubes, extrapolated from very low tube yields.*

3. *Decapping is apparently (as we feared) a difficult problem. Cutting does, of course, result in decapping, but at this time, there appears to be little control of the cutting process. Their usable nanotube yield may shrink significantly unless they gain control of the system.*

4. *The upcoming pressurization experiments are crucial.*

5. *Right now, the NREL group has low yield nanotubes (by arc furnace) that will adsorb hydrogen, or high yield nanotubes (by laser vaporization) that will not. They need to demonstrate decapping the laser nanotubes, cutting them, and filling them with hydrogen (with or without pressure). Any or all of these things may be difficult.*

6. *We are not even dealing with dehydrogenation yet.*

Technical Evaluation Report

Project: Novel Hydrogen Storage Materials – Carbon Nanotubes
Company: National Renewable Energy Laboratory (NREL), Golden, CO
P.I.: Dr. Mike Heben
Date of Visit: February 15, 2001
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

The development of a hydrogen storage system based on single-walled nanotubes (SWNT) made of carbon has been going on for about eight years at NREL. The goals are (of course) demonstrated high productivity of nanotubes and high reversible hydrogen adsorption by the nanotubes. While significant progress has been made over the past several years, the project is not yet at the level of results where 6-7% hydrogen storage (or greater) is demonstrated in gram samples (or greater) of nanotubes.

According to Principal Investigator **Dr. Mike Heben**, much of the shortcoming (if we want to call it that) is due to the large increase in the level of understanding of SWNT technology over the past couple of years. The two areas of major increases in understanding are 1) in the ability to detect SWNT concentrations accurately, and 2) the realization that SWNT diameter alone does not determine its properties. What this means is that earlier reports of 60-80% pure nanotubes being produced directly from laser vaporization as earlier reported (both by Dr. Heben and by other researchers who produce SWNTs – albeit not necessarily for hydrogen adsorption) was far too optimistic, being based on inaccurate detection methods. It also means that hydrogen adsorption capability is based on a number of factors, tube diameter being only one. Dr. Heben's research has determined that another key factor is electronic configuration. Some tubes have more or less metallic properties, while others behave more like semiconductors. Furthermore, tubes produced by a particular process do not as previously thought possess a single diameter; they have a range of diameters varying by 5-10 Angstroms. This discovery has both positive and negative implications for the SWNT project as far as the Hydrogen Program is concerned. Negatively, it points out the erroneous nature of earlier nanotube concentration reports. Positively, it appears that it will lead to better understanding of what the pertinent properties of SWNTs as hydrogen storage devices will be.

Project Strengths:

- There is increased understanding in the nature of SWNTs. This is true in the areas of how to produce nanotubes, how to purify them, and what properties will make them more able to adsorb hydrogen. The more that is known, the better the likelihood of success. *(Calling this a "strength" might raise some eyebrows, but seeing that SWNTs are not as uniform as we thought, the knowledge gained is valuable.)*

- Having a Cooperative Research and Development Agreement (CRADA) with Honda, and more important, Honda's interest in carbon nanotubes lends a large amount of credibility to the effort.

- The biggest strength may be in potential. SWNTs represent an alternative (and thus a release from at least perceived safety problems) to compressed hydrogen for physical storage.

Issues that should be Addressed:

- Despite all that has been learned in the past few years, SWNT production is still measured in fractions of grams. NREL will need to parlay the recent quantum leap in nanotube technology knowledge (and that is how I would describe it) into a quantum leap in results.

- Switching laser types to the alexandrite laser in the long run might prove to be a positive outcome. (It appears that NREL had no choice, seeing that it was the only laser available that had long pulse options.) The lower hydrogen adsorption numbers presently being reported with this laser, however, is seen as at least a temporary setback. Remember the goal is to increase hydrogen storage capabilities.

- Independent laboratory testing is necessary. As part of this, a methodology for testing needs to be agreed upon by all involved.

The high-risk, high reward potential fits few projects in the Hydrogen Program any better than this one. If this were a basic energy science project, there would be few issues. But it is an applied science project requiring a steady march toward a practical goal. Much is being learned, but progress toward those practical goals is needed.

II Introduction and Background:

I visited the NREL laboratory of Dr. Mike Heben to discuss his SWNT hydrogen storage project. This was the second time that I visited Dr. Heben, the first being in June 1997. We spent a full day going over the progress that the project has made over the past 3½ years in producing, purifying, and cutting nanotubes, and in utilizing these nanotubes for the storage of hydrogen. Included were a tour of the appropriate facilities and a discussion of a series of questions.

Throughout our discussion Dr. Heben stated that much of what we all thought we knew about nanotubes in 1997 was inaccurate. Primarily this dealt with the ability to detect nanotube concentrations and accurately report yield. We also did not understand the mechanisms involved in making nanotubes and thought that using a particular method of nanotube production would result in nanotubes of one, unique diameter. It turns out that yields had been highly overstated, and that nanotubes came in many sizes including distributions of diameters and different electronic properties. We deal with these matters in the Questions and Answers and the Additional Discussion sections below.

III Tour:

The tour of NREL's SWNT facilities included revisits of some pieces of equipment visited in 1997, as well as visiting some new additions.

The temperature programmed desorption (TPD) system, used to measure hydrogen uptake, utilizes one-milligram samples. *Note that it is the limitations of the system as opposed to the lack of material that Dr. Heben claims is the basis for his not demonstrating large volumes of hydrogen storage as yet.* The one-mg. samples are placed on platinum foil and heated electronically from 90°K (-183°C) to 1400-1500°C. Liquid nitrogen is used as the low-temperature reference. As the gas (i.e., hydrogen) comes off, it flows into an MS. Dr. Heben showed me MS plots showing hydrogen (MW = 2) as the only peak. As stated earlier, no water (MS = 18) was observed. (*See also Question 3.)*

A Sievert's apparatus, used for volumetric measurements can handle markedly larger samples than the TPD system. A known volume of nanotubes is filled stepwise with hydrogen until saturation is reached. The system works well for metal hydrides, but not as well for nanotubes. Degassing is a big problem. Dr. Heben believes that perhaps a new type of measuring system for hydrogen in nanotubes is needed. *Measurement of greater than TPD quantities of hydrogen and, more important, nanotube degassing problems pose what I consider to be serious issues for SWNT hydrogen storage. There is no reason to believe that degassing of nanotubes will be easy in the real world if it is difficult to perform in the laboratory.* Both Dr. Heben and I concur that it is warranted to connect the Sievert's apparatus to an MS to confirm the identity of hydrogen at greater than TPD quantities.

The old yttrium-aluminum-garnet (YAG) laser for making SWNTs by laser vaporization (*actually, two old YAG lasers, including one that I saw in action in 1997*) has been retired and replaced by an alexandrite laser. I was given a short demonstration of this laser. It operates in a pulse mode at about 10 Hz and 0.5 – 1.0 Joules per pulse. The pulse width can also be controlled. The carbon target is placed in the center of a tube enclosed in a tube furnace with capabilities up to 1200°C. (NREL also can use an RF furnace that can heat to 1800°C.) At very high temperatures, the new laser can make short length SWNTs. The alexandrite laser is more efficient than the YAG laser in making nanotubes, producing perhaps 50% pure nanotubes as opposed to 20-30%. Hydrogen adsorption, however, is still lagging behind, with the best values for the alexandrite laser-produced SWNTs adsorbing about 4% hydrogen.

The Raman spectrograph has become a very important measurement tool, being capable of measuring partial charge-transfer of hydrogen electrons into SWNT sp^3 orbitals. Samples can be degassed, exposed to hydrogen, etc. while Raman spectroscopy tests are being run.

Finally, I was shown an ion mill that is used as a cleansing system, primarily for templates that will be used for Chemical Vapor Deposition (CVD).

IV Questions and Answers:

Prior to our meeting, I sent Dr. Heben a list of questions to be considered during our discussions. These are reproduced together with the result of our discussion below.

1. **Please discuss the various methods you have used in generating SWNTs. Address generation methodology, yield, diameter, uniformity, ease of separation from non-SWNTs, and end-caps (method of removal and ease of removal).**

Quite a bit of the information that we were hearing earlier was not entirely accurate. Yields were based on Scanning Electron Microscopy (SEM). These initial assessments were not done rigorously. SEM results showed higher SWNT concentrations than were present in the bulk of the material. These erroneous measurements were not limited to NREL, but were common throughout the industry. *It would appear that SWNTs have an affinity for the periphery of a bulk system containing other carbon forms. That would explain the high values from SEM analysis, a process that is surface oriented.*

A second major issue is that it was previously believed that method of preparation defined the diameter of SWNTs produced, and that there was a single diameter for all nanotubes made by that process. Dr. Heben now says that each preparation method produces nanotubes over a range of diameters, and that diameters may vary over this range by four or five Angstroms. For both carbon arc nanotubes and laser vaporization nanotubes, the distribution is over the range of 10-14 Å. (Typically, nanotubes are between 7 and 20 Å in diameter, for all preparation methods. Tubes smaller than 7 Å cannot exist physically; tubes over 20 Å would tend to collapse.)

Diameter is not the only production issue. Chirality is also important. Looking at two planar arrays of graphite structures as shown in Exhibit 1, if one assumes they can be rolled into tubes along the designated axis, tubes can be formed with an edge having an "armchair" configuration, or a "zigzag" configuration. In addition, tubes can form along some diagonal axis, further complicating the result. (Some configurations are more stable than others, so you do not get all combinations.) As a result, tubes can have widely different properties; some configurations exhibit near metallic qualities, some are more like semiconductors. It all depends on the electronic configurations.

The type of tube can be determined by using different wavelength lasers to excite the tubes.

2. **What are the hydrogen uptake levels you have achieved for each of these methods? Please include and differentiate between measured and extrapolated and/or calculated numbers. (For instance, in the early days of your project, you had a low nanotube yield, subjected your entire sample to hydrogen, measured a hydrogen uptake weight, assumed that all of the hydrogen uptake was in the**

nanotubes, and extrapolated a hydrogen weight percentage based on a 100% nanotube yield.)

The best direct measurement number was 6.5%. This included metal alloy hydrogen. The 7.2% was by calculation, subtracting out the metal contribution. This was obtained with the old YAG laser. The best values for hydrogen adsorption to date using the new alexandrite laser are about 4%.

This brings up concerns (both real and perceived) about progress. A calculated number is not as persuasive as a measured number. Even though subtracting out a relatively small metal contribution is not the same as extrapolating to 10% hydrogen adsorption based on 0.05% SWNT yield (as in the old carbon arc discharge method) it still leaves questions. We address the metal probe used for sonifying the SWNTs in Questions 8 and 9.

The alexandrite laser hydrogen adsorption numbers are not as good as the YAG numbers. Purification of the SWNTs is easier, the tubes may be easier to cut, and eventually the hydrogen numbers may be superior, but right now, as we take a snapshot in time early in 2001, NREL is reporting lower numbers for the new laser.

3. **What method do you use to introduce hydrogen into the nanotubes and then to measure hydrogen uptake? What assurances are there that you are measuring hydrogen and not an impurity? (Recall that when the Northeastern University team were measuring hydrogen uptake, there was concern that part or all of their reported results could have been due to water vapor as opposed to hydrogen.)**

NREL uses two methods. The first is TPD. The TPD system is connected to a mass spectrograph (MS) and is calibrated using calcium hydride. Since no MS peak is seen for m/e = 18 *(the mass to charge ratio in mass spectroscopy is generally indicative of the molecular weight of the species (m) divided by the charge (e) with one electron stripped off; thus e is generally equal to one)* and water's molecular weight is 18, and hydrogen's is 2, (a large m/e = 2 peak is seen), it would appear that there is no water present.

The second method is the Sievert's apparatus, a pressure/volume/concentration system. It can handle much larger samples than the TPD, but samples are difficult to degas.

4. **Has any cycling of hydrogen in nanotubes been demonstrated yet? If so, what were the results? (Number of cycles, amount of hydrogen that could be continuously cycled.) Is there anything to indicate that nanotube structures may be compromised by multiple recycling?**

About ten cycles have been demonstrated. Over the ten cycles, there was a loss of perhaps 10% of the hydrogen.

These results appear to be preliminary, but are of concern as well. Continued decreases could be indicative of SWNT degradation, or of permanent adsorption. However, the loss could also (and perhaps more likely) be metal alloy related. As addressed in Question 9, the metal hydride is not entirely reversible. This would be a much more attractive explanation for cycling losses.

5. **You indicated in your FY 2001 Annual Operating Plan (AOP) submission that you may look at non-SWNT adsorption of hydrogen by carbon structures. What type of materials are you considering (e.g., fullerenes, activated carbon)? What do you see as the potential advantages here?**

This was simply offered as an attempt to act as a support service for testing other groups' carbon structures.

Independent testing is of utmost importance in all aspects of hydrogen research.

6. **Also in the AOP you indicate that you can make 98% pure SWNTs that can adsorb about 7 weight percent of hydrogen. What quantity of sample have you been able to produce to date that had these properties?**

A single sample only contains about 8-10 mg of SWNTs. Overall, however, NREL has made perhaps 0.5 – 1 g of SWNTs with these properties. The few mg samples are all that can be measured by TPD. NREL will use larger samples for volumetric measurements.

7. **Your FY 2000 Annual Review report describes a detailed purification process for the SWNTs involving refluxing in nitric acid, drying, and heating/oxidizing. It also describes a sonication process also in nitric acid to cut the SWNTs. Do you foresee similar processes to obtain SWNTs in "production?" Could purification and cutting steps be combined?**

NREL expects to develop better cutting and purifying processes. Eventually, there may be one process to do both, but not necessarily so.

Purity of SWNTs can be assessed two different ways. One is the use of Raman spectroscopy to observe high frequency shearing vibration modes. The second is by using thermogravimetric analysis (TGA). First, you react raw SWNTs with nitric acid to oxidize away the metals. (If you don't do this, the metals could act as a "fuse" causing defects to open up in the nanotubes.) Then after removing the metals you run a TGA. Two discrete peaks occur. Non-SWNTs decompose at about 300^{o}C, while SWNTs do not decompose until 600^{o}C. Thus, purification consists of SWNTs involves the nitric acid wash to remove metals, and a 550^{o}C oxidation step to remove non-SWNT carbon.

So, it appears what Dr. Heben is saying is that if we stick with the laser vaporization process, this will be the purification method. Depending on how often the nanotubes must be replaced, this could be a significant production cost. – But read on.

Dr. Heben believes that nanotube production using CVD may result in tubes that will be sufficiently pure so that a separate purification step can be avoided. *More on CVD later.*

8. **In the same report, you indicated that the sonication probe contained a Ti/Al/V alloy, some of which wound up in the SWNT sample. The 15 wt % alloy concentration is a very significant amount. While your calculation of 7.2% hydrogen adsorption by the SWNTs, given a 2.5% adsorption by the alloy is correct, I am more concerned by the presence of the alloy to begin with. Are there plans to change the cutting technique, change the probe, or include a step in which the SWNTs are separated from the alloy?**

NREL is addressing ways of processing the SWNTs that will not introduce metal, and is also investigating the role of the metal. They are looking at different techniques, different probes, and different alloys. In addition, NREL has performed density separations on the metal, and found that they could remove 90% of the metal particles. Dr. Heben pointed out that these are not production steps; these are analysis steps.

We need to get to production steps.

9. **Still on the alloy – under what conditions did you find 2.5 wt % hydrogen adsorption? This number is better than some hydride numbers at room temperature.**

The relatively high hydrogen weight percent for the metal hydride does not relate to a "good" storage system. The metal is in the form of fine particles, and would not easily be made into a hydride bed. In addition, the hydride formation is not entirely reversible. During our meeting, Dr. Heben actually spoke of 3.5%, not 2.5% hydrogen in the alloy hydride.

The calculation to get to 7.2% hydrogen on the SWNTs works for 2.5% hydrogen in the metal – not 3.5%.

The presence of the metal hydride is a likely reason for the inability to recover all of the hydrogen during cycling.

10. **You mention a new laser, which give you 50% SWNTs prior to purification. Are these SWNTs any different than the SWNTs from the old laser (diameter, length, ease of cap removal, etc.)?**

The "new" laser is the alexandrite laser. Alexandrite is a doped alumina silicate. Using this laser, chirality and diameter appears to be different. Cap removal appears to be about the same. Right now, NREL is only adsorbing about 4% hydrogen using the SWNTs made in this manner. *(We have already discussed the implications here.)*

The major difference with this laser is that it is a long pulse laser. Most people who try to make nanotubes by laser vaporization generally use short laser pulses using so-called "Qswitching" processes. The trouble with this is that the process causes metal particles to be encapsulated in layers of graphite. This makes purification difficult.

NREL has patented the use of long laser pulsing. The old YAG laser could be used in long pulse mode, but most new lasers cannot be used this way. The new alexandrite laser does have the long pulse capability. The alexandrite laser produces 750 nm light; the YAG laser was 1064 nm.

11. What are the biggest challenges for scaling up the system?

The biggest challenges are obtaining a high quantity of SWNTs in a cost effective manner, and then processing them (i.e., purifying, decapping, and cutting them) to make them accessible to hydrogen. Dr. Heben believes that CVD may be the answer. Dr. Heben is working on a proprietary process that will keep the catalyst clean during continuous nanotube production.

12. If you were asked to put a realistic date on when you believe a nanotube-based hydrogen storage system capable of storing and discharging, say, 6 wt % hydrogen would become a commercial reality for passenger vehicles, when would that be? How about 8%?

This may be difficult to answer. Percentages aside, Dr. Heben sees commercialization to be possible in about 10-12 years.

Perhaps. There are many steps that need to be taken to get the process out of the laboratory, however. Methodology, SWNT yield (quantity), purity, and correlation of good yield/purity with good hydrogen adsorption are still not optimized. And we haven't even begun to talk about packaging and other scale-up issues.

13. I last visited you in June of 1997. At that time, you had recently moved away from arc discharge nanotube production to a laser vaporization method. By so doing, you had increased nanotube yield from the couple of percent range, to the 60-80% range. (These were the numbers that you told me back in 1997; now it appears that the numbers were actually 20-30%, -- or am I mistaken?) However, you had found that the new nanotubes, having a different diameter, possessed very stable end-caps, and both cap removal and hydrogen adsorption were proving difficult. In the past 3+ years, what do you consider to be your two or three most significant steps forward? What remains (or has become) your biggest obstacle?

We have already addressed the problem of inaccurate SEM measurements providing erroneously high yields for SWNTs. 20-30% yields (pre-purification) from laser vaporization techniques rather than 60-80% are correct.

Dr. Heben identified the following significant steps forward:

i) NREL learning how to purify SWNTs as well as identifying the impurities

ii) Developing a capping/cutting procedure that allows the nanotubes to adsorb 6-7% hydrogen
iii) Putting together a CRADA with Honda (it was two years in the making)
iv) Identifying the partial transfer of hydrogen electrons into the sp^3 carbon orbitals as the mechanism for hydrogen adsorption.

The biggest obstacles that remain are:

i) Activating large samples and measuring hydrogen adsorption by the traditional Sievert's Apparatus volumetric technique
ii) Developing a methodology that will allow accurate validation by an outside source. It is difficult to degas a sample properly. NREL is currently working with Honda, however, and they may be able to provide the validation.

14. Also in 1997, you had some thoughts about perhaps going back to arc discharge SWNT production based on what appeared to be nanotubes with less stable end caps. At the time, you were collaborating with Prof. Bernier in France, and had mentioned that Bernier was getting 80-90 % yield of nanotubes. Are you still pursuing carbon arc discharge techniques?

The collaboration ended because of "politics". Bernier's 80-90% purity numbers were as flawed as everybody else's.

Carbon arc discharge is not likely to be the production method of choice; it is not worth spending time on. The tubes produced are "defective", and contain too much metal. There is also not much processes control compared to other processes. In addition, the high yields are not there. Dr. Heben says there are two techniques still in the running: laser vaporization and CVD. Dr. Heben mentioned that with laser vaporization there is much more control on the type and quantity of the SWNTs than with arc discharge. He says that with laser vaporization he will be able to make "grams a day" in the laboratory.

Grams a day in the laboratory would be a welcome increase. Although up to now much of the production has been based on how large a sample can be measured/tested, a leap in production quantity is sorely needed.

V Additional Discussion:

Hydrogen Adsorption Mechanism

One of the key findings over the past couple of years is the fact that hydrogen adsorption is not necessarily an entirely physical process. *Recall that in the past, there was much talk of capillary processes controlling the adsorption of hydrogen.* It appears that there is a partial charge transfer occurring from hydrogen to graphite hybrid orbitals. NREL is finding this by running Raman spectroscopy tests as well as by thermoelectric transport tests. In the latter, a heat pulse is applied to a site, and the length of time that it takes another site to heat up is measured.

Graphite, in its planar form, possesses sp^2 (planar) hybrid orbitals. As the tube is rolled-up, it takes on a degree of sp^3 (tetrahedral) character. The tighter the roll is (the smaller the tube diameter), the greater the sp^3 character and the stronger the attraction to hydrogen. So smaller diameter tubes might hold hydrogen more strongly. *Does this mean that they can adsorb more hydrogen, or does it mean that it will be more difficult to recover the hydrogen?*

The chirality of the tube also plays a part here. Comparing “zigzag” and “armchair” SWNT configurations (Exhibit 1) means you are pulling carbons into and out of radial and longitudinal positions. (Tube vibration can be seen via Raman Spectroscopy) It also plays into the metal-like vs. semiconductor properties.

So there are a whole series of things that determine how much hydrogen you’ll get, and how strongly it will be held. *Again, it’s good to see that nanotube technology is becoming better understood. It’s not good, however, to see how little was known previously. Also, the fact that there are so many factors involved may indicate that it will take a while to sort everything out. NREL will have to determine which SWNTs have what particular hydrogen adsorption and release properties. Perhaps, a Design of Experiments process might help to minimize the number of tests that need to be run. Following this, NREL would need to determine how to control the production of optimum SWNTs.*

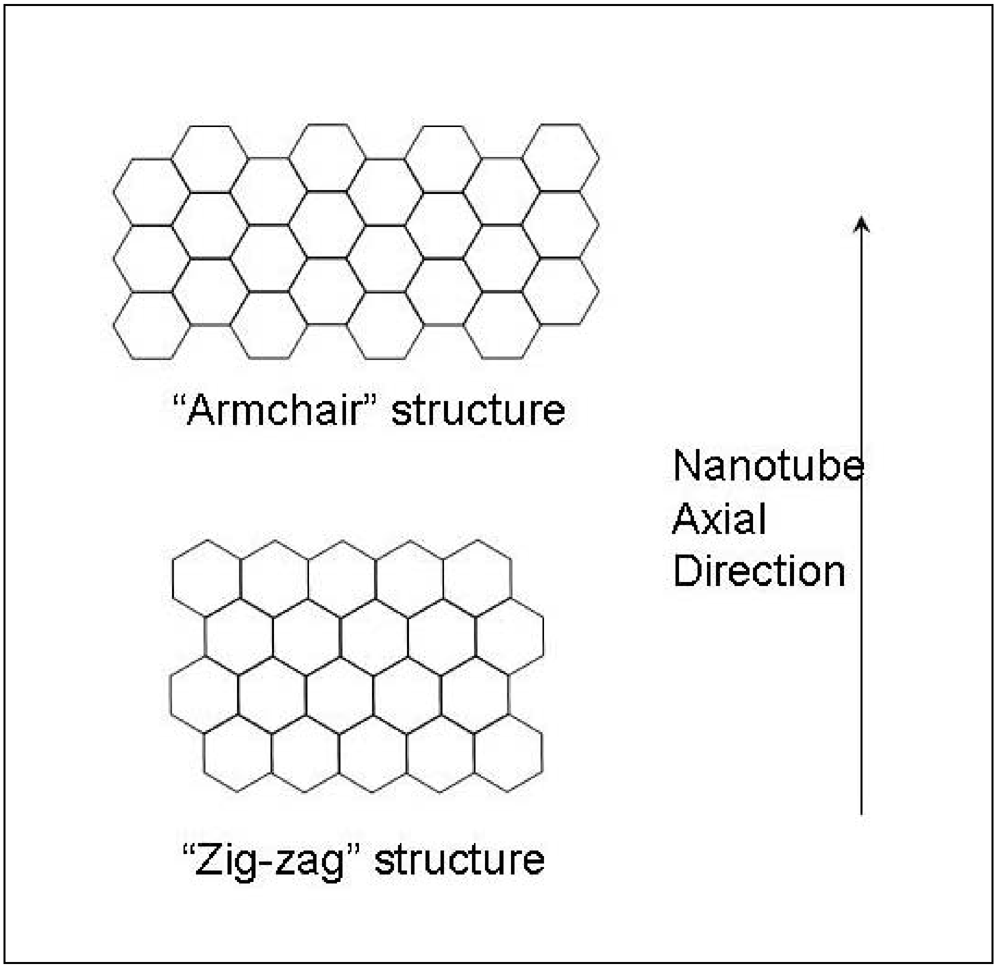
CVD

NREL is working with Honda, their CRADA partner, on CVD nanotube production. Much of the information on this process is proprietary between NREL and Honda, but in a simplistic manner, it involves decomposing methane or CO onto a catalytic surface. Depending on how it is done, one can get a variety of graphite species (SWNTs, multiwall NTs, nanofibers, etc.). Dr. Heben is very excited about the possibilities here, and believes that CVD may eventually become the bulk SNT producer. *I am intrigued also, but at the same time I am concerned by the fact that we may be dealing with yet another method with its own set of surprises.*

CRADA

One other issue that Dr. Heben brought up is that at times, the direction necessitated by working with CRADA partner Honda is not aligned with the DOE Program direction. The DOE general goal is to *(paraphrasing)* ‘make lots of SWNTs, fill them with lots of hydrogen’. There is not enough money to do this and satisfy the CRADA partner as well.

Exhibit 1. Planar views of carbon nanotube arrays.



This page intentionally left blank.

Technical Evaluation Report
Project: Hydrogen Storage in Metal Hydride Slurries
Company: Thermo Power Corporation, Waltham, MA
P.I: Dr. Ron Brault
Date of Visit: June 9, 1998
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

Thermo Power Corporation (TPC) is working on two projects for the DOE Hydrogen Program. They involve the use of metal hydrides in slurry form to transport and store hydrogen for both on-board and stationary storage applications. The methodology being studied is somewhat unique within the portfolio of hydride storage being investigated by the DOE program.

In all, the TPC project so far contains much to be impressed with. Slurry work is going well, proceeding toward a light-weight, high energy-density system, and hydrogen generation tests appear to be proceeding acceptably as well. The concept set forth for on-board systems appears sound, but needs to be demonstrated. Stationary storage systems, the original concept appears neglected for the time being, but also appears to be a viable concept. The overall regeneration process is the biggest problem right now. It needs to be the focus of future work.

Project Strengths:

- They have identified a hydride carrier (light mineral oil) that is a good medium for this type of slurry, and that also protects the particle surface from premature or a too rapid reaction.

- They are concentrating on materials that have the potential to give a high hydrogen loading, especially lithium hydride (LiH), which produces 2 grams of hydrogen for each 8 grams of hydride; and calcium hydride (CaH_2), which produces 4 grams of hydrogen for each 42 grams of hydride:

$$LiH + H_2O \rightarrow LiOH + H_2 \qquad [1]$$

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2 \qquad [2]$$

Sodium would only provide two grams of hydrogen per 24 grams of hydride:

$$NaH + H_2O \rightarrow NaOH + H_2 \qquad [3]$$

- They are making slurries that have solids loadings that are up to 90% by weight, that are pourable and appear easy to handle.

Issues that should be Addressed:

- They have not yet addressed the quite complex regeneration (of hydride) sequence. This could be a real show stopper because:
    - The thermodynamics and efficiency of the proposed reaction sequence may not be sufficient to make the process economical.
    - Maintaining water/hydride management (not allowing contact when it's not wanted) needs to be demonstrated.
    - The regenerated hydride will likely not be easily slurried. Perhaps the reconstituted slurry will be as costly to make as the original one.
    - The regeneration reaction scheme generates CO_2. This weakness is shared by many of the Program projects.

- The overall on-board system including the presence of spent hydroxide, the amount of water needed to augment fuel cell-generated water, and the overall refueling system must be addressed in much greater detail than has occurred to this point. For instance, the calculation for the percentage hydrogen in the on-board system needs to include the hydroxide. Slurry stability in a moving vehicle has been inadequately addressed, as have pumping tests.

II Introduction and Background:

TPC (formerly Tecogen), located in Waltham, MA, is currently involved in two projects for the DOE Hydrogen Program. One is in the R&D portfolio, and is involved with the use of a hydride slurry to produce and store hydrogen. The second is a validation project that is concerned with an on-board storage system for hydrogen again utilizing slurry technology. The two projects are closely tied together, with much that is to be accomplished in the first project (slurry technology, regeneration of the hydride) being used in the second. I visited TPC on June 9, and met with **Dr. Ron Brault**, who is the Principal Investigator on both projects. He made a semi-formal presentation that covered a composite of the two projects. He and his coworkers showed me several slurries and ran a hydrogenation demonstration, and he also provided answers to the questions that I had sent him prior to my visit. We divide the following discussion into matters relating to slurries, hydrogen generation, on-board activities, and hydride regeneration. The questions are included at the beginning of each section.

III Questions and Answers:

Slurry Materials and Processing Considerations:

1. **TPC's report indicated that a 38% NaH slurry had a viscosity of 250 to 300 cps. What viscosities did the LiH and CaH_2 slurries have? What type of viscometer was used in the measurements? Are the slurries Newtonian or are they affected by shear rate? Do the added dispersants affect slurry rheology?**

2. **Is the aluminum powder premixed with the slurry or the water? What role does the aluminum take in the hydrogen release reaction? Does it eventually form $Al(OH)_3$? Will it then be an additional problem during the later separation step?**

3. **Were fluid CaH_2 slurries ever made, and if so, what were their properties?** *At the time of my sending the questions to Dr. Brault, all of his reports were indicating that no pourable slurry had been made to date with calcium hydride.*

4. **Is there any effort to tailor the particle size distribution (PSD) of the hydrides to increase the slurry solids loading? What is the modality of the PSD?**

After working with preliminary systems that featured sodium hydrides in various carriers (notably acetone), TPC is now concentrating on lithium and calcium hydrides, and has settled on mineral oil as the liquid medium. In choosing lithium and calcium, TPC has chosen probably the best two choices for hydrides based on weight percentage potential. *The selection, of mineral oil, I would consider to be in the nature of a mini breakthrough*. Mineral oil serves as both a carrier and a reaction controller. Its hydrophobic nature prevents premature or too rapid dehydriding of the solid. Mineral oils also have a low vapor pressure. The particular mineral oils used by TPC have been acid-scrubbed, so they are inert. *One caveat might be the fact that "mineral oil" is a generic term. Product consistency could be a problem unless TPC takes steps to better identify the material and determine its batch-to-batch consistency.*

When TPC began their work, they first looked at sodium-based slurries. This was because sodium hydride was readily available, and is not extremely reactive. When they began to make the slurries and generate hydrogen from them, they found that the production reaction appeared to be pH limited. That is, as water was added, hydrogen was being generated, and NaOH was being formed, raising the pH of the mixture. At a pH of about 13.6, the reaction stopped. As a result, TPC tried adding powdered aluminum to the slurry as a means of scavenging the NaOH. (Aluminum will dissolve in base to give the aluminate ion, AlO_2^-.) While this approach was successful in controlling the reaction rate for the sodium system, TPC meanwhile moved on to Li and Ca systems to increase potential storage capacity. Since LiOH and $Ca(OH)_2$ are much less soluble than is NaOH, the base limitation never occurred. Therefore, the need for aluminum no longer exists, and this potential bottleneck is no longer an issue.

TPC has considered lithium and sodium borohydrides as well; these materials are not as reactive as the straight hydrides, and therefore hydrogen generation might be more controllable. However, the boron acts as a buffer, which limits hydrogen generation. In addition, the regeneration of these more complex materials would also be more complex.

Note: Despite the presence of four hydrogen atoms in each borohydride molecule, these materials are only slightly more efficient a hydrogen producer than the straight hydride on a weight basis when one looks at the whole system:

$$NaBH_4 + 4H_2O \rightarrow NaOH + B(OH)_3 + 4H_2 \quad [4]$$

$$LiBH_4 + 4H_2O \rightarrow LiOH + B(OH)_3 + 4H_2 \quad [5]$$

For instance, comparing $LiBH_4$ with LiH: 22 grams of $LiBH_4$ produces 8 grams of hydrogen, but also produces 24 grams of LiOH and 62 grams of $B(OH)_3$. (8.5% hydrogen). In reaction [1], 8 grams of LiH produces 2 grams of hydrogen, and 24 grams of LiOH (7.7% hydrogen.)

TPC is making laboratory slurries in small jar mills (about one quart size) using ceramic cylinders as the grinding medium. They have demonstrated slurries that are above 90% by weight. Proprietary dispersants are used - one percent by weight for lithium and two percent for calcium. *These dispersants could become a cost issue, but we have no information.*

Lithium hydride slurries are very easy to mill. (They mill wet.) Calcium hydrides are somewhat more difficult, but they are making good progress on both, being in the over 90% by weight range. One interesting phenomenon: Lithium hydride is less dense than mineral oil. When separation occurs, the hydride floats to the top. *This would make remixing easier in a scenario where the slurry would be shipped in barrels.*

A photomicrograph is used to determine particle size distribution, and a Zahn cup measures viscosity. They measure stability using paint industry standards. Slurry particle size distribution is more or less monomodal and in the 5-10 micron range. No attempt has yet been made to tailor the particle size distribution. Viscosities are in the 100-300 centipoise (cps) range at low shear rate. Dr. Brault mentioned that the slurries appear to be Bingham plastics, having a yield point. *There is not a lot of attention being paid to slurry properties at this point. There is no attempt to raise the solids loading or increase the stability by particle size adjustment, or to address the non-Newtonian rheology that appears to exist. Pumping tests will have to be addressed soon if TPC wishes to pump their slurries over any distance; slurry pumping problems could cause a drastic reformulation of these slurries. On the positive side, this team is quite knowledgeable about slurries, and these issues will be addressed.*

<u>Hydrogen Generation:</u>

5. **One of the monthly reports indicated that LiH only released about 41% of the expected hydrogen and that more experiments were planned. Were they ever completed? Success with LiH appears to be of extra importance due to its higher weight percentage of hydrogen, all else being equal.**

6. **Many of the reported tests are indicating that the hydrogen generation reaction does not go to completion due to pH and pressure effects. This implies that some of the hydride remains unreacted. Will this pose a problem later when the mixture is removed from the reaction chamber and the pressure is released? In other words, can it lead to hydrogen generation occurring downstream?**

TPC has now demonstrated 95 percent hydrogen recovery from their hydride slurries. They believe that when they build an engineered reaction chamber, they will do even better.

LiH generates hydrogen somewhat faster than does CaH_2, but they are more or less in the same range.

Dr. Brault and his associates provided a demonstration of hydrogen generation from CaH_2. They mixed the hydride and water in a 1 to 2 molar ratio in a reaction tube, producing hydrogen in what appears to be a controlled reaction. The heat of reaction drove the temperature up to about 300^oF (lithium hydride gives off less heat; the temperature is generally around 200^oF.) The reaction appears to be pressure limited. Dr. Brault indicated that reaction during the recycling process could indeed be a problem if hydrogen generation was not complete when intended. One of the goals is to make a slurry with a lot of fines so that there is a high surface area. This will cause an accelerated reaction rate early in the process, and help ensure reaction completeness. *However, it might prevent the slurry from being optimized for solids loading and, therefore, energy density.* Dr. Brault pointed out that they need to get away from their current bench-scale batch process for hydrogen generation, and begin some flow tests for the hydrogen generation data to be realistic. *I agree about the need for flow tests to authenticate the data. Reaction completeness may be a problem in a practical setting, however. We discuss this more in the On-Board section.*

Dr. Brault mentioned another application for a batch hydrogen generation system: If you run the pressure-limited reaction in a canister, you can stall the reaction until you release the pressure. This could have military applications.

<u>On-Board Considerations:</u>

7. **In determining the storage capacity of the on-board hydrogen system, is the amount of water being carried taken into account?**

8. **In incorporating a hydride slurry for on-board applications and transporting of hydrogen as well, what sorts of tests have been performed or are planned to ensure slurry stability?**

Dr. Brault spoke of using water produced by the fuel cell as reaction water to generate hydrogen. He stated that they would need about a one-liter start-up water tank to generate sufficient hydrogen to get the system going. *One liter of water weighs one kilogram, and equals 55.6 moles of water. This will produce 55.6 moles of hydrogen either from LiH or* CaH_2*, which in turn is equal to about 0.11 kg of hydrogen. At 93 miles/kg of hydrogen, this would allow about a ten-mile range in addition to the fuel cell water.*

The numbers reported by TPC do not include the extra liter of water. *Complete analysis would have to include it, as well as the weight of the hydroxide formed. The simplest way to do this is merely calculate the hydrogen produced as a fraction of all the reactants (as* *opposed to just the hydride). For instance, for the lithium system in equation [1], two grams of hydrogen are formed from eight grams of lithium hydride and eighteen grams of water. This amounts to about four percent hydrogen, but this is provided without adding heat.*

Dr. Brault indicated that on start up, a small battery would run the slurry pump to move slurry into the reaction chamber. Water from the reserve would be added, and hydrogen is generated for the fuel cell. The water reserve would also come in to play for peaking operations such as hill climbing.

TPC sees that the methodology of refueling of a vehicle should mimic the existing infrastructure as much as possible. Thus, they would consider a slurry system as mimicking the existing gasoline infrastructure. One difference would be that you would need to pump spent hydroxide out of the vehicle while you pumped new hydride slurry in to the vehicle. Dr. Brault envisions a bladder tank to separate the spent from the unspent fuel. *This immediately brings two problems to mind. First, it would mean either requiring one hundred percent conversion of hydride to hydroxide prior to removing the spent fuel. If this was not done, we would both suffer an efficiency loss (dumping good fuel) and be exposing the recovery system to further hydrogen generation, as both unused hydride and water would be present in the mix. Second, handling of the spent material would be a problem. It is unlikely that the spent material would still be in the form of easily handleable, pumpable slurry. Perhaps these problems could be solved by 1) multiple fuel tanks in the vehicle, so that one could be totally exhausted of hydrogen and the second would be in use when refueling the first, and 2) using a make-up carrier; perhaps more mineral oil to re]slurry the spent material. Note that these are solutions to two problems (not an either/or situation), and both could probably be quite costly as well as inconvenient. I don't believe refueling will be easy with this kind of system.*

The hydrogen generation process is exothermic. Dr. Brault sees simply employing a radiator on board to dissipate the extra heat. In a stationary application, combined heat and power could be an option. *Theoretically, it would be beneficial if the heat could somehow be used in the regeneration of hydride, but I guess that could not be done on board.*

In an attempt to simulate vehicular motion, TPC runs tests on shaker tables. This, according to Dr. Brault, duplicates the "sloshing" motion in a vehicle. *I believe that real vehicle tests are needed. Realistic motion in a real on-board tank cannot be simulated by a jar on a shaker table.*

<u>Recycling/Regeneration</u>**:**

9. Does the overall process involve the pumping of a hydroxide slurry? If so, is there any evidence that the slurry will be pumpable without additional processing?

10. Have any laboratory scale tests on the reaction scheme that regenerates the hydride been carried out yet?

Dr. Brault envisions that spent slurry will be pipelined back to a central location for regeneration, and that a centrifuging method would be used to remove the mineral oil from the hydroxide before regeneration. Dr. Brault also mentioned that the particle size distribution of the spent slurry is not that much different from that of the hydride slurry, but that the viscosity is different. This, says Dr. Brault, may be a function of the stoichiometry. He believes that they may have to add water to make the slurry pumpable. *I am surprised by the fact that the particle size distribution did not change. I would think that the size and the shape of the particles would be affected greatly by the chemical reaction. Perhaps it didn't show up clearly in the photomicrographs. We have already mentioned that pipelining a slurry that has not been properly formulated will be difficult to handle at high loadings. Substituting a hydroxide in a slurry tailored for a hydride will likely be difficult. It will be further complicated by the solubility of the hydroxide in the excess water. While this will help reduce the solids loading and viscosity, it will further complicate the regenerative process. The centrifuging process may be inadequate. An evaporation step may be necessary. This part of the process needs to be investigated as a priority; it will dictate the available options for regeneration.*

TPC have not yet approached the regeneration process experimentally, but plan to address it in the fall. They will first perform static experiments in the furnace, and then proceed to small flow tests. The reaction scheme for regeneration can be expressed by the following (using the Ca system as the example):

$Ca(OH)_2 \rightarrow CaO + H_2O$ (+15.5 kcal/mole) [6]
$CaO + C \rightarrow CO + Ca$ (+125.5 kcal/mole) [7]
$H_2O + C \rightarrow CO + H_2$ (+41.9 kcal/mole) [8]
$H_2 + Ca \rightarrow CaH_2$ (-45.1 kcal/mole) [9]
$\underline{2CO + O_2 \rightarrow 2CO_2 \quad (-135.3\ \text{kcal/mole})}$ [10]

Overall: $Ca(OH)_2 + 2C + O_2 \rightarrow CaH_2 + 2CO_2$ (+2.6 kcal/mole) [11]

TPC is considering electric arc heating for regeneration, but hope to be able to get a large portion of the needed heat from the exothermic reactions. There is a sizable efficiency penalty for using electric heating.

Dr. Brault thinks that they will probably be driven toward the lithium system, primarily due to its requiring less heat during the regenerating process than does calcium. (As mentioned before, lithium hydride has a higher energy density as well.)

It may be too early for us to assess this aspect of the process since TCP hasn't begun the testing yet. It seems that they have devoted a lot of time to the thermodynamics of the process, finding an overall essentially thermally-neutral reaction scheme. It is a very complex system, however, and I'm not sure how the kinetics will all play out, or if they can make a viable reaction process that will indeed be basically self-sustaining. They *won't find out until they go to the flow tests. It's a good overall process; it's too bad that they're making* CO_2*, however.*

IV Final Thoughts:

TPC's closest analog is the unfunded Power Ball concept, and I believe, the TPC process is superior. I prefer the slurry as a mode of transport, and also feel that the LiH system, providing more hydrogen per unit hydride, is a better storage system.

Technical Evaluation Report
Project: Hydrogen Storage in Metal Hydride Slurries
Company: Thermo Technologies, Waltham, MA
P.I: Andrew McClaine
Date of Visit: August 21, 2000
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

Thermo Technologies is developing a means by which hydrogen can be stored on-board a vehicle in a fine particle metal hydride/mineral oil slurry. As the slurry becomes mixed with water, the subsequent hydrolysis reaction releases hydrogen, and forms a metal hydroxide byproduct. Runaway hydrolysis is prevented by the presence of the mineral oil, which limits hydride-water contact. Spent hydroxide is shipped to a central location where the hydride is regenerated via a carbo-thermal process.

In the past couple of years, Thermo Technologies has demonstrated their ability to produce a useable LiH slurry, demonstrated hydrogen evolution from the slurry with the hydrogen being used to run a pickup truck with a modified internal combustion engine (ICE), and most importantly, has begun to address the regeneration issue as a top priority.

Project Strengths:

- Thermo Technologies has shown that slurrying a hydride with mineral oil does indeed allow one to control the rate at which hydrogen is evolved by the hydrolysis reaction, and that the rate can be made practical for on-board use.
- The potential for an economical regeneration process has been improved by the experimental finding that the temperature of the regeneration process can be made significantly lower by continuous removal of product.
- The overall process enables the use of on-board hydrogen while transferring CO_2 emissions to a centralized location where they can be more readily sequestered.

Issues that should be Addressed:

- The fate of all the lithium in the system must be accounted for. This is a very important and unanswered question at this stage. Lithium has been hypothesized to remain as a hydroxide needing recycling, to be wicked into the carbonaceous material, to remain as a liquid in the reactor, or to be swept out of the chamber as a vapor co-mixed with CO. It could also be all of the above.
- The economic analysis performed for Thermo Technologies is not complete. For one thing, it does not include transportation costs for transporting the hydroxide or the hydride. Nevertheless, the data is taking advantage of large scale (centralized)

regeneration. This would result in the likely need of several hundred miles of transportation, equivalent to several dollars/MMBtu hydrogen cost. For another thing, the LiOH is apparently being shipped in a mixture of water and mineral oil of which the LiOH is only about 27 % by weight. Overall round-trip economics from unprocessed byproduct being removed from the vehicle to hydrogen ready for use in the vehicle must be included in determining the overall cost of hydrogen.

- All slurry stability testing to date has been either under static conditions or on a standard "shaker table" with no variable parameters. No stability tests have been performed to date on the slurries under real-life conditions such as several hours on the road, or in a pump loop.

- Safety considerations should include methodology to ensure all the hydride is reacted prior to shipment to the regeneration center.

II Introduction and Background:

I visited Thermo Technologies in Waltham, MA, meeting with Principal Investigator (PI) **Andrew McClaine** and his team. Thermo Technologies is the new name for Thermo Power, which originated from Tecogen. The company (under all names) is and has been a Thermo Electron Company. Mr. McClaine assumed the PI role for the hydrogen storage project with the resignation of Ron Breault in June. (Dr. Breault has started a new career as a college professor). Mr. McClaine's team includes **Dr. Ravi Konduri**, Project Engineer and **Jonathan Rolfe**, Senior Project Engineer. Both were present for the meeting. **Daniel Nathanson**, Business Development also attended the meeting, and **Fred Becker**, the Program Manager was present for part of the time.

The full day's meeting included a presentation by Mr. McClaine, extensive discussions primarily centered around the series of questions that I had sent to Mr. McClaine, a demonstration of hydrogen production from LiH in the laboratory, and a demonstration of a pickup truck being powered by a hydrogen internal combustion engine (ICE), with the hydrogen coming from a LiH slurry. All of these events will be discussed below.

III Tour:

Mr. McClaine and his coworkers first took me into their laboratory where they demonstrated the effect of squirting water into a pool of LiH slurry. The reaction is easily controllable if not sluggish. It is necessary to stir the reactants in order to release all of the hydrogen. *There will not be a problem of a runaway reaction; the mineral oil adequately limits hydride/water contact. In fact, if anything should be considered worrisome at all, it is that care needs to be taken that mixing of the reactants is sufficiently complete to release all of the hydrogen. Aside from being an efficiency issue, there may be a safety aspect as well. If unreacted hydride remains, it is conceivable that it could release unwanted hydrogen when being transported to the regeneration site in the hydroxide/mineral oil/water mixture. It does not seem like a showstopper, but might be a safety issue that should be addressed.*

I was also given a demonstration of a pickup truck running on hydrogen that was being stored in a 60% LiH slurry. The truck is a Ford Ranger that had previously been used at the South Coast Air Quality Management District (SCAQMD) as part of the Clean Air Now Program. The truck utilizes a modified ICE that can run on hydrogen. The hydrogen storage/production components are mounted in the truck bed.

The system is not extremely sophisticated at this point, but is not meant to be. For instance, the slurry is kept in a five-gallon can with clamps holding the top on. The slurry is mixed with water using a screw-type mixer, and the resultant hydrogen is pressure-fed to the ICE. I observed the truck running around the Thermo Technologies parking lot with no obvious difficulties. The 60% LiH slurry has an energy density of 5,400 Wh/kg, and the overall system (container and reactor) has an energy density of 2,492 Wh/kg and 1,225 Wh/liter.

The hydrogen generation system takes up the better part of the truck bed and looks rather ungainly. Nevertheless it demonstrates what it should demonstrate – that the system can produce hydrogen in a controlled manner, and that the hydrogen can power a vehicle. It's their first demo, and it works. That's what is important. Anything more than this is secondary to solving regeneration issues.

Mr. McClaine also mentioned that no slurry settling could be detected as a result of driving the truck around the parking lot.

Encouraging, but not definitive in itself. We address settling later.

IV Questions and Answers:

Prior to our meeting I sent Mr. McClaine a group of questions/discussion topics. A large number of these dealt with hydride regeneration issues, which, I believe, is the biggest "show-stopper" facing this project. Other questions dealt with hydrogen storage and generation issues.

Regeneration Issues:

1. **What is the status of the carbon-based regeneration work? What have the bench scale tests shown to date? Where do your regeneration plans go from here?**

"We are continuing to evaluate the carbo-thermal regeneration process. Our analyses indicate that the carbo-thermal process offers the lowest cost system because it produces hydrogen as well as reforms lithium. Our experiments indicate that lithium oxide and lithium hydroxide can be reformed in the presence of carbon at reasonable temperatures. We are learning a lot about the process and have identified several alternative process options. We feel that we are nearing the end of the experiments that we can perform on the laboratory apparatus that we have constructed.

"To date, the bench scale tests have shown that lithium hydroxide produces more carbon monoxide than it should if only the lithium is reducing. This indicates that the anticipated decomposition of lithium hydroxide to lithium oxide releasing water vapor that reacts with hot carbon to form hydrogen and carbon monoxide is taking place.

“We have tested lithium oxide with carbon to eliminate the production of carbon monoxide with the water vapor. We have observed the production of carbon monoxide sufficient to account for yields of 50% to 100% of the lithium. We have observed that higher yields result when the sample has a larger fraction of carbon. This indicates that carbon contact with the lithium oxide is important. Thus in a scaled up device, the reactants should be mixed or they should be in a solvent.

“During the last several months we have been working to observe the resulting lithium. Lithium may remain as a liquid, it may be wicked into the carbon crucible, or it may be evaporated and leave the crucible. We have observed qualitatively the presence of lithium in the exhaust gases leaving the furnace. (When the exhaust gas is directed into a hydrogen flame, we observe a pink emission indicative of lithium). We are currently attempting to perform a mass balance on the lithium by measuring the amount of lithium left in the crucible and the amount deposited in a water trap after bubbling the exhaust through the water. We are using a lithium ion detector. The results of this mass balance should allow us to focus future research.”

Identifying and controlling the fate of the lithium is one of the top priorities for this project. Lithium that can be recycled represents an inefficiency to the system, but may be manageable. Lithium that escapes in the vapor phase is another story entirely. Mr. McClaine comments on this below. Nevertheless it is essential that the lithium be accounted for. A mass balance is needed. Mr. McClaine estimates that likely half of the lithium is not being transformed from the hydroxide, and must be recycled.

“The next set of experiments should be performed with an apparatus that can evaluate samples considerably larger than the samples we now evaluate. There are several experiments that should be performed.”

(At this point in the discussion, Mr. McClaine mentioned another regeneration scheme that they would like to evaluate, but wished to keep the methodology proprietary until they can formulate an invention disclosure. I will comment on this scheme once it becomes known.)

“We would also like to evaluate the use of lithium hydroxide as a solvent for the reaction. One on the outcomes of the solvent tests may be that lithium must be recovered as a gas in the exhaust products of the furnace. If so, we will need to evaluate aerodynamic quenching as proposed in the patent literature. This would be an improvement to the carbo-thermal magnesium process used in the Kaiser plant in operation during the 1940’s in Permanente, CA.”

2. **Some of your reports show a significant lowering in the temperature of the regeneration reaction if product is quickly swept out of the reactor. (I assume this is due to LeChatelier’s Principle). Is the effect compromised by sweeping reactant out of the reactor as well? Does the plan include recycling of unreacted LiOH?**

“In our preliminary system design and economic analysis, we assumed that lithium hydroxide is heated in the presence of carbon. Above about 900°K, lithium hydroxide decomposes to lithium oxide and water vapor. We noted in our experiments that the water vapor reacts with carbon at about 1000°K. Upon further heating the lithium oxide and carbon to 1350°K, we observe sufficient quantities of carbon monoxide to conclude that large fractions of the lithium oxide are being reduced to lithium. This temperature is considerably below that predicted by equilibrium chemistry. This effect is expected as a result of LeChatelier's Principle because we are diluting the carbon monoxide in large quantities of argon. At 1350°K, the vapor pressure of lithium is relatively low so the evaporation rate should be low. This may allow the lithium to form a pool. In the event that the reduction does result in vaporized lithium, we may be able to condense the lithium by aerodynamically expanding the exhaust to cool the lithium before the back reaction with carbon monoxide converts it back to lithium oxide. We have not yet been able to define the reaction rate of the back reaction."

This is further indication that Thermo Technologies is not certain where the lithium is. The assumption that the reaction is working is based on the indirect method of observing carbon monoxide. ($2LiOH \rightarrow Li_2O + H_2O$; $Li_2O + C \rightarrow 2Li + CO$) *They admit, however, that the CO may be at least in part formed by reforming of the carbonaceous material. They believe that Li vapor is being carried out with the CO gas. Could lithium hydroxide also be swept out of the reactor by the carrier gas under this new reaction process? Mr. McClaine admits it is possible. I think it is a likely fate of a portion of the lithium. Perhaps they need to look at filtering and recycling of LiOH, as well as methods to separate Li from CO.*

"Our preliminary design assumed that half of the lithium produced back reacted with carbon monoxide to lithium oxide. Thus the regeneration system is sized twice as large as ideally required."

If this is what indeed happens once (or if) the process is ironed out, it may indicate that sweeping the reactant out of the chamber and recycling is reducing the efficiency of the process. This process needs to be traded off against running at the higher temperature. I look forward to seeing the sensitivity analysis that Thermo Technologies has promised to send me.

3. What are the latest economic figures on this process? (We should spend part of the day going over these).

"The latest cost estimates conclude that hydrogen will be produced and stored at a cost of $6.04/MMBtu for a carbon cost of $50/ton to $11.30/MMBtu for $150/ton of carbon.

"We will be performing a sensitivity analysis on the following variables: cost of lithium, amount of lithium hydride to include in the analysis, cost of carbon, and maintenance and repair cost. I plan to send you a copy of this analysis in September.

"The current results are summarized in [Exhibit 1]."

"This chart compares the cost of stored hydrogen from lithium hydride and from several alternate hydrogen production processes. The chart shows the cost of hydrogen production as well as the cost of stored hydrogen, using the selected production method, as a liquid and a compressed gas. The costs of stored hydrogen are obtained by adding a fixed cost for the energy required to liquefy or compress the hydrogen. These figures were taken from an NREL report summarizing the process costs. The costs represent the lowest costs for large storage systems."

This analysis was performed by a consultant under contract to Thermo Technologies, and using two references [1,2] as a basis. The analysis assumes that there is a one-time charge for lithium hydride, and the lithium can be repeatedly recycled. It also assumes a *large central plant that can treat enough lithium to serve about 4,000,000 vehicles. Such a plant would by necessity likely be located hundreds of miles from some of the refueling sites.*

The chart shown above predicts a cost for hydrogen of 6 to 12 \$/MMBtu, based on the cost of carbon. This cost is based on the cost of carbon delivered to the recycling plant. It does not, however, include the cost of transporting the spent hydroxide to the plant, nor the cost of transporting the reconstituted hydride back to the refueling stations.

We performed a similar analysis in FY 1999 [3] and found these costs to be significant – of the order of several dollars (perhaps about \$6 for the distances estimated here) per MMBtu hydrogen. In addition, our analysis assumed a low-cost scenario in which the spent hydroxide and the hydride slurries could be transported by rail in units similar to covered coal cars. Truck transport in tanker-like containers would undoubtedly be more expensive. Transportation costs cannot be ignored.

Mr. McClaine was unable at this time to give me an estimate of the cost differential between running at 1,400K and 1,850K. The old analysis (at 1,850K) which produced a cost of hydrogen of \$4/MMBtu was "back of the envelope" while the 1,400K analysis was done more rigorously. (Our concerns with the latter analysis, however, have already been stated.)

4. What is the expected full cycle recovery efficiency of lithium (or the metal of choice)?

"We expect that lithium return for recycle should be nearly 100%. We will evaluate the possible loss mechanisms and the effect of these on the costs in our sensitivity analysis."

I am more concerned with the fate of unrecovered lithium than I am with the cost. If the lithium is being swept out by the carrier gas and lost, or is being vaporized and then being mixed with product hydrogen, steps must be taken to ensure 100% recovery.

The fact that the cost of unrecovered lithium is even being considered is significant in itself. Mr. McClaine estimates that for \$50/ton carbon, the loss of 5% lithium results in an increase in cost of about \$2/MMBtu. As I said, however, more important is – where did the 5% go?

5. What is the fate of unrecycled lithium species?

"We have not identified any unrecycled lithium species. If the hydride slurry is placed in a container with a bladder so that hydroxide product can be returned to the container on the other side of the bladder, lithium hydride should be pumped out of the container, reacted, and lithium hydroxide should be returned to the bladder. A proper generation system will not have buildup of materials so there should be no loss of lithium.

"Lithium losses may occur in the regeneration process however this will imply that there is a waste product from the regeneration process. We do not envision a waste product at this time."

The fact that Thermo Technologies believes that there will be no waste product is encouraging – they are addressing the issue correctly. The fact that early experiments are showing that at least some of the lithium is not being recovered indicates that there is a ways to go, however.

6. **How do you expect the regeneration of LiH to be effected by the use of actual hydrolysis byproduct as opposed to pure LiOH? What process steps are anticipated to move from the on-board byproduct to the regeneration reactor feedstock?**

"We anticipate that the lithium hydroxide will be returned as a compound of lithium hydroxide, water, mineral oil, and dispersant. The first step of the process will be to separate the water, oil, and solids. The water will need to be evaporated to recover the lithium hydroxide dissolved in it. The oil will be heated to remove lithium hydroxide and water vapor so that it can be reused in the production of the new lithium hydride slurry. The solids will be heated to remove excess water. At temperatures above 100°C, the hydrate of lithium hydroxide decomposes. The dried lithium hydroxide will then be introduced to the regeneration process. As this reactant is heated, any oils or dispersant remaining will be pyrolyzed leaving carbon that will be consumed in the regeneration.

"As noted above the processes are: separation of the water, oil, and solids, removal of water from the three parts, recycle of the oil, mixing of the lithium hydroxide with carbon, and heating."

The cost of the process steps indicated above are included in the analysis. Handling the material to make it ready for transport may be a cost over and above the transportation costs we spoke about earlier.

Mr. McClaine also pointed out that if the process results in contamination by other metals, the system might have to be purged periodically.

7. **Explain the methodology for electrochemical regeneration of hydrides from spent hydroxides. What are the reasons for considering this method? What are the drawbacks? What are the economics?**

"The electrochemical regeneration is currently the method used for reformation of lithium. It consists of contacting the lithium hydroxide with hydrochloric acid to form lithium chloride and then electrolytically separating the lithium and chlorine. The chlorine is then recycled to make more lithium chloride.

"I thought we should evaluate the electrolytic method of producing lithium so that we knew the upper range of the cost for lithium regeneration. We have calculated the electrical energy consumption. Assuming $0.03/kWhr, we conclude that the cost of electricity to produce lithium would be about $15/MMBtu.

"In the event that we want to produce large quantities of lithium hydride slurry in the near term, we will likely need to use existing technology to regenerate the lithium. This might be a step in the introduction of the technology.

"The drawbacks of electrochemical regeneration are that it appears to be more expensive than the carbo-thermal process and it requires purchased hydrogen to produce lithium hydride.

"We have only evaluated the cost of electricity for the electrolytic separation. Based on a process description we found for an electrochemical reduction of sodium hydroxide to sodium metal, we are estimating that hydrogen will cost about \$15/MMBtu if electrical costs are \$0.03/kWhre."

This question was asked in response to a comment from Mr. McClaine during a phone conversation prior to my visit. At the time, it appeared that Thermo Technologies was seriously considering this process. Apparently, this is not the case. For one thing, hydrogen would have to be purchased separately.

<u>Slurry and Hydrogen Generation Issues:</u>

8. Is lithium hydride the material of choice, or is this still undetermined?

"Lithium hydride was selected for use in this program because it looked like it provided the highest gravimetric and volumetric energy density while at the same time appearing to offer the greatest potential for carbo-thermal regeneration. Several multi-metal hydrides have greater gravimetric and volumetric energy densities but they appeared to be more difficult to regenerate.

"Magnesium hydride and calcium hydride have some attractive features but they require higher regeneration temperatures than lithium. The primary attractive feature of magnesium hydride is that its hydroxide is not harmful."

During our discussion, the subject of MgH_2 *came up a couple of times. Its non-toxic byproduct makes it of increased interest despite the higher temperatures involved in regeneration. From this, I raise two questions: Is Thermo Technologies interested in magnesium because they have serious concerns as to how they will recover 100% of the lithium? Is there a market –perhaps a niche market- for a hydrogen storage system (such as* MgH_2*) that will produce a byproduct that will not be recycled at all?*

We discussed borohydrides as well. Thermo Technologies have worked with these and found pH and regeneration related problems.

9. Is hydrogen generation linear with hydride loading, or is there an ideal solids loading that maximizes hydrogen yield?

"We attempted to prepare our slurries with the largest possible hydride concentration to minimize the weight of oil. Our conclusion was that higher loading was better. If the reactants are well mixed in the reactor, hydrogen yield from the slurry should be nearly 100%. Losses in the slurry would be due to contamination of the slurry with water."

Contamination of the slurry with water equals premature hydrogen generation. I don't believe that Thermo Technologies is saying that they will have this kind of problem. I think they are saying that hydrogen yield will indeed be linear with loading. The only thing that will prevent this is <u>if</u> there were some water contamination.

The limit to loading is, of course, the ability of the slurry to be handled. Mr. McClaine uses as a rule of thumb that the slurry has to "slump" in a tank. If it does not, it won't flow uniformly out of the tank, but will “rat hole” (i.e., cavitate) instead. A 60% LiH slurry has a viscosity of about 4,000 centipoise, and will slump.

I believe that the handleability of the slurry cannot be limited to slumping. Stability during transportation and pumpability are also very important (see below.)

10. If the slurry becomes unstable (i.e., the solids settle) how easily can it be remixed?

“The latest slurry formulation is very resistant to separation. We have been running two types of tests of recent batches. A sample of the slurry has been sitting still for over one month. Viscosity measurements show that the sample experiences some increase of viscosity over time. The sample regains its original viscosity (equal to that of a continuously agitated sample and equal to its original viscosity), after a few minutes on the viscosity analyzer.

“A second test was conducted using a centrifuge to separate the slurry. After light remixing, the slurry sample was still pourable after one hour at 215 g.”

Mr. McClaine indicated that the separation of the oil from the hydride upon centrifuging resulted in a small amount of hard-packing, but the remixing was easily done.

I am more concerned with how the slurry will react to being driven around in a tank for a few days (simulating a real condition) in addition to static stability, shaker tables, and centrifuging.

11. How are the hydride slurries affected by excessive pumping?

“We interpret this question to refer to the effect of self-grinding that would occur if it was pumped excessively of if the slurry is continuously agitated. The slurry as produced has particle sizes ranging from 1 micron up to 100. Slurries thicken when significant portions of the particles are less than one micron. Thus, our slurry can withstand some milling without an increase in viscosity. To date, slurry samples have been agitated for one month, with no noticeable increase in viscosity.

“We have not attempted to pump the slurry in a loop yet. Pumping the slurry through a gear pump is the method we use to control the relative size of the particles in the slurry.”

Agitating a slurry will not simulate pumping. I suggest a pump loop test if there is any plan to pump the slurry at all.

While a slurry will indeed thicken if there is a significant portion of fines (particles smaller than 1-2 microns), a small amount of fines will actually produce a thinner slurry. Particle size technology shows that when fines have diameters of less than one-tenth the diameter of the coarser particles, they fit well in the interstices of the larger particles allowing a higher loading. Furthermore, the fines act as a pseudoliquid to the coarser particles, resulting in a thinner slurry. As the amount of fines increase, however, the slurry does indeed thicken as the packing efficiency drops.

12. **If the mineral oil has such a high vapor pressure, is there a chance that if a hydride slurry is left exposed (e.g., spilled) that the mineral oil would evaporate off and the resulting dry slurry could ignite if, say, it started to rain?**

"I should have said that the mineral oil has a low vapor pressure. It evaporates very slowly at ambient conditions, so it will protect the hydride well even in the event that the hydride gets wet in rain."

I had read the high vapor pressure statement in one of Thermo Technologies' reports. Mr. McClaine informed me that that statement was in error.

V Additional Discussion:

Thermo Technologies is now generating lithium hydride/mineral oil slurries (60% solids) in 5-gallon batches. The slurries are mixed in a gear-pump grinder using 1-2 weight percent of a proprietary dispersant (*which does not appear in the cost estimates)*, grinding to a mean particle diameter of 20 microns. The resultant slurries are pourable and pumpable, having a viscosity of about 2,000 centipoise and are shear-thinning (pseudoplastic) as measured by a Brookfield Rheometer using a cylindrical spindle.

I have found that some highly loaded slurries, when measured by rheometers such as this one, can seem to possess pseudoplastic tendencies when the phenomenon that is being observed is actually a result of particles being pushed out of the path of the spindle by centrifugal force. The slurry near the spindle is then not as highly loaded. This phenomenon, which increases with increasing spindle velocity, can therefore be mistaken for pseudoplastic behavior. A rheometer that has a narrow gap between the spindle and wall of the container such as a Haake, may provide more accurate rheological data at higher shear rate. This may prove to be valuable if the slurry will be exposed to higher shear processes such as pumping. The aforementioned pump loop is, I would think, the best measure.

The on-board reaction of LiH with water, as we know, is exothermic. Twenty-eight percent of the energy is converted to heat, captured as heat of water vaporization. The water is recondensed. About 99% of the hydrogen is available for use.

Thermo Technologies generally run their hydrolysis reaction in " a little" excess water. Their byproduct is generally removed as about one mole of LiOH with 3.3 moles of water.

Since the reaction of LiH with water is a one mole with one mole reaction, the fact that 3.3 moles of water remains indicates there is more than "a little" excess water. Perhaps this is due to too much protection of the hydride by the mineral oil. If this excess is carried over into commercial systems it represents a large unwanted weight penalty on-board.

If we carry the analysis a little further: There is also some mineral oil present. If the original LiH slurry is 60% LiH by weight, there is about 5.33 grams of mineral oil for *each 8 grams (one mole) of LiH. Since the mineral oil doesn't go away, the waste product will contain 5.33 grams of mineral oil for each mole (24 grams) of LiOH, and 3.3 moles (59.4 grams) of water. Thus the LiOH will need to be separated out of a mix that is 27% by weight LiOH, 6% by weight mineral oil, and 67% by weight water.*

Mr. McClaine spoke of removing LiOH from the oil and water by vacuum distillation, centrifuging, or filtration. The cost of the separation process has been factored into the regeneration cost. The assumption is that the material will be transported to the central plant for separation prior to regeneration. *We already spoke of the need to include transportation costs to the overall economics. We see now, however, that these costs will be additionally burdened by the fact that the shipped material will weigh nearly four times that of LiOH alone. (LiOH being an estimated 27% of the total byproduct weight)*

Thermo Technologies is considering looking at magnesium slurries because magnesium byproducts are much more benign. Mr. McClaine mentioned that the Mg system might be more useful for stationary rather than vehicular systems.

MgH_2 is only 7.7% hydrogen by weight, while LiH is 12.5%. This is not as serious an issue for stationary systems, where space constraints are usually not as important. The fact that Thermo Technologies is looking at alternative systems is encouraging in that they are aware of the consequences of losing lithium, but at the same time raises the concern that they may not be confident in their ability to recycle all the lithium.

Thermo Technologies is considering attempting a demonstration of a process in which hydrides would be used as off-board hydrogen generation devices. Mr. McClaine feels that they could generate high-pressure hydrogen that could be used to fill on-board hydrogen cylinders more inexpensively than a steam methane reforming and compression process.

I would think that the hydrogen head pressure would slow the hydrogen generation reaction considerably.

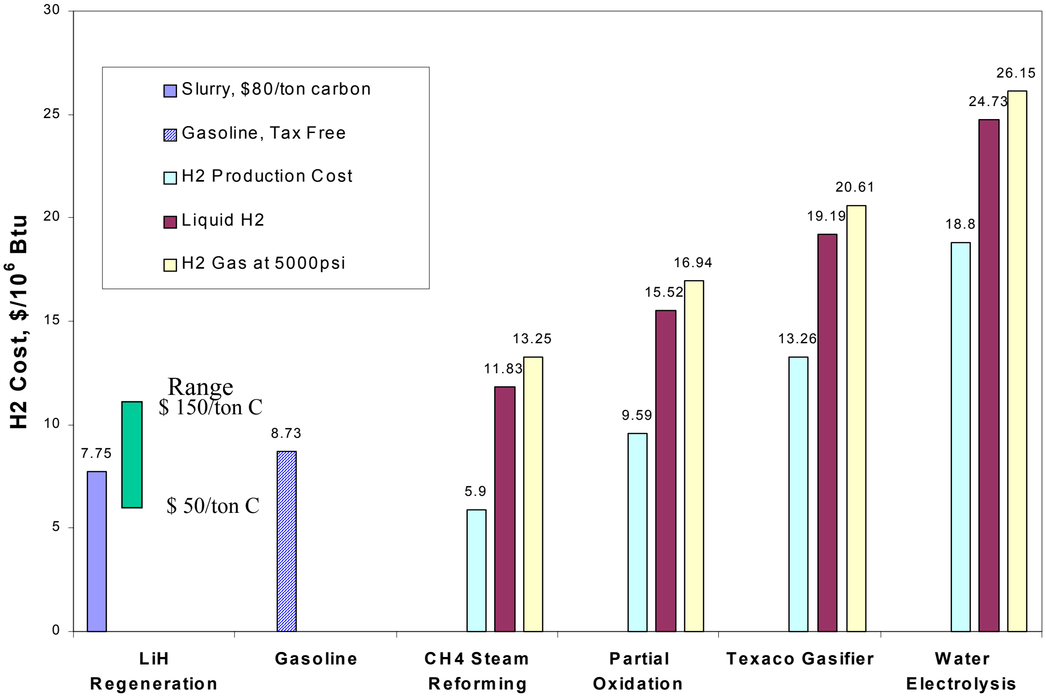
References**:**

[1] Peters, M.S. and K.D. Timmerhaus*, Plant Design and Economics for Chemical Engineers, 4th Edition*" McGraw-Hill, (1991)

[2] Ulrich, G.D. *A Guide to Chemical Engineering Process Design and Economics*, Wiley, (1984)

[3] Skolnik, E.G., J. P. DiPietro, and Z. U. Haq, "Technical Assessment and Analysis of Hydrogen R&D Projects" in *Proceedings of the 1999 US DOE Hydrogen Program Review, NREL/CP-570-26938* (1999)
(Available at http://www.eren.doe.gov/hydrogen/docs/26938toc.html)

Exhibit 1. Hydrogen Cost Comparison for various production methods, Hydrogen cost is shown as produced as a liquid and as a compressed gas at 5,000 psi.



Technical Evaluation Report
Project: The Use of Fullerenes to Store Hydrogen
Company: Oak Ridge National Laboratory (ORNL), Oak Ridge, TN
P.I.: Dr. Fang Chen
and
Company: Material and Electrochemical Research Corporation (MER), Tucson, AZ
P.I.: Dr. Raouf Loutfy
Dates of Visits: February 25, 1998 (Dr. Chen in Washington, DC)
August 14, 1998 (Dr. Loutfy in Tucson, AZ)
Evaluation by: Edward G. Skolnik, Energetics Inc.

A Meeting with Dr. Chen

I Introduction:

The use of fullerenes, primarily C_{60} structures, as a means to store hydrogen is being studied by a team from Oak Ridge National Laboratory (ORNL) and Material and Electrochemical Research Corporation (MER). On February 25, I met in Washington with **Dr. Fang Chen**, the ORNL Principal Investigator, and spent about an hour with him discussing this project. During this February meeting, we held a preliminary discussion and I saw some small samples of fullerene powders and pellets, both with and without associated hydrogen. We also planned for a more formal meeting at MER later in the year.

II Fullerene and Hydrogenated Fullerene Appearance/Description:

Dr. Chen carried with him, fullerenes as a bulk powder, as a pellet, and deposited in a thin film on aluminum foil. He is especially excited about the thin film version, as he envisions a lightweight heat-transfer system. Although no cost of fullerene production has been offered, Dr. Chen indicated that MER believes that it can be made "inexpensively" in volume in an arc furnace. (They use a process similar to what Dr. Smalley of Rice University uses.) The bulk density of fullerene powders is about 1 gram/cc.

Hydrogenated fullerenes take on distinctive coloration, said to be as a result of light scattering. Dr. Chen had samples of stable hydrogenated fullerenes in powder form. A sample that was approximately 3 percent by weight hydrogen had an orange color, while a 4 percent hydrogen sample was an olive green. This phenomenon, its reproducibility, and possible uses is something that we will need to discuss with MER.

III Discussion:

Hydrogenation and Dehydrogenation Process:

The hydrogenate is relatively easy to make, and is quite stable. Without a catalyst it requires about $400^{\circ}C$ or more, and 4,000-5,000 psi to produce. It is stabilized by cooling and depressurizing. Using a catalyst reduces the required temperature and pressure considerably. Dr. Chen indicated that pressures would be in the 500 psi region and temperatures would vary depending on the catalyst, but would probably be closer to 200°C.

The need for catalysis for dehydrogenation is greater, as the uncatalyzed dehydrogenation reaction requires 160 kJ/mole, as opposed to 100 kJ/mole for the hydrogenation reaction. The currently ongoing work involves the finding/developing of the proper catalyst. The research team has been looking at solid, liquid and solution catalysts. This would be yet another subject of discussion during the visit to MER.

Theoretical Hydrogenation Limits:

The limiting factor as to what amount of hydrogen can be associated with a quantity of fullerene is unclear. If one hydrogen were chemically associated with each carbon, that is, $C_{60}H_{60}$, the theoretical limit would be 7.7 percent by weight hydrogen. However, it is unclear, according to Dr. Chen, whether the association between the carbon and hydrogen is chemical or physical.

I believe that a clue as to the answer to this may come from the kinetic expression that is associated with the dehydrogenation step. According to Dr. Chen, the rate of dehydrogenation of the uncatalyzed, hydrogenated fullerene obeys the equation:

$$Rate = A\ (C/C_{max})\ e^{-E/\kappa T} \qquad (1)$$

where C is the hydrogen concentration in the fullerene and C_{max} *is its maximum concentration, A is the Arrhenius pre-exponential factor, E is the activation energy, κ is the molecular gas constant, and T is temperature. Since the rate of a chemical reaction, (dr/dt) is a function of the reactant concentrations and a rate constant, the rate of a reaction*

$$aA + bB + \ldots nN \rightarrow Products \qquad (2)$$

can be expressed as:

$$(dr/dt) = Rate = k\ [C_A]^a [C_B]^b \ldots [C_N]^n \qquad (3)$$

where k is the rate constant and C represents the concentration of the species in question.

The Arrhenius expression for the rate constant, k, can be expressed as a function of temperature by:

$$k = A\ e^{-E/\kappa T} \qquad (4)$$

Therefore, the expression for the dehydrogenation process can be expressed as:

$$Rate = k\ (C/C_{max}) \qquad (5)$$

This is the form of a first-order reaction, dependent only on the concentration of C, in this case, the concentration of hydrogen. This would indicate that since the reaction rate is not dependent on the rate of concentration of the fullerene hydrogenate, that the fullerene hydrogenate is not a chemical species, but that the hydrogen is physically held within the fullerene structure. At least, it indicates that the rate-determining step is the physical removal of hydrogen from the matrix. This means that the theoretical chemical limit to the degree of hydrogenation may not be the actual limit.

IV Interim Conclusion:

The project appears viable at this stage, especially if 6-7 percent hydrogen is a reality. I hope to learn a lot more later on when I visit MER (see below). While I developed an understanding of the thermal management calculations involved, I think that I will learn more as to what is going on chemically at MER. I'll also get a better feel for the degree of difficulty of making fullerenes in these forms.

The path that ORNL/MER is taking now – getting a catalyst that will lower dehydrogenation temperature seems sound. Their initial efforts indicating that liquid or solution catalysis is preferred, again makes sense from the approach of addressing reactant/catalyst contact.

B Trip to MER

I Summary:

Of the three projects that are referred to as "carbon structure" storage projects, the one being conducted by the team of Oak Ridge National Laboratory (ORNL) and Materials and Electrochemicals Research Corporation (MER) is by far the furthest along. They are at least at the several kilogram level in producing their storage material, fullerenes, and have demonstrated close to theoretical hydrogen take-up levels. On the other hand, theirs is the only carbon structure that definitely requires both heat and pressure to "move" hydrogen. Because of this, the ORNL/MER team has added a new element to their project. They are now looking at not only fullerenes but at "organic hydrocarbon" hydrogen storage as well.

This group is probably closer to a "real" system that meets DOE goals than any other with the exception possibly of U Hawaii's work. It provides higher storage loadings than the metal hydrides, and is farther along in terms of scale-up than the other carbon structure work.

Project Strengths:

- The thermal management approach appears to be very sound. Much of what ORNL predicted when running the thermodynamics and kinetics of the fullerene processes appears to have been proven in experiment.

- MER, as an expert in carbon structures appears a good choice as a CRADA partner.

- The already achieved storage numbers of over six percent by weight hydrogen (non-system base) and over 90 kg/m^3 on a volumetric basis (based on a stated material bulk density of 1.5 g/cc for pelletized fullerene) meets the DOE goal.

- The group may not have much farther to go in reducing the temperature, especially if higher temperature PEM fuel cells become available.

Issues that should be Addressed:

- The effort is now being split to include a very different system. Can both the fullerene system and the new organic hydrocarbon system be pursued to the necessary level without diluting the effort?

- In what way does the hydrocarbon system differ from work being done elsewhere? (such as the University of Hawaii). MER's expertise is in fullerenes. This is not a fullerene system.

- What will the effective degree of hydrogenation be for either the fullerene system or the new system? If each hydrogen atom comes out progressively more slowly, it may be too difficult or too costly to get sufficient hydrogen out. System thermodynamics/kinetics need to be matched up with the needs of a practical system.

- The practical system needs to be mapped out. (Actually two systems, the fullerene and the organic hydride) How would it look on a vehicle?

- There was, initially, some misconception as to the state of hydrogen in the storage system. ORNL reported several times that the rate of the uncatalyzed dehydrogenation process was proportional to the "concentration of hydrogen in the fullerene." I interpreted that to mean that hydrogen was entrapped in the fullerene by a physical process, and was told at first, that the storage could very well be physical. In actuality, the storage is chemical, and the relationship is with the number of hydrogen atoms in the molecule $C_{60}H_x$. In the meeting at MER, it was made definitively clear that the species was chemical; there was no question.

II Introduction and Background:

I met with **Dr. Raouf Loutfy**, the President of MER, on August 14th at his facility in Tucson, AZ. Also present at the meeting were **Rick Murphy** and **Jim Wang** of Dr. Chen's staff at ORNL

MER has a CRADA with ORNL in which MER is responsible for the production and hydrogenation of fullerenes, while ORNL is responsible for the thermal management activities. Thus, ORNL determines and tests the conditions under which fullerenes can best be hydrogenated and dehydrogenated, while MER produces the materials and runs the experiments.

MER, established in 1985, has historically been involved with fullerenes due to its proximity to the University of Arizona. Although fullerene production methodology was invented by Professor Smalley of Rice University, it was the University of Arizona that brought fullerene production into practice; they have the license. MER is the world leader in fullerene production. Among its other interests are carbon/carbon composites, and fuel cells.

<u>III Discussion-Fullerenes:</u>

<u>Production of Fullerenes:</u>

MER basically uses the Smalley method to produce fullerenes; that is, they use an arc furnace to vaporize carbon rods. Their bench-scale facility can produce about 0.5 kg/day of fullerenes by this method. Production of fullerenes includes the usage of thin carbon rods as the anodes for the arc discharge. The thinness of these rods and their lack of bulk lend them to vaporization and fullerene production. Thicker carbon electrodes would transfer too much of the arc-derived heat away from the surface, and make the process inefficient.

In the development of the methodology for scale up of this process, one must consider the fact that using bigger, thicker rods would lead to inefficiency. MER, however, has developed a proprietary process by which they maintain high efficiency. Dr. Loutfy estimates that the cost of producing fullerenes in the bench scale process is about \$12,000/kg. Using the scaled up (lab-scale/PDU) process that could produce up to 30 kg/day of fullerenes the cost would drop by a factor of about 100, to \$120/kg. This is still an intolerably high cost, but keep in mind, we are still talking about a PDU.

Dr. Loutfy feels that to justify a scale-up to, say, pilot plant size, they probably need two or three applications for the fullerenes. Hydrogen storage would be one of the applications. MER revealed that there is another currently proprietary application being spearheaded by a Japanese chemical company. Consequently, they have sold a license to this company to promote this unnamed product in Japan. (MER would retain the rights in the U.S. and Europe.) About another order of magnitude decrease in the cost of fullerene production is needed to make the material competitive. Dr. Loutfy stated that a breakthrough will be needed for this to happen, and is looking for the Japanese to lead the way initially.

<u>Physical vs. Chemical Sorption of Hydrogen</u>:

In the earlier report, we discussed the possibility that the hydrogen take-up by fullerenes may be physical rather than chemical. We had brought this hypothesis forth based on an ORNL report that the dehydrogenation process rate expression obeyed the relationship:

$$\text{Rate} = A\,(C/C_{max})\,e^{-E/\kappa T} \qquad (1)$$

In which "The dimensionless factor (C/C_{max}) is intended to capture the trend that at a given time, the hydrogen escape rate is proportional to the amount of hydrogen present in the sample." Since the rate of a reaction cannot be dependent on its products, but only on its reactants, I concluded that the hydrogen/fullerene association must be physical, and the dehydration rate controlled by the diffusion of hydrogen out of the fullerenes. Dr. Loutfy now informs me that the factor (C/C_{max}) actually refers not to the hydrogen concentration, but to the value of "x" in the chemical species $C_{60}H_x$ – the fullerene hydride. In other words, the species is indeed chemical, and the rate of dehydrogenation is based on the concentration of the reactant in the reaction:

$$C_{60}H_x \rightarrow C_{60}H_{x-1} + \tfrac{1}{2}\,H_2 \qquad (6)$$

As the value of "x" decreases, the reaction slows. Thus, complete dehydrogenation is difficult. This may be the most serious consequence of the process. The ORNL/MER project is already hampered by hydrogenation/dehydrogenation temperature and pressure conditions. One would not wish to resort to yet higher temperature to squeeze out more hydrogen. At the same time, if you can't get the hydrogen out, it doesn't count.

Physical adsorption of hydrogen by fullerenes, in fact, according to Dr. Loutfy is limited to about 0.2% by weight. It takes about 2.5 electron volts (60 kcal) to penetrate the fullerene cage; Dr. Loutfy says that this is less than the energy of C-H bond formation. (Bond energy tables show the C-H bond energy to be 80 kcal.) Regardless, since the kinetics follow reaction #2, it has to be chemical. Thus, the species is chemical, and therefore, an organic hydride. Thus, the chemical saturation of $C_{60}H_{60}$ is valid, and the theoretical hydrogen concentration (exclusive of system) is 7.7% by weight.

Fullerene Hydride Make-up and Appearance:

As we mentioned above when reporting on our conversation with Dr. Chen, fullerene hydrides can be pelletized without any loss of structure. At that time, Dr. Chen reported a bulk density of about 1.0 g/cc. Dr. Loutfy now reports that they have achieved bulk densities of up to 1.5 g/cc. We also noted that fullerene hydrides take on various colors, depending on the hydrogen concentration. This has been explained as having to do with the fact that as the amount of hydrogen in the fullerene increases, the material becomes more paraffin-like in nature. $C_{60}H_{60}$ as a cage structure would be a paraffin – no double bonds, saturated in hydrogen. The typical high molecular weight paraffin is white in color, and as the fullerene hydride adds hydrogen, it becomes lighter in color. A reasonable argument, and one that also would have been good to have earlier when we were considering the system to be a physical adsorption system.

Hydrogenation and Dehydrogenation of a Fullerene:

The major problem facing this project is the fact that currently it still takes too much heat and too much pressure to hydrogenate and dehydrogenate a fullerene. As reported earlier, without a catalyst it takes about 4000-5000 psi at 400°C to hydrogenate fullerene, but one can essentially reduce the pressure by an order of magnitude, and reduce the temperature into the 200°C range by using a catalyst. A key factor with using a catalyst for hydrogenation and especially dehydrogenation is in the degree of contact between the fullerene and the catalyst. Most early-on results involving catalysts involved solid catalysts and solid-solid contact. Later, MER dissolved the catalyst in a proprietary solvent to promote better contact. This provided a medium in which hydrogen atoms can better be transported, thus reducing the activation energy for the process.

IV Discussion-Liquid Systems:

The success that ORNL/MER has had with the concept of improved contact has led them to investigate new all-liquid systems. In other words, these are systems that no longer contain fullerene(!) Using a proprietary material that they simply refer to as Organic Hydride #1 (or OrgHyd1) and a new, proprietary liquid catalyst system, MER is currently achieving up to 7% by weight hydrogen under 350-400 psi at 180°C. Dr. Loutfy indicated that they could currently recover up to 75% of the hydrogen. The activation energy for the dehydration step with this system is only half of what it was for the fullerene system (84 kJ/mole vs. 160 kJ/mole). Dr. Loutfy described OrgHyd1 as a "very low cost feedstock," and one that would require a system volume only about ten percent more than gasoline.

The new system has the thermal advantage over fullerenes, but may suffer in other respects. For instance, how easy is it to separate hydrogen from the liquid system. Two problems; i) is hydrogen at all soluble in the organic material and ii) how easy is it to separate the gaseous hydrogen from the organic vapor? Of course, these two problems are also potential problems with the solvent systems for the fullerene catalysts.

V Other Topics:

Nanotubes:

On a different topic, Dr. Loutfy mentioned that MER has made some nanotubes for Mike Heben (NREL) using the carbon arc-discharge method. In a two-hour period, they made about 30 grams of material of which about 20 percent was single-walled nanotubes (SWNT). They performed hydrogen adsorption tests with the material, and found that they were getting about 2.5% by weight hydrogen adsorption on a total material basis. Interestingly, they found that if they milled the material, breaking up the nanotubes, they actually somewhat increased the amount of hydrogen adsorption.

Still on the subject of nanotubes, Dr. Loutfy brought up the name of Mayya Papan. He is a theoretician at NASA Ames who has run some calculations on the use of SWNTs as storage media. He believes that SWNTs may close if heated. This may also be the case for the spacings between graphitic plates of nanofibers. Thus, this may become an issue for both the NREL and Northeastern nanostructure projects, especially, if one or both projects evolves into something that requires some heat to speed up the hydriding or dehydriding process.

Fuel Cells:

Among MER's other interests is the fuel cell business. Their expertise in carbon/carbon composites has led to their making bipolar plates of this material for PEM fuel cells. They are currently making 50-watt stacks under an Army contract for use by foot soldiers. The fuel cells have an energy density of 150 watts/kg. In addition, MER has a contract with DOE for fuel cells for buildings.

Technical Evaluation Report
Project: High Efficiency Stationary Hydrogen Storage
Company: Arthur D. Little, Inc. (ADL), Cambridge, MA
P.I.: Dr. Scott Hynek
Date of Visit: June 8, 1998
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

The work being carried out at Arthur D. Little (ADL) was originally based on the development of tailored phase change material (PCM) systems. There were touted for use as temperature controllers for the hydriding and dehydriding of magnesium for stationary hydrogen storage. It then evolved to the investigation of nickel coatings to enhance the hydriding kinetics, and then evolved further to the study of thin coatings that could be selectively penetrated by hydrogen. The application for this work has now become support of on-board hydrocarbon reforming. It appears that the driver behind this progression is ADL's thrust in on-board reforming. Apparently, ADL wants this research to support that thrust.

The PCM project seems to have more-or-less become a coatings study on its own. It appears, however, that the attempt to use magnesium nitride coatings (Mg_3N_2) as the hydrogen "filter" has not been successful, and that, if research continues, it will involve looking for a new coating candidate. Thus the direction of the research is going toward on-board reforming of liquid fuels, not toward the storage of hydrogen.

II Introduction and Background:

I met with **Dr. Scott Hynek** of ADL at their facility in Cambridge, MA. The purpose of the meeting was to learn about the hydrogen storage activities that are currently taking place at ADL and to determine how these activities were progressing. Emphasis was placed on determining how they had evolved from ADL's work of the past few years. I had previously sent Dr. Hynek a list of questions that I wished to discuss as part of our meeting, and asked for a demonstration as well.

Dr. Hynek's current project involves the identification/development of surface coatings for magnesium that will selectively admit hydrogen from a mixture of hydrocarbon reformer product. Thus, the coated magnesium serves as both a purifier and storage (as hydride) medium for hydrogen. Dr. Hynek suggested that the system was being developed to enable on-board reforming. Recall that, earlier, Dr. Hynek had been looking at stationary storage systems, where a PCM made up of a mixture of metallic salts was used to control the hydriding and dehydriding of a magnesium-based storage system.

During the meeting, we discussed the project(s) at length and covered all of the questions. A copy of the questions is attached, but the answers are included in their appropriate places in the following discussion. I also saw the system used for hydriding the magnesium, although I was not given an actual demonstration. The discussion topics are characterized below.

III Questions and Answers:

Prior to our meeting, I forwarded a series of questions to Dr. Hynek. The questions and discussion based on them are shown here.

The PCM Project:

1. **What is the status of the phase change material project that you were involved with earlier? Were any data generated confirming the theory; how many cycles were possible?**

Dr. Hynek stated that the PCM project was successfully completed and that he had submitted a final report. According to Dr. Hynek, a phase change reactor was made that works. The system was very heavy however, and only applicable for stationary systems. (*Interestingly, it was for stationary systems that the project was geared in the first place.*) In addition, the PCM system chosen was very corrosive, especially at the temperatures needed to hydride magnesium. Therefore, it was necessary to use stainless steel vessels.

According to Dr. Hynek, however, the system was tested successfully, and run for a "few cycles". At this point, they ran out of funding, and the reactor was decommissioned. Due to this, they "never gave it the opportunity to break down." *I always had my doubts as to how many cycles a rather delicate balance could have been maintained for the relative concentrations of a three-component system that relied on fairly small temperature differences to drive the hydriding/dehydriding sequence.*

Nickel Coated Magnesium Powder:

The original PCM project evolved to focus on coatings of the hydride material. This was due to protect the magnesium, and to increase the kinetics of the hydriding reaction. Thus, the current project was supposedly "Stationary Storage and Purification of Hydrogen using Nickel Coated Magnesium Powder". Indeed, that was how the project started. While nickel coating did improve the kinetics, it was not impervious to impurities, and broke down.

2. **What would the magnesium hydride system weigh on a per kg H_2 basis? Is this compatible with on-board storage?**

When working with the nickel coated magnesium powder (NCMP), the ADL group was able to obtain about six percent hydrogen on a hydride-only basis. Dr. Hynek indicated that in addition to the container, the only additional system weight would be some tubing and a check-valve. Dr. Hynek indicated that he thought this system was too heavy for conventional, primary storage, but it might be compatible with buffer storage. (*See discussion below on their current surface work.*)

3. How effective were NCMPs in storing/regenerating already purified hydrogen, simulating electrolyzer-produced hydrogen?

The dehydriding temperature of the system is 300-350^{o}C. Thus, NCMP was very effective in storing and regenerating already purified hydrogen, and even worked well with commercial grade hydrogen. It just doesn't work with reformate, and that right now is the ADL direction of choice.

4. During your recent annual review presentation, you spoke of magnesium nitride coatings. Are these in place of NCMPs or are you still looking at the nickel coatings also?

The work on NCMP is not being pursued. The title of the annual review presentation addresses NCMP only because this was the original title of the project. The only work currently going on involves thin coatings for selective penetration by hydrogen.

The Current Surface Treatment Project:

The project that is currently being undertaken by ADL involves the use of Mg_3N_2 as a coating for magnesium particles. The goal was to develop or identify surface materials that would selectively pass hydrogen. This would allow the use of on-board hydrocarbon reformers to be used, and result in sufficiently pure hydrogen being passed to the fuel cell.

The thinking was that if any coating can be made thin enough, it will selectively pass hydrogen. Magnesium nitride was chosen because, since it is a salt of magnesium, it would more likely adhere to magnesium. In addition, the nitride can be made in an inexpensive process by reacting magnesium with ammonia. At the right temperature, the reaction is self-limiting, so the coating will be thin.

5. When being used on-board in conjunction with an on-board reformer, is the intention for the system to be used only during the period of time that the reformer is warming up?

Dr. Hynek believes that a potential application may be to use the coated hydride to provide buffer storage, i.e. use the hydride to provide hydrogen to the fuel cell until the reformer is hot enough to begin producing its own hydrogen. Additionally, it could be used to provide peaking power for hill climbing. It could be a fairly simple system, utilizing a pressure regulator and a check valve.

6. Do you envision NCMP as a purification system, a storage system or both? Is it exclusively an on-board system, or would it have an application for, say, a replacement for PSA or membrane purification systems on a stationary reformer?

It could conceivably take the place of a PSA system. It might also reduce a pre-compression step. The temperatures would be about right for this type of an application.

7. You have spoken of the "temperatures of interest" for the hydride system to be 300-400^{o}C. The DOE program is looking for hydride storage systems operating in the 150^{o}C range to be more compatible with PEM fuel cells. How does this particular system fit in?

The 300-400^{o}C "temperatures of interest" is not compatible with either the operating conditions of the PEM fuel cell, nor is it near the DOE storage temperature goal. There are two answers: first, a cooling system will be needed anyway to handle the reformate. Secondly, since this will be a buffer system, rather than a primary storage system, the issue is not as important. *While it is true that a buffer system is not going to have the capacity of a primary storage system, the question remains: why have the cooling problem at all? Why not look at a lower temperature system? The answer is, I think, that they are committed totally to the on-board reformer concept – a concept that is much more compatible with the higher temperature storage system.*

Dr. Hynek indicated that the magnesium nitride coating was not as robust as expected, and only lasted a couple of months. He believes, however, that recoating can easily be accomplished. Perhaps also, ammonia can be left in the vapor phase above the hydride for continuous regeneration. *Recoating every couple of months seems excessive. An ammonia atmosphere permanently set over the hydride seems like it would lead to a complex separation process. Would you need a second infrastructure to keep an ammonia supply available?*

8. Are there any plans to address coatings for hydriding materials other than magnesium?

Nickel is not a candidate coating for a reformate purification process, although during our conversation, Dr. Hynek came upon the thought that a Ni/Mg nitride might be a good coating candidate. It might be better kinetically than the straight magnesium nitride. The nitride coating is not as good kinetically as was the NCMPs. With the nitride system, Dr. Hynek has been using platinum as a dissociation catalyst, and concedes that he may need a platinum washcoat.

Dr. Hynek believes, however, that the answer lies with a different coating material, and that's the direction in which he'd like to see the research go. He indicated that they have a couple more coatings to look at. Their identity is proprietary, however.

<u>IV Tour:</u>

The hydride facility is a stand-alone 6 x 15-foot structure. A bank of six hydrogen tanks attached to a manifold stand outside the building. Inside the building, the reactor consists of six test vessels each containing coated hydrides. Each vessel has its separate heating system, and is equipped with thermocouples and pressure transducers. A data logger records pressure and temperature for each vessel. Current hydriding conditions are two hours at 300 to 350°C.

Using a new gas manifold, each test vessel can be filled with a variety of gas mixtures (to simulate reformate feeds) consisting of hydrogen, CO, CO_2, and steam. Previously, the same vessels were used to apply the coating to the magnesium powder. Chemical vapor deposition (CVD) was used to form the nitride coating from ammonia:

$$2\ NH_3 + 3\ Mg \rightarrow Mg_3N_2 + 3\ H_2 \qquad [1]$$

This reaction is self-limiting, with the formation of a thin, complete coat. Dr. Hynek indicated that the new, proprietary coatings might require a "fancier" mode of application.

In the previous work, NCMP were produced by a CVD process using a nickel carbonyl [$Ni(CO)_5$] precursor. This was not a pleasant material to work with.

V Additional Issues:

ADL is looking at on board reforming as a major thrust. They would "not be happy" with a project that emphasized on-board hydrogen storage. Therefore, Dr. Hynek is looking at options that will support on-board reforming. ADL does not see hydride storage upon a vehicle as practical because it is too heavy.

The ADL view is somewhat infrastructure based. The thought is that if a refueling station is built, it should mirror the on-board system. If the on-board system is metal hydride, there should be stationary metal hydrides in the refueling station. If you have a liquid infrastructure, the on-board hydrogen source should also be liquid.

Right now, there are no plans to investigate non-magnesium storage systems. Magnesium was chosen for its low cost, and high storage capacity. (Recall that the original application for the PCM-based system was stationary storage, and that the current thrust is on-board reforming. The magnesium system is more compatible with both applications than it is with on-board hydrogen storage for PEM fuel cells.) Dr. Hynek did concede that maybe it would be worthwhile to look at other, lower temperature hydrides even if their capacity is not as great, especially if you are just looking at a small buffer system.

This page intentionally left blank.

Technical Evaluation Report
Project: Hydrogen Storage Development
Company: Sandia National Laboratories, Livermore, CA
P.I.: Dr. George Thomas
Date of Visit: September 17, 1998
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

Sandia National Laboratories (SNL) in Livermore, CA is probably the premiere metal hydride laboratory for the DOE Hydrogen Program. The expertise of **Dr. George Thomas** and his staff, the extensive diagnostic equipment resource, and the tie-in with the combustion and systems side of the house (led by **Dr. Jay Keller**) presents a formidable package for the Program. Dr. Thomas is leading a hydride storage effort that covers development and evaluation of metal hydride materials, development of hydride container systems (hydride beds), and integration of hydride storage into systems. The metal hydride materials effort has primarily been based on magnesium systems, but has recently grown to include alanates (materials of the form $X(AlH_4)_y$) and similar systems. A series of six modular hydride beds have been produced. They were originally intended for use on the Palm Desert vehicles, but when those plans changed, they remained at SNL, and are awaiting a home. In the systems integration area, SNL leans on systems engineering as a means to make hydrides an integral part of a process. Thus, hydride materials, beds and operating labor are all part of an equation. SNL is also heavily involved in the coordination of the Remote Application Power Program (RAPP).

The work being performed by Dr. Thomas' group is mainstream to the program. Key strengths include Dr. Thomas' overall knowledge of hydride chemistry, the vertical nature of the SNL approach (hydride materials, hydride beds, systems), the interaction of Dr. Thomas with Dr. Keller, and the understanding of what the limits are with a hydride system.

It appears to me that Dr. Thomas, similarly to the group at ECD, has basically written off magnesium systems for wide scope usage. It appears that the combination of low temperature and high energy density will not be reachable with these systems.

The collaboration with Craig Jensen in Hawaii on alanate systems likely will (and should) take up a large part of the SNL research effort. While some magnesium work will continue, it likely will be strongly geared toward applications. Dr. Thomas states that there is much to be done with storage systems rather than hydride chemistry.

II Introduction and Background:

On the above date, I visited Dr. Thomas at his laboratory at SNL The purpose of the meeting was, as usual to gather information through discussions and a tour, that would help in my assessment of the technology in question. In addition, given Dr. Thomas' overall expertise in storage technologies, a discussion on the overall package of hydrogen storage activities was held. **Steve Guthrie**, who is on Dr. Thomas' team, and Jay Keller who acts as Program Manager for the SNL hydrogen work, and who also leads SNL's remote power and combustion efforts in hydrogen, were also present for large fractions of the day.

During the day, we primarily discussed the magnesuium hydride systems, the collaboration with the University of Hawaii on the relatively new alanate storage systems, and the status of the hydride bed modules that SNL constructed earlier. We also spent some time discussing SNL's role in RAPP. I also was given a tour of many of the facilities of the Materials and Engineering Science Center, focusing primarily on surface analytical capabilities. Finally, I was able to pulse Dr. Thomas on his opinion of various storage technologies and the associated ongoing projects.

Dr. Thomas' laboratory was exceedingly active on the day of my visit. Representatives from Plug Power and the University of Alaska, Fairbanks were present, setting up for some quick-turn-around reformer/fuel cell assembly and testing that needed to be completed by the end of the fiscal year as part of RAPP.

III Discussion:

Magnesium-based Systems:

Dr. Thomas' team have been working on magnesium based hydride storage systems for the past several years. Dr. Thomas feels at this time that these type of systems will probably not exceed about 3.5% by weight hydrogen (material weight) at any temperature approaching PEM applicability. Maybe 120^{o}C can be achieved at this weight percentage. For this reason, the SNL team is quite excited about their relatively new undertaking in conjunction with Craig Jensen's laboratory at U Hawaii on alanates and related substances.

As to the magnesium systems themselves, Dr. Thomas is specifically addressing Mg/Zn/Al systems. He is using a new ball mill/melt process to get higher plateau pressures. You need a higher pressure at a particular temperature. Dr. Thomas' goal is to be able to produce the so-called "R" phase of the Mg/Zn/Al system with consistency. The R phase has a higher hydrogen capacity than the alternative configurations.

Aluminum-based (and Analogous) Systems:

Alanates [*a rather strange name in my opinion; it implies the presence of oxygen*] and similar compounds provide an opportunity for reasonably high hydrogen loading. The base compound, $NaAlH_4$, contains 7.4% hydrogen by weight; the analog $LiAlH_4$, contains 9.8% hydrogen. The collaboration with Jensen's group originated with the finding by Bogdanovic that alanates can be hydrided reversibly in the presence of appropriate catalysts:

$$X(AlH_4)_y \leftrightarrows XH_y + Al + (3/2)y\, H_2 \quad [1]$$

"X" can be Na, Li, Mg or Zr. Zirconium particularly may be interesting as the reaction may occur at or near room temperature. Dr. Thomas stated that the analogous boronate (using the same type of nomenclature) systems, which would provide the potential for higher hydrogen loadings (boron has an atomic weight of 11 versus 28 for aluminum) are probably not reversible. Depending on the level of use, $NaAlH_4$ could either be purchased, or produced from Na/Al mixtures in a hydrogen atmosphere. If X were something other than Na, it would probably be difficult to purchase.

Reaction [1] is actually composed of two steps. Using $NaAlH_4$ as an example:

$$NaAlH_4 \leftrightarrows (1/3)\, Na_3AlH_6 + (2/3)\, Al + H_2 \quad [2]$$

$$(1/3)\, Na_3AlH_6 \leftrightarrows NaH + (1/3)\, Al + ½\, H_2 \quad [3]$$

Reaction [2] might require high pressure to recycle the hydride – perhaps about 1500 psi, but Reaction [3] would appear to lend itself to low pressure low temperature operation.

Current work is focused on determining optimum catalytic systems for the hydriding/dehydriding cycle. These materials do not appear to degrade during recycling. The key to these systems, according to Dr. Thomas, is fabrication and synthesis.

Storage Modules, RAPP, and Other Projects:

SNL is sensitive to "useless demonstrations". Thus, they are holding on to their six hydride bed modules for the time being. They were, at one time going to be used on the Palm Desert project, but now they believe that other storage systems may have better applicability for Palm Desert. Thus, the modules (or 5 of the 6, at least) are sitting on a test stand in one of the laboratories, waiting for an application. Dr. Thomas mentioned wheelchairs as possibly being appropriate if the right scenario could be found.

Dr. Thomas is sensitive about an apparent misconception as to the speed of filling hydride systems. He mentioned that he believes that DOE has been stating that metal systems are hydrided slowly, making this one of the disadvantages of this type of storage system. The existing modules can be filled in six minutes by adding hydrogen in short bursts and using a cooling line.

As previously mentioned, my visit coincided with a rush of activity concerning SNL's role in the RAPP Program. As my visit occurred about two weeks before the end of the fiscal year, SNL was busy trying to test/demonstrate operational fuel cells by the end of the month. The plan is for three competitive 3.5-5 kW reformer/ PEM fuel cell systems, probably with hydride storage. The concept being addressed is: home-level distributed power generation, with, perhaps, the reformer built oversized to provide heat as well. The fuel of choice (or more accurately, of necessity) is diesel.

The hydrogen people at SNL are interested in systems. All that they do with hydrides must ultimately lead to making storage devices that are part of an integrated system. Their approach is thus tied strongly to systems engineering analysis. Dr. Thomas believes that it is on storage systems, rather than hydride chemistry, that the work must focus. For instance, successful hydride storage systems must use inexpensive hydride materials, inexpensive hydride bed materials, and low manufacturing costs.

IV Tour:

SNL, as one would expect, has a vast array of analytical tools at their disposal. I was given a tour of some of the facilities within the Materials and Engineering Science Center, focusing on the equipment that is applicable for hydride work. The Center has several scanning and transmission electron microscopes (SEMs and TEMs) including a hot filament SEM, a field emission SEM and a field emission TEM. (Field emission systems produce very high electric fields resulting in high resolution micrographs), and an electron microprobe. The group is thus able to obtain both morphological and elemental compositions. Other techniques used by Dr. Thomas' team includes: Inductively Coupled Plasma Mass Spectrometry (ICP-MS) x-ray tomography, laser ablation and x-ray defraction (to identify phase).

Standard hydriding tests are performed with a pressure/composition/temperature (PCT) manifold in the hydride R&D lab. Kinetics experiments done on the system tie in with microstructure analysis. Since much of the understanding of hydride systems is surface-oriented, SNL also employs x-ray photoelectron spectroscopy (XPS) and Auger Spectroscopy to characterize the chemistry of the material surfaces for both the hydriding and dehydriding processes.

During the tour, I was also shown and allowed to operate a model remote-controlled car, which was powered by an H-Power provided fuel cell and included hydride storage.

V The Overall Hydrogen Storage Program:

Following the "formal" part of the meeting, Dr. Thomas and I reviewed the overall hydrogen storage component of the DOE hydrogen program. Given the importance of hydrogen storage in the overall program, Dr. Thomas feels first and foremost that there is not nearly enough money being spent to enable the necessary ventures into new research. The program, however, needs to ensure that the projects being supported are enabling technologies. Specifically, Dr. Thomas feels that there is not enough being done in the area of non-vehicular storage. The increase in prominence of distributed utilities make them a good candidate for stationary hydride storage systems.

There is a key need to lower the costs of metal hydride systems. Currently, the "AB" hydride systems (e.g., Mg_2Ni) cost about \$20/kg. This needs to be lowered to the \$5/kg range.

One interesting comment made by Dr. Thomas is that he does not consider projects where hydrides are reacted with water such as the Thermo Power Corp (TPC) process to be a storage process because the hydriding is not reversible. He believes it should be moved to the production side. *This is not a trivial argument, since the Program weighs production dollars vs. storage dollars. I agree that the TPC project does not represent classical, reversible hydride technology. However, it includes (if successful) a remote regeneration process. More important is the fact that its purpose is to provide an on-board source of hydrogen. It provides a material on-board that undergoes a chemical reaction to ultimately power a vehicle. In this manner, it is much like a tank of gasoline. Thus, I believe that the storage section is appropriate for the TPC project*.

This page intentionally left blank.

Technical Evaluation Report
Project: Vehicular Hydrogen Storage Using Cryogenic Hydrogen
Company: Lawrence Livermore National Laboratory, Livermore, CA
P.I.: Dr. Salvador Aceves
Date of Visit: September 22, 1999
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

The pressurized cryogenic hydrogen storage tank project being carried out by Lawrence Livermore National Laboratory (LLNL) under the direction of **Dr. Salvador Aceves** is one of the group of storage projects that is of great importance to the eventual utilization of on-board hydrogen as a fuel cell feedstock. It provides the potential of a relatively inexpensive, long-range storage option. Nevertheless many technical, safety (both real and perceived) economic, and logistical hurdles need to be addressed.

The concept, briefly, involves the development of an on-board hydrogen storage tank that is strong enough to hold over 3,000 psi of compressed hydrogen, and is also sufficiently insulated to hold liquid hydrogen with only minimal evaporation. In this way, if one is traveling short distances, one can use the less expensive compressed hydrogen. However, if one requires a longer range, one can switch to the more costly, but more compact liquid hydrogen.

The LLNL group has conducted extensive techno-economic analyses on the concept, identified tank and insulation materials, constructed prototype tanks, and cycled (pressure and temperature) and burst-tested the tanks. Pressure cycling is performed with pressures up to 3,500 psi. Helium is used as the cycling gas. Most of the temperature testing has been done at liquid nitrogen temperatures (77^{o}K) due to safety considerations in using liquid hydrogen. At the time of my visit, Dr. Aceves and his team had recently completed their first cycling test with liquid hydrogen. In order to perform this test, the participants had to go to a remote testing area, far removed from the laboratory, and had to spend 2 or 3 days virtually locked in a bunker.

Project Strengths:

- An effort to make a single system that can be both a low cost hydrogen storage strategy for a “commuter” vehicle and a high capacity hydrogen storage strategy for long trips is technically a good one.
- The group is making significant progress using virtually “off-the-shelf” technology.
- Much of the testing that has been performed to date (temperature cycling, pressure cycling, burst testing) has been successful.

- The tank has been shown to never totally lose its supply of liquid hydrogen as a conventional liquid hydrogen tank would. Due to its insulation, there will always be hydrogen present on which to run the vehicle.

Issues that should be Addressed:

- There needs to be more thought put to scenarios where a user of a vehicle equipped with one of these tanks would switch back and forth between gaseous and liquid hydrogen.

- Testing with hydrogen has just started, and is apparently difficult to do at LLNL from a permitting standpoint. If the difficulty persists it could unduly stretch out the project. In addition, it leads to a public perception that hydrogen is a uniquely dangerous material.

- Since hydrogen testing is just now starting, much of the designing to date has been based on extrapolation from liquid nitrogen temperatures. While the colder temperature of liquid hydrogen points to only a slight contraction of the case material, and less off-gassing of the fibers, testing under real conditions are needed.

- A better dissemination of information is needed. For instance, referring to the insulation overwrap as “multi-layer vacuum super insulation” without any further explanation, is insufficient at best.

- Better bond data (or a better bond) is apparently necessary for the fiber/epoxy composite. We were told that it “fails somewhat” within the composite – not at the composite to aluminum interface. We were also told that the internal pressure presses everything together.

Overall, I think that this is a good project, but it needs a better understanding of what the potential market actually will be. Using two fuels (gaseous and liquid hydrogen) for two ranges sounds good in theory, but how applicable is it on a large scale? Some real world scenarios need to be addressed.

II Introduction and Background:

I met with Dr. Salvador Aceves at his laboratory at Lawrence Livermore National Laboratory to discuss his project. Dr. Aceves made a presentation that was updated from his Annual Review Presentation. We discussed the project in detail including a series of questions that I had forwarded to Dr. Aceves prior to my visit. Dr. Aceves also showed me the facilities, samples of tank materials, and prototype tanks.

The project has been going on for several years, initially as an analytic study of methods to provide low-cost, long-range hydrogen storage. The current design emerged as the most promising. It couples the lightweight of pressure vessels with the smaller overall volume/higher storage density of cryogenic vessels. The storage system is based on the premise that a personal vehicle can serve two purposes: it can be a short-range commuter vehicle, and it can be a vehicle used for long distance travel. Thus, the storage system is designed to hold either high-pressure (3,500 psi) gaseous hydrogen for commutes, or liquid hydrogen for long distance travel. Since gaseous hydrogen is used only for short-range driving, the tank can be relatively small (alternatively, the extra design for an ultra-high pressure tank is avoided). Since expensive liquid hydrogen is only used when necessary for long rang driving, the cost is relatively low. In addition, the "super insulation" keeps evaporation low.

LLNL is partnered with Standard Composites Industries (SCI) of Pamona, CA. SCI is performing testing at no cost. Dr. Aceves mentioned that they are planning a demonstration of the tank in FY 2001. A possible site is Palm Desert.

III Tour:

The tour of the facilities was more-or-less routine. I saw prototype tanks, bare and insulated; I saw joints and fittings designed to facilitate the filling and emptying of the tank; I saw pressure test facilities and assemblies. I did not see the area where actual hydrogen testing was (had been) going on. This site was several miles away from the laboratory, and was not easily accessible.

I was shown a roll of (and given a small piece of) the "multi layer vacuum superinsulation." It more-or-less-resembles a papery aluminum foil. This is discussed below.

IV Questions and Answers:

I sent Dr. Aceves a set of discussion questions prior to my arrival. He responded in writing and we also discussed the questions and answers in detail.

1. **Please describe in terms of pressure and temperature cycles, the conditions under which the vessel would operate between "fill-ups." Consider situations in which the vehicle i) would make several short trips (maybe 20-30 km a day, back and forth to work) ii) would make a single long trip.**

"See [..Exhibit 1 ..] with the results of the run. Also see [..Exhibit 2...] with a plot of the temperature and pressure shown on a property diagram for hydrogen."

Exhibit 1 shows the appropriate pressure and temperature cycles and Exhibit 2 shows a plot of the state and density of hydrogen as a function of time for the same process. The data show a 95 liter cryotank filled with 5 kg of liquid hydrogen, driven 20 km per day. Each day's consumption is about 0.15 kg.

A couple of interesting points emerge. First of all, only the first part of the question was answered. Note that my question did not specify whether the hydrogen was gaseous or liquid. All of the previous reports on the system indicated that the tank would be filled with compressed, gaseous hydrogen for short daily commutes and with liquid hydrogen *for long trips. Yet in a scheme that would seem to clearly call for gaseous hydrogen, Dr. Aceves modeled liquid hydrogen. This goes along with his many comments indicating that the system may be best run on liquid hydrogen only.*

Second, the curve shows that after about a week, the remaining hydrogen is all vapor. As the hydrogen continues to be depleted and the temperature rises, the maximum pressure in the vessel, which is a little above 1,000 psi, is reached after about two weeks.

2. How does refueling a vehicle that uses the insulated pressure vessel differ from refueling a liquid hydrogen vehicle?

"Ideally, an insulated pressure vessel would be fueled with compressed hydrogen for most of the time, and it would be fueled with liquid hydrogen only when this is needed for long range. When fueled with liquid hydrogen, the fueling of an insulated pressure vessel would be different than the fueling of a liquid hydrogen tank because the insulated pressure vessel may have its contents under pressure. Ideally, the tank would be filled with liquid hydrogen at high pressure t avoid losing the gaseous hydrogen contained in the vessel. If this is not practical or economical, then the high pressure hydrogen would have to be vented before filling it with liquid hydrogen."

The insulated pressure vehicle would be filled with liquid hydrogen at high pressure to avoid losing the gaseous hydrogen already contained in the vessel. This is based on the assumption that the tank already most likely contains some pressurized gaseous hydrogen as a result of its primary day-to-day use. If the high-pressure fill is not economical or practical, the gaseous hydrogen would have to be vented prior to the liquid hydrogen fill up.

The need to vent gaseous hydrogen in order to fill up with liquid hydrogen is an item that came up quite a bit during the day. It appears that this may be one of the major drawbacks of the system. It raises costs, increases safety concerns, and may turn the system into one with limited appeal. It also reduces the likelihood of a conceptual home filling system.

3. If a cryogenic hydrogen vessel were to fail – say in a collision with another automobile, how would the consequences compare to those that might be suffered by a compressed hydrogen tank or by a liquid hydrogen tank?

"This depends on the state of the hydrogen at the moment of the failure. If the stored hydrogen is in a gaseous state, then the consequences would be similar to having compressed hydrogen tank fail. If the tank contains liquid hydrogen, then the accident would be similar to having a liquid hydrogen tank fail. In either case the failure would be quite benign, since hydrogen evaporates and diffuses so quickly. Failure of pressure vessels is in general unlikely to occur, as can be derived from the good safety record that exists for natural gas tanks."

If the tank were filled with gaseous hydrogen, the consequences would be similar to the failure of a standard compressed hydrogen tank. If it were filled with liquid hydrogen, results would be similar to those for a standard liquid hydrogen tank. Dr. Aceves stressed the benefits of quick evaporation and rapid diffusion of hydrogen as limiting the negative effects of a tank failure.

What Dr. Aceves says is certainly true, although I would hesitate to agree with his use of the word "benign" when discussing a potential failure.

4. What plans are there to address potential seal failures?

"Seals are a big problem when high-pressure hydrogen has to be contained, especially considering that in this case we have to keep a vacuum space around the pressure vessel for the insulation. For this reason, we decided to onlu use welded joints in all the ducts that contain hydrogen. We also use an explosion-bonded part between the aluminum tank and the stainless steel shell. Seals between the vacuum space and the environment are much easier to handle and regular vacuum seals are used."

Dr. Aceves believes that seals are a very important consideration, especially in light of the fact that the insulation surrounding the case needs to contain vacuum space. Thus, LLNL is using only welded joints for all ducts that contain hydrogen. The seal between the aluminum tank liner and the stainless steel shell is an explosion-bonded aluminum/stainless steel joint. (Explosion bonding is produced by setting off an explosive charge next to adjacent plates of the two metals to be bonded. The explosion "pushes the two plates into each other.") Seals that do not come in contact with hydrogen (such as those within the vacuum insulation) are not a problem; "regular" seals are used.

This question was prompted by some of the concerns of the Peer Review Panel at the Annual Review. Dr. Aceves indicated that a bimetallic joint did indeed show leakage, and had to be replaced. This will bear careful watching. One question that arises is whether the intricate welding process that may be necessary to make a sound joint can be cost-effective.

LLNL appears to be well aware of reviewers' concerns. They are performing extensive cycling and leak checking. These need to be done with hydrogen, however.

5. What are the materials that make up the multi-layer insulation (If this is proprietary, please just provide whatever generic information that you can.)

"The multi-layer insulation is made of aluminized mylar with a layer of very thin gauze in between the layers to reduce conduction heat transfer. This is a commercial product. We only cut it into pieces that fit around the vessel."

The insulation is a commercial product, made up of layers of aluminized Mylar separated by thin layers of gauze. The gauze reduces thermal conductivity, while the shiny aluminum surface provides the reflectivity that cuts down on radiative heating. LLNL only cuts the insulation to shape.

The only objection I have here is the use of the term "multilayer vacuum superinsulation" together with its acronym "MLVSI" and without much in the way of description, if any, in many of Dr. Aceves' publications it becomes confusing.

6. The vessel itself has been described as a kevlar/aluminum or carbon fiber/aluminum vessel, and has been depicted as having an aluminum base with

a fiber overwrap. Is there a binder (resin) component to the fiber? What temperatures is the fiber wrap exposed to? Has the wrap material been exposed to mechanical properties testing as a function of temperature, and if so what were the results?

"Yes, the tanks have a Kevlar/epoxy overwrap. The fiber overwrap will be exposed to liquid hydrogen temperature (20 K). The individual fibers and the resins have been tested (not by us) down to liquid helium temperature (4 K). The results indicate that the fiber stiffens as the temperature drops. We have made a table of properties for the fibers and the resins and these will be used in a detailed finite element analysis of the tanks."

The overwrap is kevlar or carbon with an epoxy binder. This overwrap will see temperatures as low as 20^{o}K (liquid hydrogen temperatures.) Testing has been done (not by LLNL) on the fibers and the epoxies (*apparently separately*) using liquid helium (4^{o}K). The fibers stiffen as the temperature drops. LLNL has compiled a table of fiber and resin properties and is using these data in a finite element analysis.

Failure testing at low temperatures would be of value.

7. Has there been, or are there any plans to perform aging tests on the vessel or its components?

"Aging is always an issue when an accelerated cyclic test is conducted (as we are doing). Kevlar is indeed known to age, and for this reason, the safety factor for Kevlar vessels (3.25) is bigger t6han the value used for carbon fiber vessels (2.5). However, this appears to be the only effect of aging. Once this effect is taken into account (by increasing the safety factor), an accelerated test should be able to reflect the material behavior during regular use. Pressure vessels fail suddenly when a high pressure is applied. There is no evidence that the pressure vessel will fail by creep under a sustained load."

LLNL is conducting accelerated cycling tests, but apparently not aging tests. The Kevlar issue "appears to be the only effect of aging." With this being controlled by the increased safety factor, the accelerated cycling tests should accurately reflect real material behavior.

I would think that some accelerated aging tests would be of value to supplement the Kevlar aging database. Aging properties of epoxy, bond interfaces, and any material coming into direct contact with hydrogen should be evaluated thoroughly.

8. When vessels were burst-tested, what were the failure modes?

"The vessels failed by hoop mid cylinder separation. This is the preferred mode of failure. See [Exhibits 3 and 4..]."

The burst testing was performed after a cycling series; the vessel burst at 13,657 psig. This number was better than (but not outside the statistical range of) other similar vessels that had been burst tested.

9. Are you still considering the microsphere option at all?

"No. Multilayer insulation is inexpensive enough and easy enough to install that we are planning to continue using it in the future. We have proven to ourselves that we can keep a high vacuum in the insulation space by generating an initial vacuum with a vacuum pump. The vacuum is then improved as the vessel is filled with liquid hydrogen due to cryopumping (adsorption into the fiber that occurs when the vessel is cooled down)."

10. At what temperature (approximately) is the interface between the exterior of the fiber wrap and the innermost layer of the insulation?

"Most of the thermal resistance in the insulated pressure vessel is in the multilayer insulation. Therefore, the outer surface of the fiber overwrap reaches a temperature that is very close to the temperature of the interior of the vessel. This was verified in our recent experiments where it reached the temperature of the cryogenic fluid to within 10 K."

The exterior of the fiber wrap (and thus, the innermost layer of insulation) is very close in temperature to the internal temperature of the vessel. That is, with liquid hydrogen inside the vessel, about 20^{o}K.

Note: This question was asked due to my mistaken notion that the insulation is bonded to the composite case (which would raise the question of bond strength at cryotemperature) As the MLVSI is physically wrapped around the case, but is not bonded, this is not an issue. I do believe that the LLNL researchers need to be a little more careful in how they describe their system, so that misconceptions are not generated.

V Additional Discussion:

Extensive testing has taken place on the inner vessel, but not much yet on the insulated vessel. They have tested a small (1 kg H_2) insulated pressure vessel with liquid hydrogen. They held it for two days without any problems seen.

At low temperatures, the fiber wrap will be less tough (less resistant to impact) but would burst at a higher pressure. A ten-meter drop test is being scheduled for a tank filled with liquid nitrogen.

Good test, but liquid hydrogen is colder, and would likely decrease tank strain capabilities.

All the testing and cycling that has been done on the tanks is performance-based. The problem is that no one is certifying these types of tanks. LLNL is looking for a way to make this happen.

The vessel does emit a considerable amount of gas. This is not composite-based hydrocarbons, but primarily water (70%) and nitrogen (30%). At cryogenic temperatures, the vessel actually absorbs gas.

The insulation appears to be working well. Conventional liquid hydrogen systems start losing hydrogen at about two days, and have lost all hydrogen after about ten days. According to Dr. Aceves, this insulated cryohydrogen system loses hydrogen only very gradually, and actually reaches what appears to be equilibrium. Some hydrogen (3.5 kg in a tank designed for 5 kg) remains, and will be around for "years".

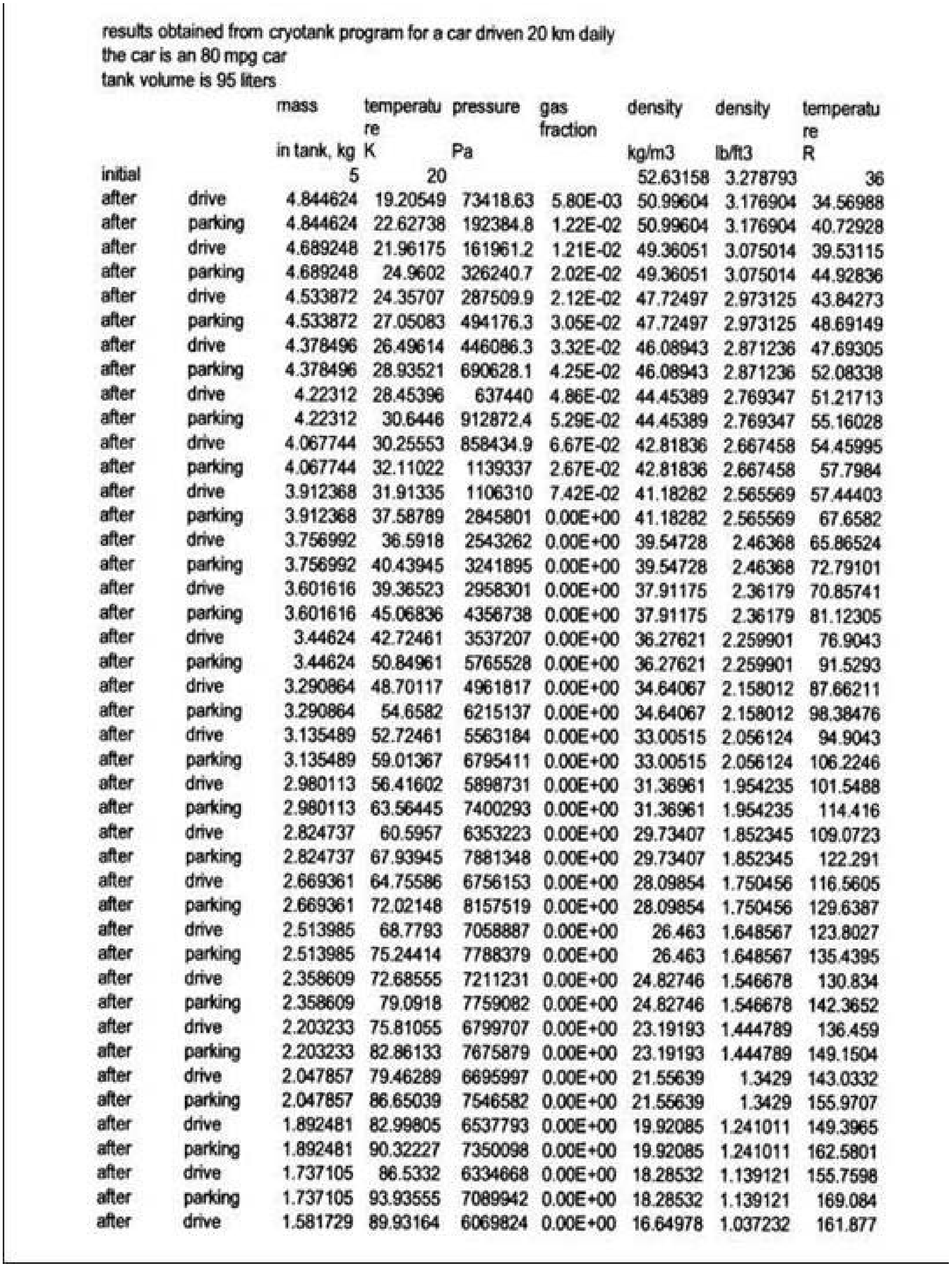
VI Final Thoughts:

A tank that can either hold pressurized, gaseous hydrogen or liquid hydrogen allows both relatively inexpensive daily commutes (on gaseous hydrogen) and long-range (400 miles) travel (on liquid hydrogen). Say that you are commuting to work every day, so you fill up with compressed hydrogen. Then on the weekend, you plan to drive a few hundred miles to another city, so you fill up with liquid hydrogen. But how can you, when you haven't used up all of the gaseous hydrogen from the previous fill-up? What do you do? Do you vent the excess hydrogen? Sell it back to the hydrogen dealer? Have two tanks? All of these options increase safety concerns and/or system cost.

Dr. Aceves mentioned that perhaps if you are planning to use your vehicle for long trips you fill it with liquid hydrogen all the time. This is a more costly option. Dr. Aceves likened the situation to owning an SUV. You pay for the "status" associated with owning the vehicle even though you don't utilize its intended advantages. I'm not sure that I agree. Also, if you are going to do this, the tank will simply serve as an insulated liquid hydrogen tank. Why give the tank an excess of high-pressure capability? The curve that Dr. Aceves presented to us shows that the pressure goes a little above 1000 psi.

It appears that an analysis is warranted in which the methodology and cost of using the system with only liquid hydrogen is considered.

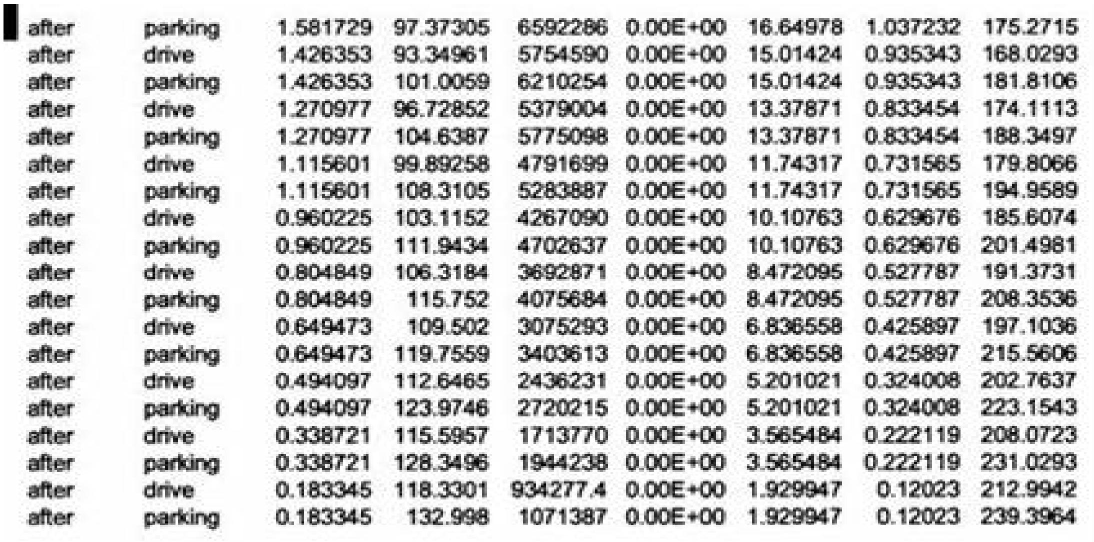
Exhibit 1. Table of Temperature and Pressure Cycles



results obtained from cryotank program for a car driven 20 km daily
the car is an 80 mpg car
tank volume is 95 liters

		mass in tank, kg	temperature K	pressure Pa	gas fraction	density kg/m3	density lb/ft3	temperature R
initial		5	20			52.63158	3.278793	36
after	drive	4.844624	19.20549	73418.63	5.80E-03	50.99604	3.176904	34.56988
after	parking	4.844624	22.62738	192384.8	1.22E-02	50.99604	3.176904	40.72928
after	drive	4.689248	21.96175	161961.2	1.21E-02	49.36051	3.075014	39.53115
after	parking	4.689248	24.9602	326240.7	2.02E-02	49.36051	3.075014	44.92836
after	drive	4.533872	24.35707	287509.9	2.12E-02	47.72497	2.973125	43.84273
after	parking	4.533872	27.05083	494176.3	3.05E-02	47.72497	2.973125	48.69149
after	drive	4.378496	26.49614	446086.3	3.32E-02	46.08943	2.871236	47.69305
after	parking	4.378496	28.93521	690628.1	4.25E-02	46.08943	2.871236	52.08338
after	drive	4.22312	28.45396	637440	4.86E-02	44.45389	2.769347	51.21713
after	parking	4.22312	30.6446	912872.4	5.29E-02	44.45389	2.769347	55.16028
after	drive	4.067744	30.25553	858434.9	6.67E-02	42.81836	2.667458	54.45995
after	parking	4.067744	32.11022	1139337	2.67E-02	42.81836	2.667458	57.7984
after	drive	3.912368	31.91335	1106310	7.42E-02	41.18282	2.565569	57.44403
after	parking	3.912368	37.58789	2845801	0.00E+00	41.18282	2.565569	67.6582
after	drive	3.756992	36.5918	2543262	0.00E+00	39.54728	2.46368	65.86524
after	parking	3.756992	40.43945	3241895	0.00E+00	39.54728	2.46368	72.79101
after	drive	3.601616	39.36523	2958301	0.00E+00	37.91175	2.36179	70.85741
after	parking	3.601616	45.06836	4356738	0.00E+00	37.91175	2.36179	81.12305
after	drive	3.44624	42.72461	3537207	0.00E+00	36.27621	2.259901	76.9043
after	parking	3.44624	50.84961	5765528	0.00E+00	36.27621	2.259901	91.5293
after	drive	3.290864	48.70117	4961817	0.00E+00	34.64067	2.158012	87.66211
after	parking	3.290864	54.6582	6215137	0.00E+00	34.64067	2.158012	98.38476
after	drive	3.135489	52.72461	5563184	0.00E+00	33.00515	2.056124	94.9043
after	parking	3.135489	59.01367	6795411	0.00E+00	33.00515	2.056124	106.2246
after	drive	2.980113	56.41602	5898731	0.00E+00	31.36961	1.954235	101.5488
after	parking	2.980113	63.56445	7400293	0.00E+00	31.36961	1.954235	114.416
after	drive	2.824737	60.5957	6353223	0.00E+00	29.73407	1.852345	109.0723
after	parking	2.824737	67.93945	7881348	0.00E+00	29.73407	1.852345	122.291
after	drive	2.669361	64.75586	6756153	0.00E+00	28.09854	1.750456	116.5605
after	parking	2.669361	72.02148	8157519	0.00E+00	28.09854	1.750456	129.6387
after	drive	2.513985	68.7793	7058887	0.00E+00	26.463	1.648567	123.8027
after	parking	2.513985	75.24414	7788379	0.00E+00	26.463	1.648567	135.4395
after	drive	2.358609	72.68555	7211231	0.00E+00	24.82746	1.546678	130.834
after	parking	2.358609	79.0918	7759082	0.00E+00	24.82746	1.546678	142.3652
after	drive	2.203233	75.81055	6799707	0.00E+00	23.19193	1.444789	136.459
after	parking	2.203233	82.86133	7675879	0.00E+00	23.19193	1.444789	149.1504
after	drive	2.047857	79.46289	6695997	0.00E+00	21.55639	1.3429	143.0332
after	parking	2.047857	86.65039	7546582	0.00E+00	21.55639	1.3429	155.9707
after	drive	1.892481	82.99805	6537793	0.00E+00	19.92085	1.241011	149.3965
after	parking	1.892481	90.32227	7350098	0.00E+00	19.92085	1.241011	162.5801
after	drive	1.737105	86.5332	6334668	0.00E+00	18.28532	1.139121	155.7598
after	parking	1.737105	93.93555	7089942	0.00E+00	18.28532	1.139121	169.084
after	drive	1.581729	89.93164	6069824	0.00E+00	16.64978	1.037232	161.877

Exhibit 1 continued



after	parking	1.581729	97.37305	6592286	0.00E+00	16.64978	1.037232	175.2715
after	drive	1.426353	93.34961	5754590	0.00E+00	15.01424	0.935343	168.0293
after	parking	1.426353	101.0059	6210254	0.00E+00	15.01424	0.935343	181.8106
after	drive	1.270977	96.72852	5379004	0.00E+00	13.37871	0.833454	174.1113
after	parking	1.270977	104.6387	5775098	0.00E+00	13.37871	0.833454	188.3497
after	drive	1.115601	99.89258	4791699	0.00E+00	11.74317	0.731565	179.8066
after	parking	1.115601	108.3105	5283887	0.00E+00	11.74317	0.731565	194.9589
after	drive	0.960225	103.1152	4267090	0.00E+00	10.10763	0.629676	185.6074
after	parking	0.960225	111.9434	4702637	0.00E+00	10.10763	0.629676	201.4981
after	drive	0.804849	106.3184	3692871	0.00E+00	8.472095	0.527787	191.3731
after	parking	0.804849	115.752	4075684	0.00E+00	8.472095	0.527787	208.3536
after	drive	0.649473	109.502	3075293	0.00E+00	6.836558	0.425897	197.1036
after	parking	0.649473	119.7559	3403613	0.00E+00	6.836558	0.425897	215.5606
after	drive	0.494097	112.6465	2436231	0.00E+00	5.201021	0.324008	202.7637
after	parking	0.494097	123.9746	2720215	0.00E+00	5.201021	0.324008	223.1543
after	drive	0.338721	115.5957	1713770	0.00E+00	3.565484	0.222119	208.0723
after	parking	0.338721	128.3496	1944238	0.00E+00	3.565484	0.222119	231.0293
after	drive	0.183345	118.3301	934277.4	0.00E+00	1.929947	0.12023	212.9942
after	parking	0.183345	132.998	1071387	0.00E+00	1.929947	0.12023	239.3964

Exhibit 2. Plot of Temperature/Pressure

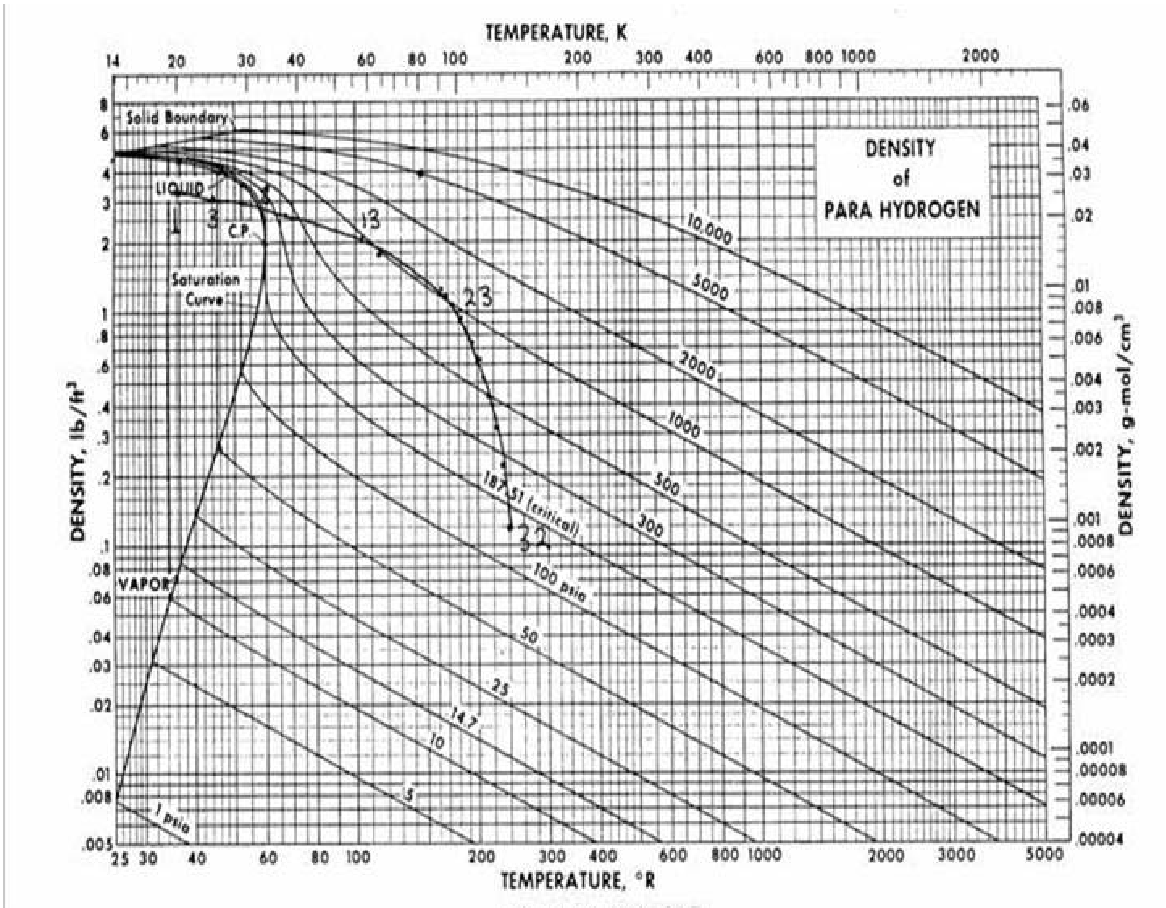


FIGURE 3.15. Density (P-ρ-T).

Exhibit 3. Burst-tested Kevlar/Aluminum Pressure Vessel

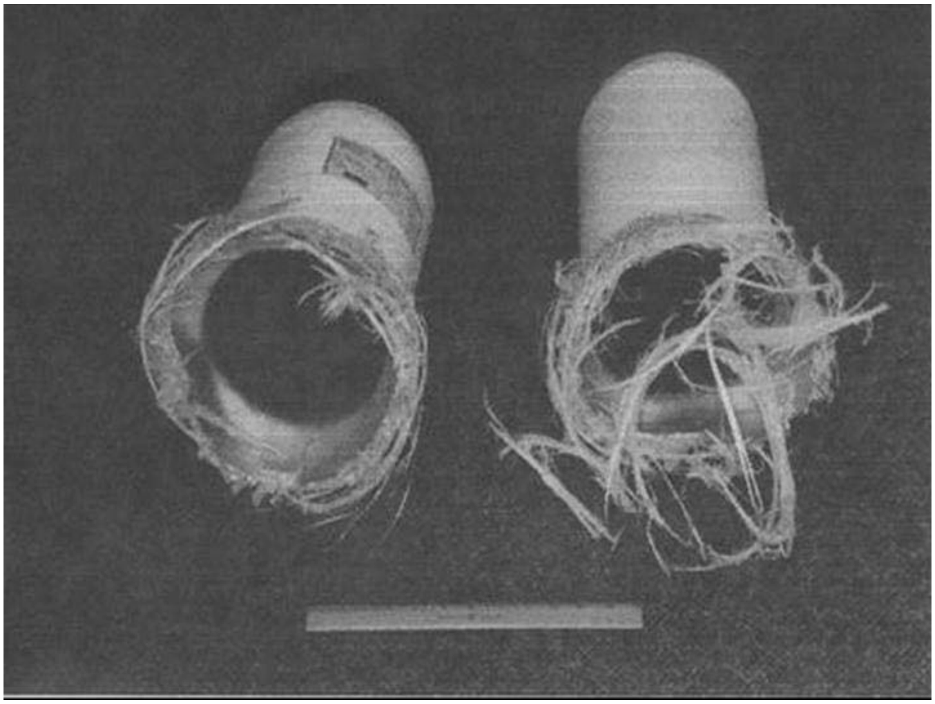
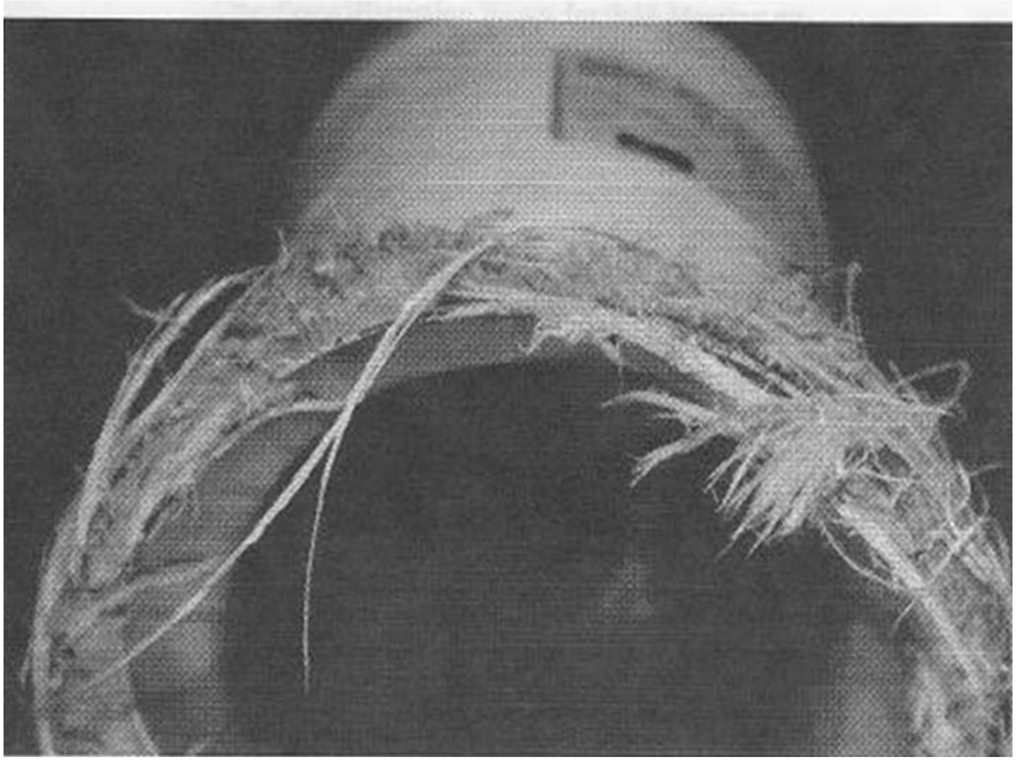


Exhibit 4. Details of burst-tested vessel



This page intentionally left blank

Technical Evaluation Report
Project: Vehicular Hydrogen Storage Using Cryogenic Hydrogen
Company: Lawrence Livermore National Laboratory, Livermore, CA
P.I.: Dr. Salvador Aceves
Date of Visit: May 2, 2001
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

The Lawrence Livermore National Laboratory (LLNL) cryogenic hydrogen project is centered on the concept that on-board hydrogen storage can be addressed by realizing that although a driving range of a few hundred miles is sometimes required, it is not always required. The cryogenic pressurized tank is designed to hold compressed hydrogen gas (C-H_2) for short commutes to work, and to hold liquid hydrogen (L-H_2) for longer-range trips. Since it can hold either form of hydrogen, it can be built smaller than "standard" compressed hydrogen tanks, requiring lesser amounts of C-H_2 when used to commute to work, and relatively infrequent fill-ups of the more costly, denser L-H_2 for longer trips.

In the approximately twenty months since I last visited this project, LLNL has moved from the small sized (1 kg H_2) prototype to the full size tank (6-7 kg H_2), which they are now building and testing. The tank consists of an aluminum liner, a composite (carbon/ or aramid/epoxy) overwrap, and layers of aluminized Mylar insulation over this. The entire tank is encased in a stainless steel shell.

Project Strengths:

- There is definite progress. LLNL has moved from prototypes to full-scale tanks, and most aspects of the project are proceeding as expected.
- LLNL has a demonstration partner in SunLine who has and will have the proper vehicles, facilities and infrastructure to enable a meaningful demonstration. This will provide meaningful data that will represent a good first step in validating this type of tank.

Issues that should be Addressed:

- The fact that LLNL is not ready to test actual hydrogen systems remains a serious concern in my mind. How do you tell a potential customer that even though the laboratory researchers had to shield themselves in a bunker to perform tests with hydrogen, its all right to have a full tank of hydrogen under your car? The SunLine demonstrations will help, but aging tests of tank materials in the presence of hydrogen, including some overall tank structural tests are needed.

- The possibility of unbonding between the liner and composite remains an issue. It happened with the smaller tanks. Will it happen with the full-size tanks? Does it matter? Is an actual liner/composite physical bond necessary?

- The failure of one bimetallic seal in one of the prototype tanks has not been resolved yet. In addition, seal testing needs to be done in the presence of hydrogen.

- A lot of thought/analysis is needed to map out usage and infrastructure scenarios. If this project is to be a success, we need to know if the dual hydrogen scenario will be workable. This needs to emphasize "people" aspects – how easily will people adapt to a dual fuel infrastructure.

- Consideration needs to be made for hydrogen transfer into the tank. (How does one put L-H_2 into a tank half full of C-H_2?)

II Introduction and Background:

I visited **Dr. Salvador Aceves** at his facility at LLNL to review progress on his cryogenic, pressurized hydrogen storage tank since my last visit in September 1999. We discussed the project in detail and toured the assembly and pressure testing laboratories. Dr. Aceves has been working on the cryogenic pressurized tank concept for the past several years, first choosing this approach from a series of alternate storage scenarios (including glass microsphere storage); designing, building, and testing prototype vessels; and now building and preparing to test full size tanks.

III Tour:

The tour consisted of stops in two different buildings at LLNL, one housing high-pressure testing facilities, and the other, a new location for the assembly of tanks. In the high-pressure laboratory, Dr. Aceves and I were joined by **Tim Ross**, **Chuck Borzileri**, and **Vern Switzer**, whose functions include oversight of the high-pressure facility and safety coordination. When I arrived, there were two full size tanks in the facility, and structural pressure and leak tests were scheduled to be run at a later time.

In a "manned" area, LLNL insists on a 5X safety margin for high-pressure vessels.

The test bed is basically the same as it was 20 months ago, but some of the instrumentation has been upgraded. Also, more consideration has been given to handling the tanks. A full size, insulated tank filled with water (for pressure testing) or liquid nitrogen (for cryogenic testing) weighs about 900 pounds.

[Dr. Aceves mentioned that the primary pressure cell was the same one where LLNL previously performed their glass microsphere hydrogen storage system tests. They were looking to see how quickly they could pressurize the microspheres, using helium at the time. They had just gotten certified to test with hydrogen (*so apparently it can be done at LLNL*) but the contract got terminated and the Principal Investigator left the laboratory.]

In the second building, we were met by **Mark Fowler** who led us through the new facility where tanks are being assembled. It is here that following leak testing (at the pressure facility) the composite tanks are wrapped with the multi-layer insulation. (The tanks themselves currently are manufactured at SCI.) Following this, a vapor shield (a series of heat transfer tubes welded to a jacket, with spaces filled with thermal epoxy) is installed. This reduces heat transfer loses. More insulation is wrapped over the vapor shield. Finally, a stainless steel outer shell is placed around everything. The plan is to "fit out" or assemble the entire tank in this facility. Any welding will be done here as well.

The shields and shells are made by an outside contractor. In actuality, LLNL does not have a shell yet; Dr. Aceves cites contractor problems.

IV Questions and Answers:

I sent Dr. Aceves a set of discussion questions prior to my arrival. He responded in writing and we also discussed the questions and answers in detail.

1. **We have discussed previously the problems that arise logistically when wanting to test hydrogen-filled tanks. Has anything happened recently to alleviate the situation? If not, how will this important (in my opinion) part of materials and components testing be addressed?**

"Nothing has changed. Being a DOE laboratory there are a lot of regulations for us to follow. The energy in the hydrogen exceeds the maximum energy limit for our high-pressure cells. We can move to our high explosives facility, but this is expensive. Instead, we'll try to do the tests at either SCI or SunLine, where we are away from DOE regulations."

The bottom line is that it is too expensive. When Dr. Aceves used LLNL's remote test facility for three days in 1999, it cost about 1/3 of that year's budget. The use of the remote high explosives site is part of LLNL's policy; there is "too much energy" to allow testing in LLNL's standard high-pressure laboratories. To test in the normal laboratories, the tank would have to be approved by the Department of Transportation (DOT). But, Dr. Aceves claims, they are moving beyond that need. Testing will be performed at one of their partners' facilities – either Structural Composites Industries (SCI) or SunLine Transit Agency. Hydrogen testing should be easier to accomplish there, where the laboratory limitations won't stand in the way. Dr. Aceves recognizes the fact that the tank needs to be certified.

While the current program does include some off-laboratory testing, it does not include hydrogen testing. I think I would test with hydrogen at the first opportunity.

2. **You had a milestone in which you tested 5 insulated pressure tanks. You indicated six tests – four cycling tests (cryogenic, ambient temperature, environmental, and thermal), a hydraulic burst test and a gunfire test. While the last two are destructive tests, the cycling tests (I hope) are not. How were the tests apportioned among the five tanks? Did any tank see a series of, say, all**

cycling tests? Are some of these tanks the same ones that will be used for the upcoming bonfire and drop tests?

"We originally built 5 tanks with insulation.

- One tank was used for the ambient temperature cycling test and then for the gunfire test.
- One tank was used for the environmental cycling test and then it was burst tested.
- One tank was used for the thermal cycling test and then it was burst tested.
- One tank was used for cryogenic cycling. This will be now used for the bonfire test.
- The remaining tank will be used for the drop test."

The tanks referred to here are all the small, 1-kg tanks. All of them were aramid fiber tanks, not carbon fiber. The tanks that were burst after cycling all passed a 3X burst pressure threshold, and failed in the hoop direction. They essentially acted like new tanks, according to Dr. Aceves. The 3X criterion was imposed for aramid tanks to compensate for the fact that aramid ages faster than does carbon. No aging studies have been done, however. Dr. Aceves indicated that they are proceeding according to DOT regulations.

All except the fifth tank were cycled thousands of times. The fifth tank was only subjected to thermal shock via liquid nitrogen cooling. It will be next subjected to a drop test.

3. **Have any cycling tests been performed (or are being planned) to simulate "real life" conditions? For instance: something like three cycles with compressed hydrogen (or even nitrogen) followed by a cycle with liquid hydrogen, with the process repeated several times.**

"We did cryogenic cycling, where we did a cryogenic cycle with LN followed by 10 cycles with gaseous helium. We believe this may be close to "real-life" conditions, with the only exception of using helium and nitrogen to replace hydrogen."

That's a very important exception!

Dr. Aceves recognizes that some hydrogen testing will eventually be necessary. When the National Hydrogen Association's (NHA) standards become International Organization for Standards (ISO) standards (sometime in the next few months, hopefully), there will be more direction. Dr. Aceves believes that the NHA standards will be similar to DOT or ISO standards for compressed natural gas (CNG).

He believes, however, (*as do I*) that testing with hydrogen is needed for materials compatibility. Dr. Aceves stated that he believes that NHA is not adequately addressing materials compatibility issues with hydrogen. Embrittlement is the main concern.

Dr. Aceves noted that it might be a little easier to test with hydrogen at LLNL after the NHA standards come out – at least for gaseous hydrogen. Cryogenic conditions still represents a problem that needs to be addressed. Perhaps, suggests Dr. Aceves, SAE tests for liquid natural gas (LNG) can be used as a model. The SAE tests consist of a drop test and a bonfire test.

Anything that will make people more comfortable with hydrogen is worthwhile.

4. **Are you using both aramid and carbon composites at this time, or have you down-selected?**

"We are using only aramid vessels, mainly due to availability. The size that we required was only made in aramid. In the long term a decision will be made probably based on cost. In the foreseeable future I believe aramid will be cheaper than carbon fiber, so we'll probably keep using aramid."

Even though the aramid version is twice as heavy, it's one-sixth the cost of the carbon fiber version when purchased from SCI. *(This is based on aerospace grade carbon fiber; perhaps a cheaper grade could be used.)* Since the system drivers appear to be cost and volume rather than weight, aramid tanks are more likely to be the choice commercially. Dr. Aceves cited a Ford study that showed that the main item for the additional cost (about \$3000) for a hydrogen car over a conventional car would be the tank. The analysis was for a C-H_2 tank.

Cost estimates I've seen for a hydrogen tank are more of the order of \$1000. In my 1999 analysis of the PowerBall process, I made a comparison to a C-H_2 *tank, and I used \$750, based on some Sandy Thomas analyses.*

To estimate the cost of his tank compared to a C-H_2 tank, Dr. Aceves considers the costs to be proportional to the amount of fiber used. Since his tank is roughly 1/3 the size of a C-H_2 tank, he estimates that it will cost about 1/3 to 1/2 that of the C-H_2 tank.

5. **When I visited in 1999, we discussed the composite to aluminum bond, and you told me that the bond "fails somewhat." Is this still the case? Is this failure mode present both with aramid and carbon composites?**

"We only did ultrasonic testing in the aramid vessels, so we don't know for sure if the carbon fiber vessels present the same form of detachment. In the cryogenic tests it is possible to hear the tanks making slight popping sounds during the first few cycles. We interpreted these sounds as an indication that some detachment is occurring at the liner-fiber contact. We heard these sounds both in the carbon and in the aramid vessels, so we believe that yes, there is debonding in the carbon pressure vessels. We have not done cryogenic testing of the full-size pressure vessels, so we don't know whether the same effect will exist."

It is important to know if unbonding is really occurring and what its consequences are. Some of the compressed hydrogen tank designs do not bond the liner to the composite. They use the theory that it is safer to design without a physical bond rather than to bond the two components and have a bond failure.

6. **Last time, we spoke about seal issues, and you mentioned that you were having some leak problems with a bimetallic seal. What is the seal situation now?**

"The bimetallic seal failed in one of the tanks we made. This only happened one time. We talked to the company that makes the bimetallic seals and they told us that it was a very rare event. We also shipped the failed part to them to see what went wrong with it."

The seals were manufactured by High Energy Metals in Seattle. Of the 14 seals that LLNL purchased, there was only the one failure. These seals are necessary to bond together the aluminum liner and stainless steel filler tubes. The filler tubes need to be high strength to accommodate filling the tank with C-H_2, and low thermal conductivity to fill the tank with L-H_2 efficiently. Aluminum will not do this. Meanwhile, the liner itself needs to be aluminum to minimize embrittlement (*although low temperature testing is needed)* and cannot be plastic to survive cryogenic temperatures. Therefore the tank needs stainless steel filler tubes, an aluminum liner, and bimetallic seals.

I am concerned by the 93% reliability record (13/14) and not assuaged by the "very rare event" statement from the manufacturer. I think this needs further investigation. In addition, the seal testing must include exposure to high pressure and cryogenic hydrogen.

Dr. Aceves wondered about the capacity expansion capabilities of the explosion-bonded bimetallic seal "industry" and whether a new business will evolve if the pressurized cryogenic tank becomes a commercial product. *It certainly will be a serious consideration necessary for mass production of pressurized cryogenic tanks. The failure is of more pressing importance however.*

7. **Please describe the nature of the upcoming demonstration with SunLine. As a bus company, I would think that SunLine's requirements would tend to a frequent refueling capability and a relatively short driving range. How does this sort of duty cycle translate to bona fide tests for the pressurized cryogenic tank? Is it actually the SunLine pickup truck that will be used for long-range liquid hydrogen fills?**

"The superbus is used for long distance trips, carrying commuters from Palm Springs all the way to Los Angeles area. The pickup truck is used for general services over a wide range of conditions. So both vehicles do require a long-range capability. The pickup truck may have a more variable schedule, which may be more similar to the schedule of a personal vehicle."

This justifies the use of the two vehicles as stated.

8. **Will the two vehicles at SunLine be equipped with ICEs or fuel cells? You note that the "superbus" is fueled (currently, I assume) with LNG. Is the plan to switch to LH2 exclusively, or to run on blends?**

"The vehicles at SunLine run with ICEs. The pickup truck uses hydrogen fuel, and the superbus is fueled with LNG. So our pressure vessels will be used with LNG in the superbus. No attempt will be made of running on mixed fuels. This will be a good first attempt at demonstrating insulated pressure vessels. Also, SunLine already has a fueling station for LNG. SCAQMD likes LNG so it is good to demonstrate LNG use to enhance our opportunities to obtain complementary funding."

There is no plan to use hydrogen on the "superbus" at all. The bus actually has several tanks on-board, the cryotank will just be one of them. While the DOE Hydrogen Program is funding production and installation of the tanks for both vehicles, the South Coast Air Quality Management District is funding the LNG part of the project.

I agree that the superbus is a good first demonstration of the tank in use – as long as we remember that it's not a hydrogen tank in this instance – different fuel, different temperature.

Currently, the pickup truck is using electrolytically produced hydrogen that is stored in a low-range (50-60 miles) pressure vessel.

SunLine will have a L-H_2 facility within a year. While they get the facility ready, LLNL will be installing the tanks in the truck and superbus.

9. **Do the finite element analysis tests include results for both liquid hydrogen temperatures and liquid nitrogen temperatures (I believe from our previous discussions that you do much of your cryogenic testing with liquid nitrogen)? Does the plastic deformation that you report after five cycles manifest itself at liquid nitrogen as well as at liquid hydrogen temperatures? If so, how does the deformation differ at the two temperatures?**

"The finite element analysis was done for liquid nitrogen temperatures because most experiments were done with liquid nitrogen. We are planning to run an analysis with liquid hydrogen temperatures. It will be interesting to see how the results compare."

The liquid nitrogen finite element analysis matched up well with experimental data according to Dr. Aceves.

10. **In 2000, the Annual Peer Review team had concerns about the potential difficulties of developing two infrastructures – a gaseous hydrogen infrastructure and a liquid hydrogen infrastructure. How do you envision refueling stations? Gaseous hydrogen stations in the cities and liquid on interstates, all stations having both fuels, etc. Has any thought been given to the infrastructure question?**

"Ideally, people would have an electrolyzer in the garage that would produce enough hydrogen for the daily fill-up. This would make refueling much easier for people. This could be complemented by compressed hydrogen stations in the city. Then, liquid hydrogen would be sold on the highways for people to use in long trips."

Dual stations that sell both forms of hydrogen are possible. However, if you made C-H_2 from L-H_2, there would be no savings. The project's forte is in minimizing the amount of L-H_2 you have to make. If the dual station evaporated L-H_2 to make C-H_2, there would be no savings. The electrolyzer scenario appears to be more economical.

These thoughts seem to make sense. However, I think a more in-depth infrastructure scenario analysis needs to be performed to make sure that we are not going to produce a product that will require an unwieldy infrastructure. The analysis would have to include a means to determine whether consumers would be able to (and willing to) adapt to the dual fuel approach.

Dr. Aceves likened the home electrolyzer scenario to the electric vehicle (EV) system. Women especially liked the EV concept because they never had to go to a refueling station.

11. (This question is a little different from the others) The overall premise of using compressed hydrogen for commuting and liquid hydrogen for long trips is a clever one. My concern is that people who drive cars are not necessarily clever. People will have to refuel with what will be to their way of thinking, two different fuels. It will likely take some getting used to, especially in cases where people are driving intermediate distances, or change their plans, or several other scenarios. Is there any plan to develop sets of instructions (or training) for the driver as to what fueling options to use? (I assume the last thing that a driver would want to do is vent half a tank of compressed hydrogen to take on a tank of liquid hydrogen.)

"I totally agree with this comment. We can't count on people to optimize their use of hydrogen. However, I think that in the long term, when we switch to renewable hydrogen, energy will be more expensive than today and people will have a greater motivation to optimize hydrogen use. Then our vessels may achieve their full potential. Some instructions on how to minimize energy consumption (or money spent) would be necessary at that time. In the meantime, while we can buy gasoline at $1.50 per gallon, hydrogen will never be used in big scale."

This can be a real issue. Education will certainly be needed.

The infrastructure analysis indicated above should include provisions for training/educating the various types of drivers that would be using the cryogenic tanks. The alternative would be to modify the tank design (if possible) to allow, say, filling the tank with $L\text{-}H_2$ *without losing stored* $C\text{-}H_2$.

V Additional Discussion:

- The outer shell also serves "unofficially" as a secondary containment vessel.
- To date, none of the full size, fully assembled tanks have been tested. Five of the smaller tanks were hydro burst within their outer shell.

VI Final Thoughts:

This project continues to make good progress. It appears that LLNL is going down the right path with the exception of the inability to test in the presence of hydrogen. This is worrisome. Dr. Aceves is concerned about materials issues (as am I) in the presence of *hydrogen. He recognizes the problem, but has no solution until a test site (perhaps as he suggested, SCI or more likely SunLine) can be identified outside LLNL. When the test site is determined, a rigorous test program in recommended – one that will provide data in areas that non-hydrogen testing cannot. This includes cryogenic testing at L-*H_2 *temperatures (*20^oK*), and materials aging tests.*

The other key item is the entire issue of how the tank and associated infrastructure will be utilized. I think some analyses need to be performed to see where and when the user gets the C-H_2*, where and when he gets the L-*H_2*, and whether that scenario is both economical and palatable to the consumer.*

This page intentionally left blank.

Technical Evaluation Report
Project: Hydrogen Storage Using Lightweight Tanks
Company: Lawrence Livermore National Laboratory, Livermore, CA
P.I.: Dr. Fred Mitlitsky
Date of Visit: March 21, 2000
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

Dr. Fred Mitlitsky is responsible for two somewhat related projects at Lawrence Livermore National Laboratory (LLNL) – one involving the development of regenerative fuel cells (RFC), and the other involving the development of lightweight tanks for hydrogen storage. In the tank area, the emphasis is on liner development for vehicular hydrogen storage, and it is in this area that we focused our visit. The liners serve as barriers to hydrogen permeation and also as mandrels on which to wrap composite tanks.

Quite a lot of work has been done in the liner area over the past few years. Dr. Mitlitsky's group has tested and/or characterized some fifty material candidates as to hydrogen permeability, and has assessed leading candidates for strain, toughness, corrosion resistance and processibility as well. A high density polyethylene has emerged as the leading candidate to this point. LLNL, is trying to improve the system by adding a coating (polymeric or metallic) to the inside surface of the liner. This would decrease hydrogen permeability and would allow for a thinner overall liner system.

This is an important project. Advanced compressed hydrogen tanks are very likely to be the near to mid term (*at least*) answer for on-board hydrogen storage.

Project Strengths:

- Dr. Mitlitsky and his group appear to have correctly identified the goals of high pressure storage, and are attacking them in a proper, well thought out manner.
- The team appears to be a good one.
- The focus on lightweight liners is the right direction for this overall effort.

Issues that should be Addressed:

- To date, the results appear to indicate that no single polymeric system will meet permeability requirements and be easy to process. Dr. Mitlitsky has indicated that there are a lot of potential alternatives (metal coatings, "paint-on" polymers, use of dicyclopentadiene). They need to be developed and assessed.
- Results are presented in far too complex a manner; they need to be simplified.

- An overall cost-benefit comparative analysis is needed at a stated safety level.

- More material aging studies are needed. These really need to be done in a hydrogen atmosphere.

II Introduction and Background:

I visited Dr. Mitlitsky and two of his co-workers, **Dr. Andrew Weisberg** and **Dr. Blake Myers** on March 21, 2000, spending the better part of a day with them, discussing the project and getting a tour of their laboratory.

The major emphasis of our meeting was the discussion of liner materials and systems that are being identified/developed at LLNL. Dr. Mitlitsky states that they can achieve a 12% hydrogen loading using a polyethylene-lined composite-wrapped tank. It can hold 5000 psi hydrogen, and has a 2.25 safety factor.

The key parameter, however, is permeability. Permeability units are derived from a gas transmission rate (e.g., moles per square meter per second), for a given material thickness and a given pressure.

In determining what the permeability rate should be, a comparison was made to a natural gas vehicle (NGV) specification. This spec stated that for natural gas at 3600 psi, the permeability should be no more than 0.25 standard cc per hour per liter of tankage. At this rate, natural gas leaking into a stagnant, closed standard garage would take three years to reach the lower flammability limit (5%). Based on this, LLNL believes that their goal for a 5000 psi hydrogen tank should be 1 cc per liter of tankage.

III Tour:

- The laboratory possesses a RFC test rig, on which "all kinds of" RFCs can be tested. Hydrogen can either be produced from water (in the electrolyzer mode) or can be bottled hydrogen. One can add impurities either to the hydrogen (cathode) or oxygen (anode) gases if desired in the test. The rig is currently not operational; safety features are being repaired. In addition, the RFC work is not funded during the current (1999-2000) fiscal year. (Dr. Mitlitsky is trying to obtain RFC funding from the Defense Advanced Research Projects Agency (DARPA).)

- Dr. Mitlitsky showed me a small RFC that produced hydrogen in the electrolysis mode (he demonstrated burning the hydrogen) and produced electricity (turned a propeller) in the galvanic mode.

- There were also assorted liners, cases, and parts of both in various states of completion throughout the laboratory.

IV Questions and Answers:

A large portion of our discussion time was spent going over a series of questions that I had sent Dr. Mitlitsky prior to our meeting. Dr. Mitlitsky had prepared a set of written responses, and these were referred to often during our discussion. The written responses are included in this section:

For questions directly related to the FY 1999 Annual Review Report prepared by Dr. Mitlitsky, the reader is referenced to ***http://www.eren.doe.gov/hydrogen/pdfs/26938ll.pdf***

1. **Please explain the philosophy as to why a storage system that is more likely to be vehicular, and the regenerative fuel cell, that is more likely to be stationary are considered as a unit.**

"Regenerative fuel cells (RFCs) have vehicular applications as well as stationary applications. In fact, this line of research (RFC systems with lightweight tankage) began as a result of starting with a clean sheet of paper and determining which high cycle life energy storage system would be optimal (from mass considerations) for vehicles. Vehicles designed around RFC systems with lightweight tankage have comparable cost to vehicles designed around primary fuel cell powered systems. Unlike primary fuel cell powered systems, vehicles with RFC systems carry their infrastructure onboard the vehicle. Therefore, RFCs do not require an extensive hydrogen infrastructure for initial market penetration. RFCs can be electrically recharged or rapidly refueled.

"Many classes of vehicles would benefit from closed cycle energy storage (e.g., indoor service vehicles, mining vehicles, high altitude aircraft, spacecraft, some boats, some offroad vehicles, some construction vehicles). This is similar to the niche for secondary batteries, which primary batteries cannot replace in many applications due to cost and logistics. To build closed cycle energy storage for vehicles requires the highest performance storage systems, without a superior storage system these options fail."

This may be, but I don't believe that the RFC project (at least at first) had anything to do with vehicles.

2. **Is the cryogenic tank that Salvador Aceves is working on simply a totally different concept, or are there any overlaps with the lightweight liner/tank project?**

"There is only modest overlap between Salvador's cryogenic tank project and the lightweight liner/tank project. Although the components for the pressure vessel inside Salvador's storage approach have the same names as the components of a lightweight tank, they face much more stringent operating specification. Due to huge technical risks, Salvador has not been able to innovate on these components, having found a relatively heavy option already in production. Instead his research activity must focus on heat loss and insulating systems outside the pressure vessel, in contrast to our effort focuses on weight and hydrogen permeation."

Dr. Aceves could conceivably use some of the same materials to make a plastic-lined tank. Dr. Mitlitsky thought that dicyclopentadiene might be applicable for the cryotank. This might decrease overall tank weight.

You can compare hydrogen losses from a compressed gas tank, to liquid hydrogen boil-off. Dr. Mitlitsky believes that if his liner is 0.15 inches thick, his tank will have a half-life of 6 months. Hydrogen in a cryotank would not last as long.

There appears to be very little overlap. It seems to be two storage projects that happen to be at the same laboratory.

3. You stated in your FY 1999 Report that metal liner options will "poison RFC systems." How will this happen?

"The statement from the FY 1999 Report is "Without extreme caution concerning the management of residual moisture, the available metal liner options can poison RFC systems." This statement is relevant to hydrogen sources which may have more than negligible amounts of water contained (e.g., electrolytic hydrogen production which does not have adequate drying of the gas stream). Moisture in the gas stream can react with some metal liners (e.g., aluminum or some grades of steel) and leach metal ions into the gas stream. These metals can poison PEM fuel cells and reduce lifetimes or performance.

"The term 'poison' refers to the inactivation of catalysts, although in the case of PEM, it can also refer to the occupation of sites responsible for proton transport. Industry experience has failed to confirm the irreversibility of poisoning, although it has compiled a large laundry list of ions incompatible with the intrinsically long service life of PEMs.

"If care is taken to use tank liner materials that are compatible with PEM fuel cell plumbing, or if water is prohibited from collecting in the hydrogen storage tanks (e.g., by assuring that only dry hydrogen is stored) and if water is prevented from forming in the hydrogen container (e.g., by preventing low levels of air or oxygen from entering the hydrogen tank), then liner material choice does not need to be constrained by compatibility with water and/or fuel cell plumbing."

Dr. Mitlitsky believes that it is better to use liner material that is not affected by moisture than to worry about poisoning. I would agree.

4. Why is your data normalized to MDPE for hydrogen and HDPE for oxygen? Since MDPE data appears to be available throughout, why not use it as a baseline for everything?

"The data presented in the FY 1999 Report "Table 3. Literature Survey of Some Polymers Considered for Tank Liners" was generated primarily by comparing to reference data in "Modern Plastics 1991 (Mid-October 1990 Issue Vol 67 (11), pp. 592-6 for Film & Sheet (supplemented with pp. 480-528 for Resins & Compounds)". This reference did not have both hydrogen and oxygen permeation data for HDPE, which is a marginally superior permeation barrier compared with MDPE (note that oxygen permeation is ~35% greater in MDPE compared with HDPE). In fact, HDPE was chosen as a baseline material for liner development, so it is the relevant data for comparison within this program which is focused on developing hydrogen tankage. Oxygen data is presented because it was readily available, and well-funded RFC programs might be interested in storing oxygen. At present, nobody is paying for oxygen permeability data collection (except proprietary data in the food wrap industry), so there isn't much published on materials (e.g., polyethylene variants) that might be more suitable for tank liners. Although I agree in principle that a good choice for a baseline should be the same for both gases, for this program HDPE is the relevant baseline."

The Table is shown in Exhibit 1. For the liner program, we should just concentrate on HDPE. This has become the baseline material at any rate. Anything that has shown lower permeability has failed on other grounds.

5. We need to discuss the permeation testing methodology shown in Figure 8 of your FY 1999 Annual Report. (The figure is hard to follow.)

“Figure 8 - Schematic and Photos of Permeability Test Fixture at SRI shows a permeability test fixture at SRI which is capable of screening a wide variety of liner candidates for permeation as a function of delta-P up to 5 ksi (34.5 MPa). Tests can be performed at various temperatures, induced biaxial strains, and using several different gases, including hydrogen. These tests are effectively a modified version of the ASTM gas transmission test using a Dow gas transmission cell (ASTM Designation: D 1434-82, section 9.1, 1982, Philadelphia, PA). The ASTM test is strictly defined at low delta-P (~30 psi). However, some materials exhibit unexpected permeation characteristics at high delta-P (~5 ksi), which is more representative of the design point for hydrogen tanks.

“In addition, permeation tends to be exponential with temperature, so elevated temperatures can be more indicative of worst-case design points for hydrogen tanks. Some materials also exhibit increased permeation as a function of strain cycles (that result from pressure cycles and temperature cycles to a lesser extent). A rather large database of hydrogen permeation data has been collected on this apparatus for various materials as a function of temperature, delta-pressure, and biaxial strain.”

The Figure is reproduced here as Exhibit 2.

6. Figure 9 in your 1999 Annual Report seems to indicate that permeability is actually decreasing with increasing pressure for several materials. Please explain.

“Figure 9 - Measured Hydrogen Permeability of Several Candidate Liner Materials, does show that permeability decreases with increasing delta-pressure for several materials, most notably HDPE. This phenomenon is not completely understood, has been seen by other groups, and might be due in part to the increased compressibility of some materials at higher delta-P. One possible explanation is that the increased compressibility could reduce the size of more permeable micropores within the material and thus reduce the induced permeability at higher delta-P. Note that even in cases where the permeability of the material decreases with pressure, the actual permeation (or gas transmission rate) still increases with pressure.”

The Figure is shown in Exhibit 3.

It’s best to track both permeability and permeation.

7. The same report indicates that some life cycle tests are being conducted. Have any real time or accelerated aging tests been conducted (or planned) that look at mechanical properties and permeability?

“Three different tests have been performed to study mechanical properties and permeability as the tank ages:

“Accelerated stress rupture, as defined by NGV2 (hold a tank at 125% of service pressure for 1,000 hours at 65 °C).

Leak test, ambient pressure cycle test, and repeated leak test. Mechanical tensile tests at temperature and various strain rates. This data will allow us to calculate the fatigue properties of the liner material. Can also predict creep and life expectancy of materials. A separate program was undertaken to predict the time effect of the compression set of Nitrile O-rings.

"Direct testing of cycle life issues has only taken place on integrated vessels. These tests were performed in house at Thiokol as part of a risk reduction effort to make sure this line of development could pass NGV2. When may experimental tanks with nylon liners failed cycle life tests, an in-house research program was funded at Thiokol to calibrate and predict cycle life. That program acquired strain cycles to failure on 'dogbone' test specimens, produced one excellent retrodiction (prediction of an experimental result already in hand) of nylon tank cycle life, and was abandoned due to lack of specifically useful predictions for the cluster of HDPE liner materials now used as a baseline."

I think the tests that are lacking are ones that need to be done in a hydrogen atmosphere, or after materials have been aged in a hydrogen atmosphere.

8. Have physical property tests been carried out as a function of temperature?

"Permeability and tensile properties have been obtained at -40 °F, room temperature, and +180 °F. These results are limited to the best candidate materials, while the room temperature results have been accumulated for a much wider range of plastics in order to find the best candidates."

9. What are the goals for the properties being tested?

"Obtain permeation, mechanical characterization, and life cycle data for design and analyses. Obtain more data as necessary to design a tank liner which serves as an adequate barrier with minimal weight. Numerous materials property issues have arisen in the development process that required the extension of this testing program, and future developments of even thinner liners might require additional measurements that we cannot currently justify (financially) at this time."

Goals of 2×10^{-16} moles per square meter per second for permeability at room temperature and 5000 psi will allow a reduction in liner thickness below the 0.3 inch baseline value. Trying to get better than this would likely compromise other considerations such as processing ease, temperature dependence, etc.

Strain goals are 1% for thousands of cycles.

To meet natural gas vehicle goals (NGV2), they need to show the ability to cycle 15,000 times. LLNL has the capability of performing 10 cycles per minute. They use water as a recycling fluid, as it is much safer than gas.

10. Has any down-selection been performed as to liner material? If so, to what material(s)? What are the relative strong and weak points of these materials?

"Cross-linked high-density polyethylene (XLPE) is our baseline material at this time. No other polymeric material has shown better permeability that can be fabricated into a lightweight high cycle life tank. Other polymer material with lower permeability are brittle and/or require extra processing or protection methods. High cycle life tanks using metal liners tend to be heavier and more expensive than tanks with polymer liners."

Other than polyethylene, the only material that looks somewhat promising at this point is dicyclopentadiene (DCPD). It has many superior properties (toughness, corrosion resistance, wider temperature range, ease of processing), but is not as good a barrier as polyethylene. LLNL is currently looking at "treated" versions of DCPD to reduce permeability.

11. Your FY 2000 AOP submission indicates some planned work with permeation inhibition coatings. Have materials been identified? What type of testing has been done, or is planned?

"Yes, candidate materials have been identified. These include "paint on" layers of low permeability polymers onto molded polymers. We are also examining plated metal coatings onto molded polymers. Samples have been prepared with one paint-on and two plated coatings. Another batch of perhaps two coating approaches will also be assembled shortly. All of these specimens are headed for the SRI permeation testing apparatus. Plans are underway at Thiokol, under an existing (small) DOE-funded contract, to permeation and burst test an integrated 12" vessel with plated liner."

This work, I believe, is critical to the success of the project. It does not appear that polyethylene alone (or perhaps any polymeric material alone) will be satisfactory for meeting goals.

12. Is the liner chemically bonded to the composite tank? If so, what bond tests are being performed?

"No. There may be a chemical bond formed during processing between liner and composite overwrap, but there is no realistic way to test this bond. It is clear that this bond fails during the first few cryogenic temperature cycles applied to Salvador's tanks, without harming their performance. With lightweight liners, the failure of this bond may not be so forgiving, one such failure having lead to a leak path in a prototype (thick XLPE liner, conformable) Thiokol tank. That tank's failure locus does not occur in cylindrical tanks, and no direct effort is anticipated to improve this bond which has worked well on over a dozen gH2 and NG tanks."

At one time, LLNL did make an attempt to bond liner to case, but the debonding created more problems than no bond at all.

13. What material (if it's not proprietary) is being used as the binder material for the carbon fibers in the composite tank?

"TCR® resin UF3325-93 (resin system in prepreg 93% part B - commercial cure = short cure - an 8 hr cure, low part B, therefore more flow, process is proprietary, can store at room temperature for up to ~1 year, 270 °F cure, 2 hour ramp, hold for 4 hr, 2 hour cooldown = commercial cure). Although the epoxies used as matrix materials for advanced composites are not proprietary or exotic, their handling is. Even process recipe duplication may not suffice to duplicate matrix performance. The resin just mentioned was formulated for its (proprietary) handling characteristics, and results in tanks which are tough enough to pass the "bullet test" (part of NGV2) easily."

The resin is a Thiokol product. One of its best properties is its long shelf-life in the uncured (prepreg) state.

14. **In the FY 1999 report, in the “Barriers” section, nothing is indicated as a problem in the tank liner area. Do you believe that standard R&D procedures with materials already identified will lead to meeting your objectives?**

“Yes.”

Our discussions on metal coatings might lead me to believe that they are not there yet. Polyethylene is the liner of choice, but it will either be too thick, or will need an as yet untested metal coating.

V Additional Discussion:

Liner Material and Processing

- Currently, the LLNL group uses rotomolding (a spin-melt molding process) to produce liners. For small numbers of liners, this is the economical way to go, as the tooling costs under $20K. 1-4 parts can be made per hour. For mass produced parts, they would look at injection molding. The tooling is much more expensive (up to $250K), but several parts can be produced per minute. Dr. Mitlitsky is also considering blow-molding. This would produce parts even more quickly, and could also produce thinner parts.

- Dr. Mitlitsky’s suggested that their liner technology could go in one of several directions: Crosslinked polyethylene liner is considered the baseline. From a technical standpoint, polyethylene will likely provide an adequate permeation barrier. However, for safety reasons “the way the rules are written.” it would likely have to be made too thick. Other options are to use a different liner (along with its associated problems), or coat the polyethylene with something (outside, inside or both). Many liner candidates are too expensive and/or are difficult to process. They may be difficult to rotomold or need to be processed in an inert atmosphere, for instance. One suggestion is to bond a metal coating onto the outside of the polyethylene liner material. The metal acts as a secondary permeation barrier. Injection molding may prove a cheap alternative for rotomolding, but LLNL needs someone else to do this. *The likely problem is that they can’t afford the tooling. This appears to be a good indication of the fact that LLNL is not nearly “there yet”. They have both material and processing issues.*

- So far, only polyethylene has qualified as a single-material candidate. LLNL has found that if they use ¼ inch polyethylene inside a composite, they can achieve a leakage of 1 cc/hr per liter of tankage at 5000 psi. This is barely acceptable. (*or may not even be acceptable. My understanding is that DOE wants 0.25 cc*) If you use a metal coating, you should do better by an order of magnitude. This doesn’t include high temperature usage or cycling, however.

- As far as coatings go, one potential candidate is vinylidene – basically, Seran Wrap. The material can be painted on the polyethylene, and exhibits good permeation inhibition – perhaps two orders of magnitude better than polyethylene itself. Metals are even better permeation barriers, but they have lower strain-to-failure values.

- Another option is a liner that is only metal. However, the metal will fatigue and fail before the composite, so the metal cannot be too thin. So you are increasing weight and cost.

- Strains of about 1 percent are needed for tank liners.

- In Dr. Mitlitsky's words, polyethylene "turns to butter" at 7000 psi. The use of a different material at high pressures may be warranted. *I would be concerned at 5000 psi under these conditions.*

- Some polymers including polyethylene, if heated back to the cure temperature, will perform a one time shrinkage of 6-8 percent. This fact needs to be considered when coating the liner.

  It would seem to me that the initial cure cycle is not sufficient to totally crosslink the polymer, and the recycle is finishing the process. The cure cycle should probably be changed to end this problem.

Composites

- An epoxy binder "looks great" until it is pressurized for the first time, then it starts to develop microcracks; that is why you need a liner.

- DCPD is another candidate for composite binder. It is 1-2 orders of magnitude tougher than polyethylene, is less subject to corrosion, and is easier to work with than is epoxy. LLNL thinks they can manufacture a part that won't crack and may work well.

- The tanks they currently can produce can hold 5% hydrogen. They know that they can go higher, but manufacturers think it may be too expensive. For example, they could use T-700 carbon fiber tanks, which costs about $17/pound, they may be able to accommodate 9-10 percent hydrogen.

- T-1000 carbon fiber tanks will get you to 12% hydrogen, but the fiber is $70/lb – a real problem. Perhaps the cost will come down with large volume purchases.

- LLNL has built a prototype tank (with T-1000 fibers), but have not yet burst-tested it. Thiokol, however, did successfully perform an armor-piercing bullet test on a tank at 5000 psi.

- LLNL does not do much large-scale testing on-site. They let Thiokol do it, or hire a contractor.

Regenerative Fuel Cells

This was not the topic of interest for this visit (recall that RFC R&D is not currently being funded at LLNL), but Dr. Blake Myers has a contract to look at safety issues with regard to the SRT/National Power halogen RFC project, and wanted to spend a few minutes discussing the project.

As we know, hydrogen/halogen RFCs can operate at higher efficiencies than their hydrogen/oxygen counterparts. For example, according to Dr. Myers, at 300 amps per square foot, the water system has a round trip efficiency of around 40-50%, while the HBr system is about 64%. *I think the HBr numbers are a little high.* The halogen systems, however, present many additional safety issues. For instance, Dr. Myers recommends complete body coverage in the operating area, and a “clothespin” respirator.

Dr. Myers believes that National Power, with their halogen electrolyzer experience in Europe, is a “great partner for SRT.”

Dr. Myers does not see a problem with bromine supply, citing Great Lakes and Albermarle in the U.S. and Dead Sea Bromine in Israel as the three leading bromine suppliers, each capable of supplying over 300 million pounds of bromine per year. *These three companies account for roughly 80% of the world’s output*. All of these companies have good safety records.

Exhibit 1. From Mitlitsky FY 1999 Report (Table 1)

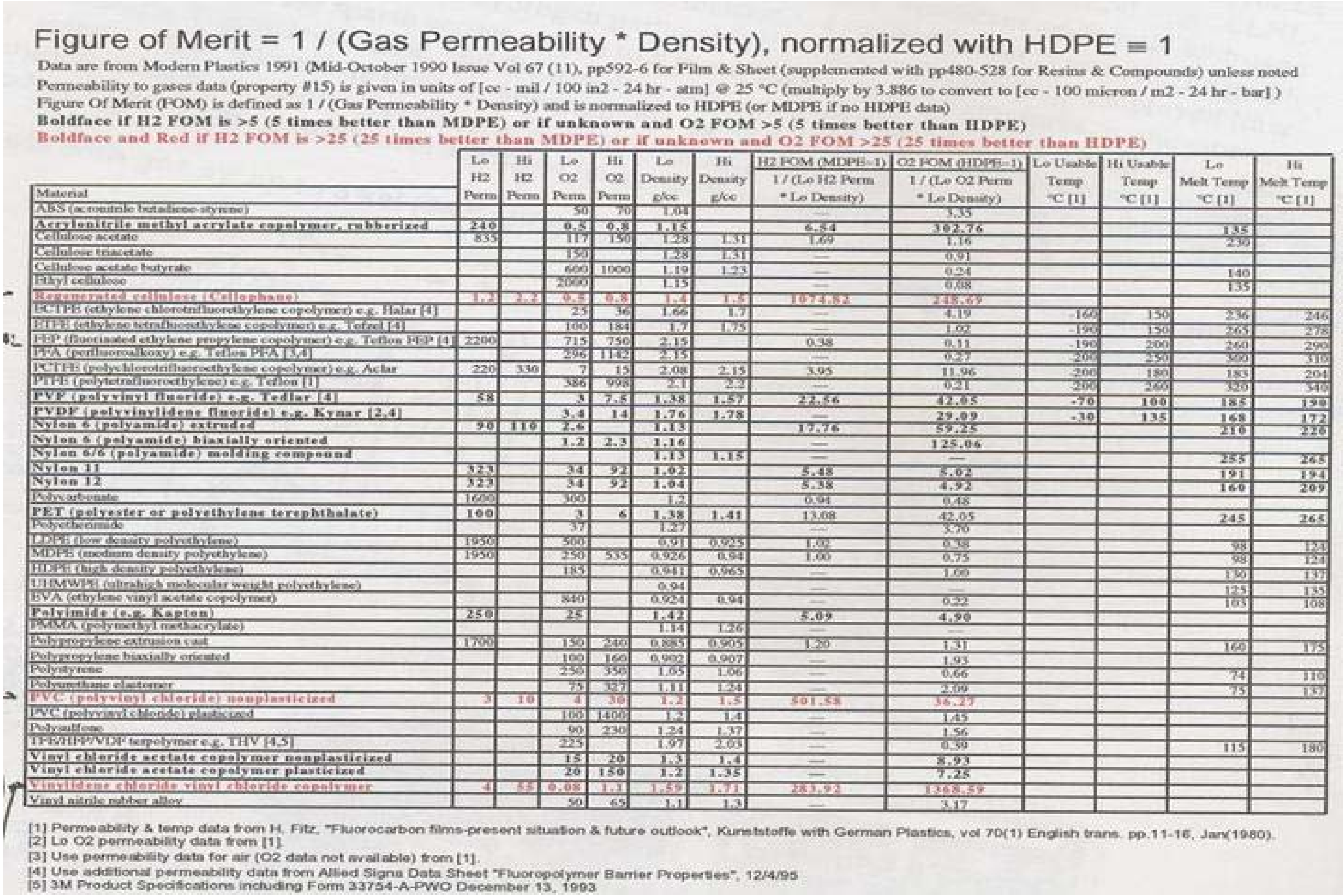


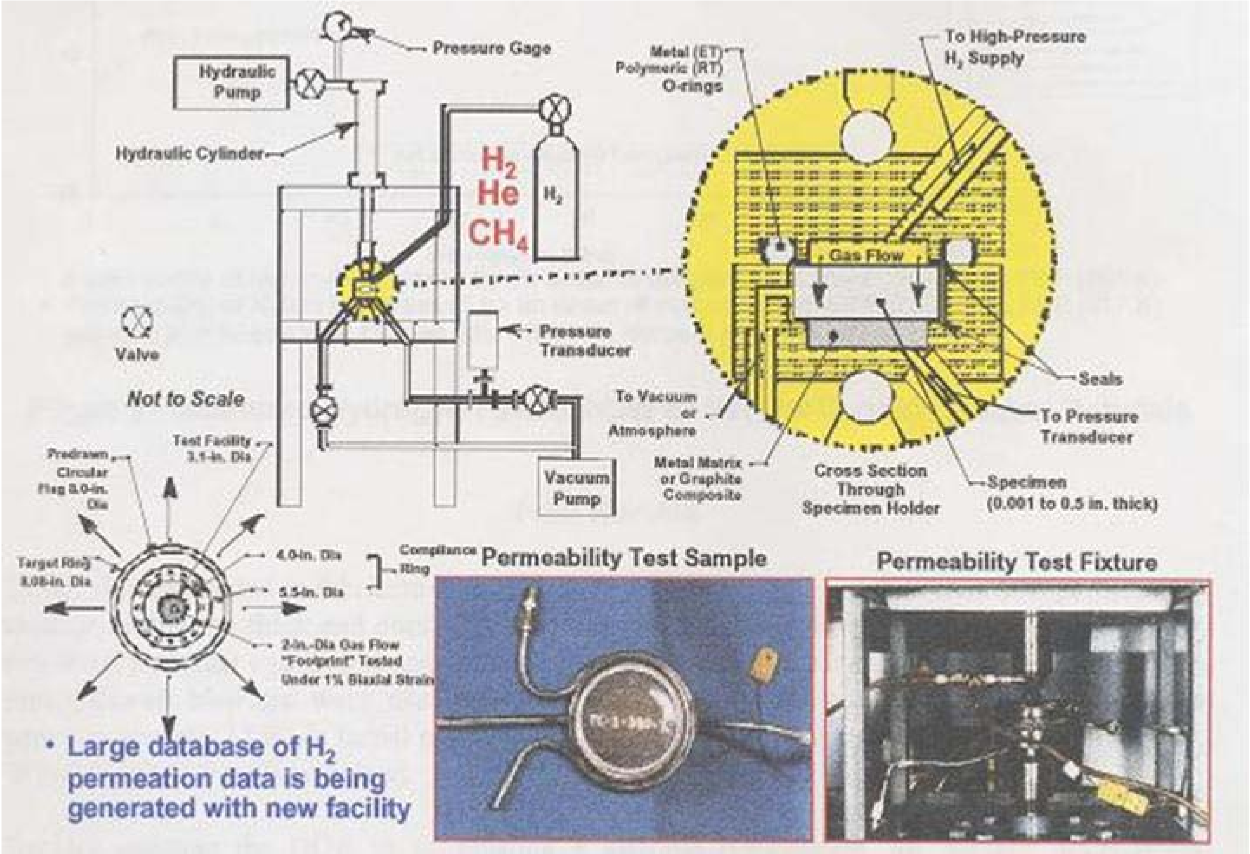
Figure of Merit = 1 / (Gas Permeability * Density), normalized with HDPE ≡ 1

Data are from Modern Plastics 1991 (Mid-October 1990 Issue Vol 67 (11), pp592-6 for Film & Sheet (supplemented with pp480-528 for Resins & Compounds) unless noted
Permeability to gases data (property #15) is given in units of [cc - mil / 100 in2 - 24 hr - atm] @ 25 °C (multiply by 3.886 to convert to [cc - 100 micron / m2 - 24 hr - bar])
Figure Of Merit (FOM) is defined as 1 / (Gas Permeability * Density) and is normalized to HDPE (or MDPE if no HDPE data)
Boldface if H2 FOM is >5 (5 times better than MDPE) or if unknown and O2 FOM >5 (5 times better than HDPE)
Boldface and Red if H2 FOM is >25 (25 times better than MDPE) or if unknown and O2 FOM >25 (25 times better than HDPE)

Material	Lo H2 Perm	Hi H2 Perm	Lo O2 Perm	Hi O2 Perm	Lo Density g/cc	Hi Density g/cc	H2 FOM (MDPE=1) 1 / (Lo H2 Perm * Lo Density)	O2 FOM (HDPE=1) 1 / (Lo O2 Perm * Lo Density)	Lo Usable Temp °C [1]	Hi Usable Temp °C [1]	Lo Melt Temp °C [1]	Hi Melt Temp °C [1]
ABS (acronitrile butadiene styrene)			50	70	1.04		—	3.35				
Acrylonitrile methyl acrylate copolymer, rubberized	**240**		**0.5**	**0.8**	**1.15**		**6.54**	**302.76**			**135**	
Cellulose acetate	835		117	150	1.28	1.31	1.69	1.16			230	
Cellulose triacetate			150		1.28	1.31	—	0.91				
Cellulose acetate butyrate			600	1000	1.19	1.23	—	0.24			140	
Ethyl cellulose			2000		1.15		—	0.08			135	
Regenerated cellulose (Cellophane)	**1.2**	**2.2**	**0.5**	**0.8**	**1.4**	**1.5**	**1074.82**	**248.69**				
ECTFE (ethylene chlorotrifluorethylene copolymer) e.g. Halar [4]			25	36	1.66	1.7	—	4.19	-160	150	236	246
ETFE (ethylene tetrafluoroethylene copolymer) e.g. Tefzel [4]			100	184	1.7	1.75	—	1.02	-190	150	265	278
FEP (fluorinated ethylene propylene copolymer) e.g. Teflon FEP [4]	2200		715	750	2.15		0.38	0.11	-190	200	260	290
PFA (perfluoroalkoxy) e.g. Teflon PFA [3,4]			296	1142	2.15		—	0.27	-200	250	300	310
PCTFE (polychlorotrifluoroethylene copolymer) e.g. Aclar	220	330	7	15	2.08	2.15	3.95	11.96	-200	180	183	204
PTFE (polytetrafluoroethylene) e.g. Teflon [1]			386	998	2.1	2.2	—	0.21	-200	260	320	340
PVF (polyvinyl fluoride) e.g. Tedlar [4]	**58**		**3**	**7.5**	**1.38**	**1.57**	**22.56**	**42.05**	**-70**	**100**	**185**	**198**
PVDF (polyvinylidene fluoride) e.g. Kynar [2,4]			**3.4**	**14**	**1.76**	**1.78**	—	**29.09**	**-30**	**135**	**168**	**172**
Nylon 6 (polyamide) extruded	**90**	**110**	**2.6**		**1.13**		**17.76**	**59.25**			**210**	**220**
Nylon 6 (polyamide) biaxially oriented			**1.2**	**2.3**	**1.16**		—	**125.06**				
Nylon 6/6 (polyamide) molding compound					**1.13**	**1.15**	—	—			**255**	**265**
Nylon 11	**323**		**34**	**92**	**1.02**		**5.48**	**5.02**			**191**	**194**
Nylon 12	**323**		**34**	**92**	**1.04**		**5.38**	**4.92**			**160**	**209**
Polycarbonate	1600		300		1.2		0.94	0.48				
PET (polyester or polyethylene terephthalate)	**100**		**3**	**6**	**1.38**	**1.41**	**13.08**	**42.05**			**245**	**265**
Polyetherimide			37		1.27		—	3.70				
LDPE (low density polyethylene)	1950		500		0.91	0.925	1.02	0.38			98	124
MDPE (medium density polyethylene)	1950		250	535	0.926	0.94	1.00	0.75			98	124
HDPE (high density polyethylene)			185		0.941	0.965	—	1.00			130	137
UHMWPE (ultrahigh molecular weight polyethylene)					0.94		—	—			125	135
EVA (ethylene vinyl acetate copolymer)			840		0.924	0.94	—	0.22			103	108
Polyimide (e.g. Kapton)	**250**		**25**		**1.42**		**5.09**	**4.90**				
PMMA (polymethyl methacrylate)					1.14	1.26	—	—				
Polypropylene extrusion cast	1700		150	240	0.885	0.905	1.20	1.31			160	175
Polypropylene biaxially oriented			100	160	0.902	0.907	—	1.93				
Polystyrene			250	350	1.05	1.06	—	0.66			74	110
Polyurethane elastomer			75	327	1.11	1.24	—	2.09			75	137
PVC (polyvinyl chloride) nonplasticized	**3**	**10**	**4**	**30**	**1.2**	**1.5**	**501.58**	**36.27**				
PVC (polyvinyl chloride) plasticized			100	1400	1.2	1.4	—	1.45				
Polysulfone			90	230	1.24	1.37	—	1.56				
TFE/HFP/VDF terpolymer e.g. THV [4,5]			225		1.97	2.03	—	0.39			115	180
Vinyl chloride acetate copolymer nonplasticized			**15**	**20**	**1.3**	**1.4**	—	**8.93**				
Vinyl chloride acetate copolymer plasticized			**20**	**150**	**1.2**	**1.35**	—	**7.25**				
Vinylidene chloride vinyl chloride copolymer	**4**	**55**	**0.08**	**1.1**	**1.59**	**1.71**	**283.92**	**1368.59**				
Vinyl nitrile rubber alloy			50	65	1.1	1.3	—	3.17				

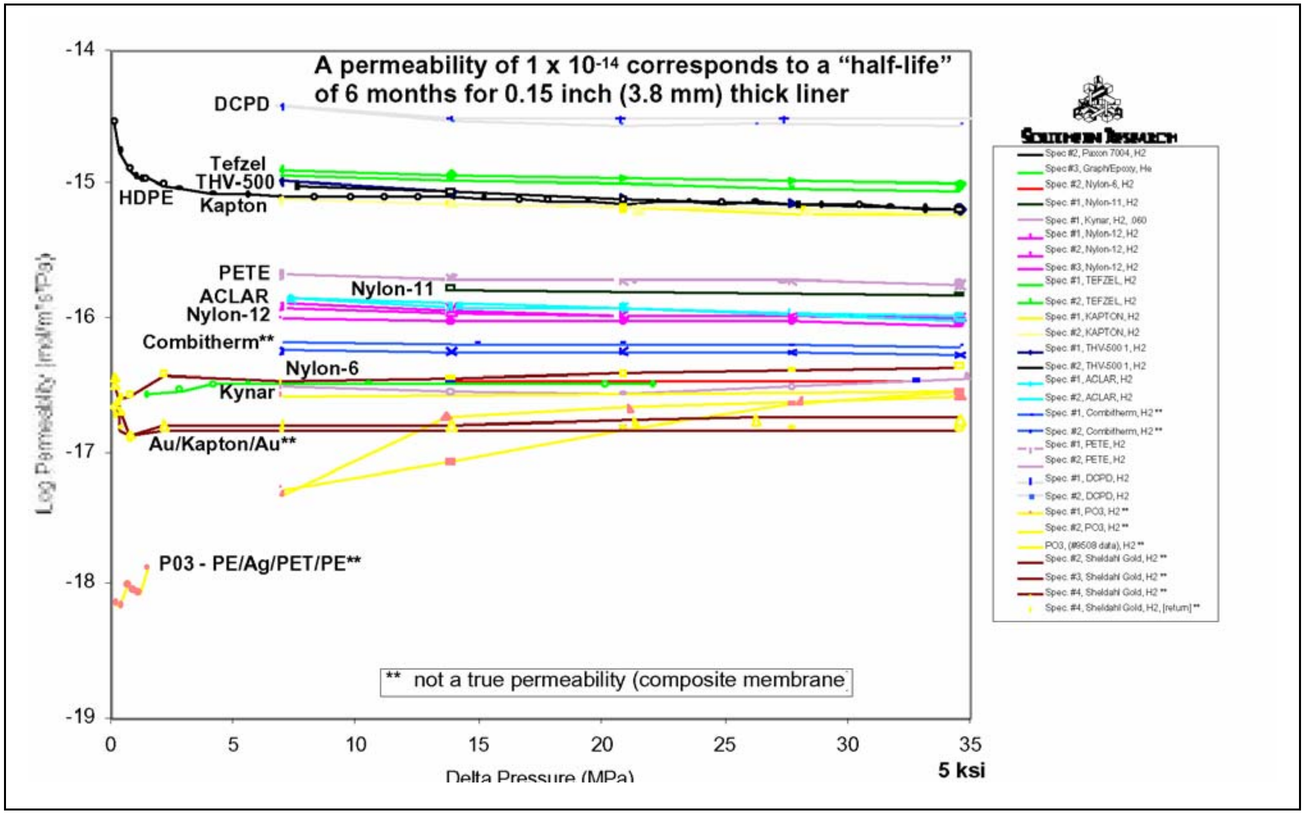
[1] Permeability & temp data from H. Fitz, "Fluorocarbon films-present situation & future outlook", Kunststoffe with German Plastics, vol 70(1) English trans. pp.11-16, Jan(1980).
[2] Lo O2 permeability data from [1].
[3] Use permeability data for air (O2 data not available) from [1].
[4] Use additional permeability data from Allied Signa Data Sheet "Fluoropolymer Barrier Properties", 12/4/95
[5] 3M Product Specifications including Form 33754-A-PWO December 13, 1993

Exhibit 2. Permeability Test Fixture From Mitlitsky FY 1999 Report (Figure 8)



- Large database of H_2 permeation data is being generated with new facility

Exhibit 3. Measured Hydrogen Permeability From Mitlitsky FY 1999 Report (Figure 9)



This page intentionally left blank.

Technical Evaluation Report

Project: Conformable Tanks for Hydrogen Storage
Company: Thiokol Propulsion, Brigham City, UT
P.I: Andrew Haaland (Site-Visit Host: Mark Warner)
Date of Visit: September 6, 2000
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

Thiokol's forte in designing and building composite cases for solid propellant rocket motors has led them to investigate similar tanks that can be used for storing hydrogen. Because volume of storage is a key parameter on board a vehicle, Thiokol is developing the idea that the hydrogen tanks should be conformable. That is, they should be shaped in a manner so as to maximize storage within the given area. Although a single cylinder would optimize volume on its own, multiple cylinders represent non-optimal volumes due to the interstitial spaces.

Thiokol has had a program in which they designed and developed conformable tanks that could hold 5,000 psi hydrogen. The present issue involves the use of conformable tanks that can hold 10,000 psi hydrogen.

There are two questions that must be asked: What are the benefits/disadvantages of 10,000 psi conformable tanks compared to 5,000 psi conformable tanks, and what are the benefits/disadvantages of 10,000 psi conformable tanks compared to 10,000 psi cylinders?

Project Strengths:

- Thiokol is one of the world leaders in the design of composite cases. If conformable composite cases are "the way to go," Thiokol is an excellent choice.
- Conformable tanks provide the potential for about 20% more hydrogen in a given envelope, at a given pressure.
- Designs for 10,000 psi tanks, both cylindrical and conformable, indicate that they will each hold about 67% more hydrogen on a volumetric basis than their 5,000 psi counterparts within their envelope. (The increase in hydrogen on a weight percent basis is small (7-10%) due to the more than 50% increase in the weight of the tank necessary to accommodate the higher pressure. This in itself, however, should not be viewed as a serious negative; the key is envelope energy density, not weight percent hydrogen.)
- The additional energy necessary to compress to 10,000 psi is not a show-stopper; for conformable tanks, it increases from 6.3% of the hydrogen that is to be compressed to 7.7%.

Issues that should be Addressed:

- Thiokol is basing aging characteristics on models. While they have shown very good correlation of models with past data, the effect of exposure to hydrogen is not part of the model. While Thiokol recognizes that aging studies that include hydrogen exposure need to be performed eventually, I believe they are of utmost importance in selecting liner material now.

- The tank design information was not easy to follow. (This, of course, does not make the design unacceptable. It just made interpretation difficult.)

- Going from 5,000 psi to 10,000 psi for either conformable or cylindrical tanks requires about a 50% increase in tank weight (a little worse for conformable tanks than for cylindrical tanks.) Note that I don't consider the small increase in hydrogen weight percentage (5.8% to 6.2% for conformable design) an issue, but the increase in tank weight itself, together with the higher materials costs may not be worth the relatively modest increase in range over Lawrence Livermore National Laboratory's (LLNL) design for a single cylinder at 5,000 psi (see analysis at end of report.)

- Even if all safety requirements are met, I am concerned about the public perception of a 10,000 psi tank – conformable or cylindrical.

- I am not at all sure that the Thiokol people themselves (or at least some of them) believe in 10,000 psi tanks.

II Introduction and Background:

I met with **Mark Warner**, Senior Principal Engineer on the conformable tank project. (The project PI, Andy Haaland, was unable to be present.) We discussed the conformable tank project in detail emphasizing 10,000 psi design. Our meeting included detailed discussion of a series of questions that I had previously forwarded as well as some more general discussion. In addition, I was given a tour of the conformable tank laboratory as well as some more general Thiokol production and diagnostic facilities.

Thiokol's work with conformable tanks originated from a meeting that they held with Chrysler in 1993. Chrysler was looking for a "square" propane tank for their RAM van. Thiokol built aluminum tanks with aerospace-quality welds for Chrysler. The filled propane tank weighed less than a steel tank full of gasoline. Thiokol built about 200 propane tanks for Chrysler, and then the project was stopped. The key to the success of the Thiokol propane tank design was the development of an interlocking joint design. This reduced both the cost and weight of the tank.

Aside from the tank for Chrysler, a 3-cell model, Thiokol has made two and four cell liquid propane tanks for Ford and GM. These have been ASME-certified.

Later, Thiokol had two conformable tank programs, one with Brookhaven for a 3,600 psi conformable compressed natural gas (CNG) tank, and one with NREL for a 200 psi propane tank. They tried to develop an injection-molded tank and were unsuccessful. Later, they were trying to mold onto a braided fiber, but ran out of money. Part of the Brookhaven project involved the development of a tank liner that would adsorb natural gas.

Thiokol made a decision that they would be "the conformable tank people." As part of their overall conformable tank program, Thiokol has had a DOE Hydrogen Program project to design and build conformable hydrogen tanks for use at 5,000 psi.

III Initial Discussion:

Conformable Tank Design:

Mr. Warner presented some basic design parameters for the 5,000 psi conformable tank. Conformable tanks, as shown in Exhibit 1 can provide a more efficient use of space than cylindrical tanks. Over 80% of the envelope volume can be used. This is especially true when the design would call for a tank volume that would require the inclusion of a fraction of a cylinder.

The overall design for conformable hydrogen tanks is very similar to that for CNG tanks with the exception that the hydrogen tank is thicker to allow for the higher pressure. Testing is essentially the same for the two types of tanks.

The "standard" tank that Thiokol developed for CNG and hydrogen is a two-cell model having a weight of 22.7 kg and an internal volume of 68 liters. It is meant to meet the NGV2-1998 test standards. Its service pressure can be either 3,600 or 5,000 psi, with a minimum 2.25X safety factor. Its cycle life design is 20 years.

IV Tour:

Mr. Warner gave me a tour of the appropriate facilities at Thiokol. For this tour, we were joined by team members **Darrel Turner** and **David Nelson**. Their "Composite Building" works on everything from resin up through the actual part – real parts for real applications. They can wind up to 37 inch diameter pressure vessels in this building. Larger composite cases (up to 160 inch diameter) are wound in a separate building. Most of their composite work involves carbon fibers, but they also work in glass, Kevlar (aramid), and polybenzoxazole (PBO) fiber.

Within the Composite Building are several winding stations utilizing four winding machines and state-of-the-art winding programs. Several different low cost mandrel technologies are also studied here. These include sand, foam, other "washout" materials, and plastic mandrels. Test specimens are also manufactured here.

Thiokol usually uses 5¾ inch diameter cases as materials testing specimens. If building motor cases, they will then generally scale up to 12,, 18, and 37 inches.

Much of the conformable tank work is done in this building as well. I saw several conformable polyethylene liners and conformable tanks as well. Typically the individual cells of the conformable case are held together with some carbon composite overwrap. A glass composite layer is wound over the top of this for labeling purposes. Mr. Warner mentioned that Fred Mitlitsky (formerly of LLNL) thought that this made the overall system too heavy. The tank assembly also has foam endcaps and more foam in the open areas between the cells. Foam protects the tank during impact and also prevents a tank mounted on a car from collecting road debris between the cells.

I also visited the "foam lab" and saw the foam-application operation. The type of foam and the application process is proprietary to Thiokol.

V Questions and Answers:

Mr. Warner and I spent several hours in discussion, a large part of which was devoted to the previously forwarded questions shown below.

1. **Compare conformable tanks with cylinders using 5000 psi designs and 10,000 psi designs. Also compare tradeoffs for 5,000 vs. 10,000 psi conformable tanks. Consider energy density by weight and volume, cost, and safety issues, real and perceived. What are the critical design issues that need to be considered in going from 5,000 to 10,000 psi?**

Design comparisons were presented, and are summarized in Exhibit 2. The 10,000 design is preliminary. They had just completed it at the time of my visit. These data represent an envelope aspect ratio of 1.6 (that is, equivalent to 1.6 cylinders will fit in the envelope.)

The 1.6 aspect ratio is close to a worst case scenario, but I think it is a fair number to use to sell the conformable concept.

The data in Exhibit 2 are somewhat difficult to follow, but we can see the case for conformable tanks over cylinders lies in the fraction of the system that carries hydrogen (V/V_e). This also manifests itself as the weight of hydrogen in the system (which would, of course be directly proportional to V/V_e assuming the pressure is constant.)

There is some concern with the meaning of some of the data in Exhibit 2. For instance, envelope energy density is a key parameter; it is the amount of energy available in the overall available space. Exhibit 2 shows that for a conformable tank system at 5,000 psi, the envelope energy density is 435 wh/liter. The same column shows that the ratio of the tank volume to the envelope volume, V/V_e, is 58%. If that is the case, the energy density of a tank would be 435/0.58 = 750 wh/liter. The table lists the energy density for a tank as 555 wh/liter. We have since learned that the 555 wh/liter number is based on the external tank volume; it has nothing to do with the V/V_e ratio of 58%. While energy density based *on external tank volume is a valid parameter for a single tank, it appears to be more or less meaningless in a situation where you have several cylindrical or conformable tanks. It's the envelope energy density that matters.*

Energy density data in Exhibit 2 do not include the weights of polar bosses, foam filling, and other ancillaries that would add a few pounds to the weight of the system.

Not included in the calculations is an additional advantage for conformable tanks over cylinders. The cylinders need to be kept somewhat apart from one another (perhaps about one-quarter inch) to allow for mounting brackets. The conformable tanks do not need this separation.

The biggest issue at 10,000 psi according to Mr. Warner is tank wall thickness. Tank volume is down compared to 5,000 psi. *It's down 11.6% for cylindrical tanks and 12.2% for conformable tanks.*

Liner durability is also very important. First of all, it may be necessary to pre-stress the liner to allow it to handle 10,000 psi. In addition, aging, creep, fatigue, and embrittlement are issues. Thiokol believes that exposure to hydrogen will shorten the liner's fatigue life at even 5,000 psi. At 10,000 psi it could be a serious problem.

I believe liner exposure to hydrogen could be the biggest showstopper for polymeric liners at high pressure – 5,000 OR 10,000 psi. Yet long term aging data in the presence of hydrogen are sorely lacking, both in the Thiokol project and elsewhere.

Other matters to consider at 10,000 psi include hardware issues – pressure relief devices and valves, for example. Also, sealing issues increase in importance at the higher pressures. The polar boss seal is an o-ring seal in the Thiokol design. At 10,000 psi, Mr. Warner believes, they will need to back it up. In addition, working at 10,000 psi is difficult because there are no standards at this pressure.

Many design issues are the same or similar for cylinders and conformable tanks. Mr. Warner says that they have been performing much of the conformable tank design using cylinder equations. One exception is the increased effort that Thiokol puts into looking at membrane loading. He expects it to be much the same at 10,000 psi.

Specifically on safety and cost, Mr. Warner says that it is too early to address cost, and that safety issues will again come back to NGV2 standards.

Overall, Mr. Warner says about 10,000 psi conformable tanks: "It can be done. I think we can get there, but it will take some work."

2. **If you were to make 10,000 psi conformable tanks for on-board hydrogen storage, how would you "sell" it to industry; to the public?**

10,000 psi conformable tanks would need to be sold on safety and cost. Mr. Warner mentioned the Hindenburg, Space Shuttle, and leakage issues (a quote he used was "the only hydrogen tank that doesn't leak is an empty tank.") as the hydrogen fears that would have to be overcome. 10,000 psi hydrogen would have to be shown to be less expensive per mile that 5,000 psi hydrogen or liquid hydrogen.

The major added problem at 10,000 psi would be that in a catastrophic failure, there would be a greater energy release and a larger damage zone. The damage zone would likely be most sensitive to the location of the tank. The likelihood of a catastrophic failure, however, would be less with a pressurized tank. Pressurizing the tank actually helps to stabilize it. Drop tests work "better" with pressurized than unpressurized tanks.

(*Yes, but do they work better at 10,000 psi than at 5,000 psi? I'm not sure of that.)*

If the tank were punctured, the mass flow would be higher, but the velocity would be the same, so the flame (if the gas were ignited) would be the same.

Mr. Warner feels that it may be worth spending some time and money to actually compare how much energy is released if a tank comes apart at 5,000 psi vs. 10,000 psi. *If 10,000 psi conformable tanks were to become a reality, this would be a necessity.*

3. **Have the materials and processing methodology used to make the conformable tanks been used by Thiokol for any other projects/purposes?**

Thiokol has made several composite rocket motor cases including the Castor 120, the Trident, and the Peacekeeper. They have also used TCR composites (the material that is being used in the conformable tank program) to manufacture ski poles, golf clubs, and other commercial materials. TCR composite uses a Thiokol-developed resin that will not cure (crosslink) at room temperature (an earlier serious problem.) It is stable at room temperature for a year; a temperature of 250°F is needed to cure the resin. *More information about TCR is available at the Thiokol website:* http://www.thiokol.com.

The fiber in the composite is M30-S. A carbon tow fiber which, at $27/lb, costs about one-third as much as the high strength "Cadillac" of carbon fibers – T-1000. Mr. Warner mentioned that in high production, they would likely downgrade to T-700 fiber which costs $17/lb. He believes that this would even be possible for the 10,000 psi tanks.

Thiokol has found that the prepreg (uncured resin) has sufficient tack to allow wrapping of the composite on the liner without slippage.

Thiokol also has abundant tank liner experience, having rotomolded 18 inch test bottles and 37 inch motor case liners. In fact, the rotomolded liner technology that they developed for conformable tanks is actually being "rolled back" into their defense work in the form of insulated rotomolded thermoplastic liners.

4. **Is there any data available on the effect of long term storage of hydrogen in conformable tanks (i.e., either real time or accelerated aging tests)? At ambient temperature? Or as a function of temperature? Please consider the properties of the plastic liner as well as the overwrap when we discuss this.**

There have been no aging studies performed to date that consider the effects of hydrogen. Mr. Warner feels that these tests can come later, given the fact that Thiokol has a large database of rocket motor aging that they can use as models. Very impressive predictions were presented for long term aging and cycling of many motor components including composite cases, o-rings, liners, and propellant grains as well as bondline interfaces. In fact, tank designs were based on rocket motor fatigue studies, and these studies were used as part of the liner material screening process.

The amount of work and data present to develop the models are certainly noteworthy and serve as a good step toward addressing aging issues. I believe, however, that it is a mistake to not move rapidly to actual hydrogen-based aging tests given hydrogen's reactivity and penetration capability as well as the pressures involved. Models are fine, but some real tests are needed. Aside from real safety concerns, perceived safety concerns are a big problem for hydrogen. Models that do not include exposure to hydrogen - high pressure hydrogen - will not mollify doubters.

5. **What material is the liner?**

The baseline liner material is crosslinked polyethylene. Many others polymeric liners have been studied as well, including Nylon 12, Nylon 11, Nylon 6, and Kynar (polyvinylidene fluoride). Aluminum liners were considered, but the cost for the tooling to manufacture conformable aluminum liners was deemed prohibitive. Coated liners, with the coating meant to reduce hydrogen penetration without adding much weight and thickness are another option.

If this looks very similar to some of the work being done at Lawrence Livermore National Laboratory (LLNL), that is because much of the liner work was done in conjunction with LLNL.

6. **What was the failure mode for the tanks in the burst tests?**

Hoop failure within the cylinder.

As desired. No "weak links" in the dome areas or near joints were identified.

7. **How robust are the tank shapes? Can they be (or do they need to be) easily modified for vehicle design changes that could occur in years to come?**

The shapes are quite robust. The center cells (*the ones with the flat sides*) can be repeated as needed. It isn't necessary, however, to maintain the rectangular nature of the center cells. For instance, it would also be easy to do a wedge-shaped cell.

Mr. Warner sees little in the way of additional problems. He believes that Thiokol would be able to work with vehicle designs in the future and build more efficient conformable tanks cheaply.

A single cell can carry about 1.5 times its service pressure before it will rupture. In addition, since it is a multicell system, a rupture to one cell would not effect other cells.

8. **Although the use of a sand mandrel is low cost for making a few tanks when compared to machined mandrels, the fact that the sand mandrel can only be used once would make it an unlikely candidate for mass producing tank liners and tanks. What type of hardware would be used for mass production?**

Sand mandrels were just used as a proof-of-concept tool. For production, they have/will invest in permanent tooling. In fact, once they got comfortable, they moved to rotomold molds.

VI Additional Discussion:

Thiokol is interested in pursuing conformable composite pressurized cryogenic tanks. Mr. Warner feels that this may be where "the future may be." *(-or does this mean that the future is not with high pressure conformable tanks??)* Thiokol has some thermoplastics that are rotomoldable and that will withstand cryotemperatures. Mr. Warner visualizes a plastic liner, composite inner tank, and a metal outer tank – a Dewar effect.

Currently, Thiokol has a wound composite tank made with a thin aluminum liner that has held 100 pounds of cryogenic hydrogen. The tank itself weighs 60 pounds. It does not have an outer metal tank as it is designed for space applications where "space acts as the Dewar." If it were to be built for normal use, where the outer insulating tank was needed, the tank weight would be doubled. *That's still 45% by weight hydrogen, if the numbers are right.*

Mr. Warner mentioned that Thiokol is considering looking for funding for a conformable, pressurized cryogenic tank, saying that this concept "makes more sense than 10,000 psi [does]." *Again, interesting choice of words. Does this mean that Thiokol does not really believe that 10,000 psi makes sense?* Thiokol has data that shows that a conformable cryogenic tank will be more efficient than a series of cryogenic cylinders. There is no bond coat between the polyethylene liner and composite tank.

VII Final Thoughts:

Following the site visit, I considered two key factors in taking hydrogen to 10,000 psi instead of 5,000 psi: the amount of compression necessary, and the increased driving range gained. These are discussed below.

Compression Work:

Although it takes more energy to compress hydrogen to 10,000 psi than to 5,000 psi, the additional work does not appear to be prohibitive.

The work required for compression, $w_{t,\ ith}$, *for isothermal compression (cooled chamber compression) is calculated according to:*

$$w_{t,\ ith} = R_{H2}\ T\ Z\ \ln\ (p_2/p_1)$$

Where:

R_{H2} = *4124 J/kgK (hydrogen gas constant)*
T = *Temperature = 298 K (assuming ambient conditions)*
Z = $(K(p_1) + K(p_2)/2K(p_1)$ *(Correction factor for hydrogen gas with* $K(p) = 1 + p/150$ *MPa)*
p_2 = *Compression level (MPa)*
p_1 = *initial pressure = 14.7 psi (0.101352 MPa), (assuming ambient conditions)*

Wt (5000 psi (34.373 MPa) = (4124)(298)*(1.12)*ln (34.373/0.101352)*
= 8,019,647 J/kg = 2228 wh/kg = 1011 wh/lb

Wt (10000 psi (68.948 MPa) = (4124)(298)*(1.23)*ln (68.948/0.101352)*
= 9,859,495 J/kg = 2739 wh/kg = 1248 wh/lb

To get 3.6 lbs of hydrogen into a 5,000 psi conformable tank, you would need 1011 x 3.6 = 3640 wh of energy. The 3.6 lbs of hydrogen would provide 3.6 lb x 14920 wh/lb = 53712 wh of energy. So it would take 3640/(3640+53712) =

6.3% of the energy to compress to 5,000 psi.

To get 6.0 lbs of hydrogen into a 10,000 psi conformable tank, you would need 1248 x 6.0 = 7488 wh of energy. The 6.0 lbs of hydrogen would provide 6.0 lb x 14920 wh/lb = 89520 wh of energy. So it would take 7488/(7488+89520) =

7.7% of the energy to compress to 10,000 psi.

Driving Range:

We can also compare the range that one could drive using Thiokol or alternative tanks in a "standard" fuel cell vehicle.

The envelope volume that can be backed out from Exhibit 2 is 123.5 liters (32.6 gallons):

For example, using the data for weight of hydrogen and envelope energy density for the 5,000 psi conformable tank:

[3.6 lb H_2 x 14920 wh/lb H_2 (LHV)] / [435 wh/l] = 123.5 liters

Performing the same exercise with the cylinders and with the 10,000 psi cases also result in the same number, confirming that Thiokol is using a constant envelope volume.

This volume is about twice that of a standard gasoline tank for an automobile. At 10,000 psi, this envelope would hold 6.0 pounds (2.72 kg) of hydrogen with the conformable tank design. At 95 miles per kg H_2 for a fuel cell vehicle, this provides a range of about 260 miles. (A hypothetical 123.5 liter (32.6 gallon) gasoline tank at 30 mpg gasoline would have a range of 975 miles.)

Looking, for comparison, at the LLNL lightweight cylinder design (we reviewed this project in March 2000) they talk of a scenario where there is a single cylinder 18 inches in diameter (outside) and 48 inches long that is filled with 8.5 pounds of hydrogen to 5,000 psi. This would have a range of about 366 miles. The outside volume of this tank is about 200 liters ($\pi r^2 h = \pi$ x 81 x 48 x 0.0164 liters/in^3 = 200.3 liters). The inside volume can be calculated from the weight and pressure of hydrogen, assuming hydrogen to be a perfect gas:

8.5 lb H_2 x 0.4536 kg/lb x 500 moles H_2/kg x 22.4 liters/mole at STP

= 43183 liters H_2 at STP. (V_1)

$V_2 = V_1P_1/P_2$ (Boyle's law): 43183 liters x 14.7 psi/ 5000 psi = 127 liters inside volume.

Thus, the "envelope" is 127/200.3 = 63.4%. The envelope energy density, calculated for the LLNL tank the same way as Thiokol did for their tanks results in:

[8.5 lb H_2 x 14920 wh/lb H_2 (LHV)]/ 200.3 liters = 633 wh/liter

If the envelope size were the same as with the Thiokol tanks, 123 liters, the LLNL tank would hold 123.5/200.3 x 8.5 lb = 5.24 lb H_2 (2.38 kg), a 226 mile range.

Exhibit 3 summarizes the various driving range comparisons we have been discussing. The data indicate that if the vehicle design can use a single cylinder, it is preferable. A conformable tank arrangement at 10,000 psi will only provide 32 more miles of range than will a single (LLNL) cylinder of equivalent envelope and 5,000 psi.

Exhibit 1 Comparison of Cylindrical and Conformable Tanks

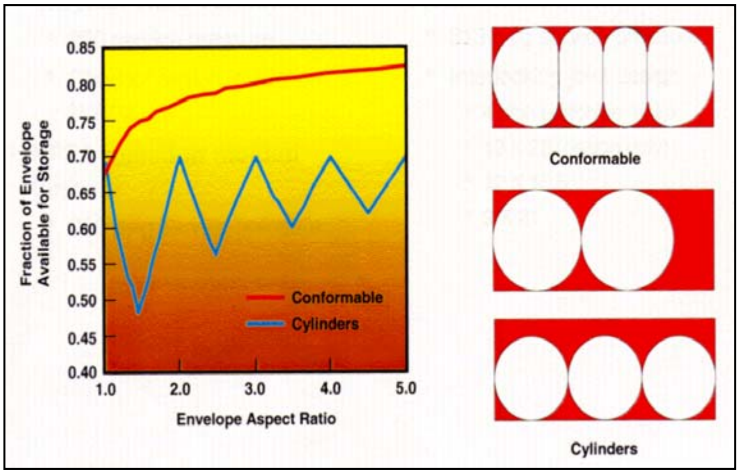


Exhibit 2. Comparison of Conformable and Cylindrical Tanks at 5,000 and 10,000 psi

Parameter	**5000 psig Design**			**10,000 psig Design**		
	Conformable	**Cylinders**	**Advantage of Conf. (%)**	**Conformable**	**Cylinders**	**Advantage of Conf. (%)**
Tank Volume, V (in^3)	4,367	3,520	24.1	3,834	3,109	23.3
Tank Wt, W, (lb)	58.3	46.8	-24.6	90.6	71.3	-27.0
Composite Wt., $W_{c,}$ (lb)	38.5	29.2	-31.9	72.2	54.9	-31.5
Fiber Wt. (lb.)	26.6	20.1	-31.9	49.8	37.9	-31.5
Liner Wt. (lb.)	19.8	17.6	-12.5	18.4	16.4	-12.1
PV/W	936,771	941,122	-0.5	1,058,453	1,090,111	-2.9
PV/W_c	1,417,873	1,508,049	-6.0	1,328,325	1,416,022	-6.2
V/V_e	58%	46%	24.1	51%	41%	23.3
$PV/W(V/V_e)$	540,293	437,541	23.5	536,026	447,616	19.8
$PV/W_c(V/V_e)$	817,773	701,114	16.6	672,695	581,440	15.7
Energy density (wh/l)	555	584	-4.9	926	980	-5.5
Specific Energy (wh/kg)	1,924	1,933	-0.4	2,057	2,114	-2.7
H_2 mass fraction (%)	5.8	5.9	-0.4	6.2	6.4	-2.7
Wt. of H_2 (lb)	3.6	2.9	24.1	6.0	4.9	23.3
Envelope Energy Density (wh/l)	435	351	24.1	727	589	23.3

P = Burst Pressure
V_e = Envelope volume
W_c = Weight of Composite

Exhibit 3. Driving Range Comparisons

Design	Parameters	Driving Range (Miles, based on 95 miles/kg H_2)
Thiokol	Cylinders, 5,000 psi	125
Thiokol	Conformable, 5,000 psi	155
Thiokol	Cylinders, 10,000 psi	211
Thiokol	Conformable, 10,000 psi	258
LLNL	Single Cylinder as designed 200.3 liter envelope, 5,000 psi	366
LLNL	Single Cylinder at envelope equivalent to Thiokol (123.5 liters), 5,000 psi	226

Technical Evaluation Report
Project: Hydrogen Composite Tank Program
Company: Quantum Technologies, Irvine CA
(a subsidiary of IMPCO and formerly known as IMPCO)
P.I.: Dr. Neel Sirosh
Date of Visit: February 20, 2001
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

Quantum Technologies is a wholly owned subsidiary of IMPCO. This new status came into being the day before my visit. Quantum is a "Tier 1" (or as they call themselves because they deal with vehicle level validations, a "Tier 0.5") supplier to automotive original equipment manufacturers (OEM). Among their areas of expertise is development and manufacture of composite tanks for the automotive industry. As experts in the manufacture of vehicular fuel (including "advanced" fuel) metering and storage equipment, Quantum understand the workings of the automobile industry and what is needed to develop a fuel storage system, and to get it up to specification, as well as validating, certifying, and manufacturing it.

Quantum has a contract with the DOE Hydrogen Program to develop, manufacture, and deliver a series of high-pressure hydrogen storage tanks. Goals are to produce tanks at 5,000 and 10,000 psi, holding 7.5–8.5 weight % hydrogen. They also produced one tank last year which was loaded to 11.3 % – a "world record!" Such tanks may be impractical, however, and Quantum personnel seemed to think that 8.5% might be more realistic.

Project Strengths:

- Quantum is well into aging tests. Many recognize the value of aging tests, but up until now, most similar projects I've evaluated have not considered aging as a priority issue in the short term. Hydrogen is highly reactive/corrosive in the presence of a variety of materials. Evaluating how prolonged exposure to hydrogen (not to some inert gas) will affect liner and tank material (since the liner is not entirely leak-proof) under a wide variety of conditions (cycling, temperature, pressure) is of prime importance. Quantum recognizes this, and is acting accordingly.

- Quantum appears to have designs that will result in very high hydrogen energy densities.

- Quantum's patented in-tank high-pressure regulator (see discussion below) is a very important safety feature that removes a concern present with many standard regulators on high-pressure tanks. The standard outside-the-tank regulator represents a weak point in an overall system. It is easier to knock off a regulator than it is to damage a tank.

- Quantum's overall commitment to quality control proved by a detailed paper trail is impressive.

Issues that should be Addressed:

- For the most part, I have very few concerns. One I do have, however, was the reaction to the mention I made of hearing about a catastrophic failure involving a Quantum tank being tested by another laboratory. (See Question 5 for details.) I would expect Quantum to have a more definitive answer than that it wasn't a real test, and they do not know why it was run. It may have been a bad test. It was, however, a catastrophic failure.

- I would recommend that Quantum look closely for any signs that bonding their liner to the composite could cause failures down the road.

- As I stated in my Thiokol report: the public perception of a 10,000 psi tank cannot help but be an issue.

II Introduction and Background:

My site visit to Quantum included a practically all day meeting with members of their Advanced Fuel Storage Group. The visit included tours of their Irvine and Lake Forest facilities.

Participants in the day's activities included **Dr. Neel Sirosh**, Director of Fuel Storage Systems, who was my principal point of contact; **Aleck Papanicopolous**, Development Program Supervisor; **Dwayne French**, Marketing Manager, who provided most of the general information on Quantum and who took me on the tour of the Lake Forest Facility; **Andre Fregeau**, Program Manager for the DOE program, who acts as an interface between technical and contract personnel; and **Maggie Vigil**, Program Analyst.

Mr. French informed me that as a company, IMPCO has been around since 1958 and is the largest manufacturer of gas equipment for the vehicular industry. The new subsidiary, Quantum, has taken over the work of providing high tech and systems development for fuels for internal combustion engines (ICE) and fuel cells. They produce platforms for liquid propane, compressed natural gas, and fuel cells, with General Motors being their principal customer. They are also responsible for power train control. In some cases, Quantum is the manufacturer of record for the gaseous fuel system.

Quantum's Irvine facility houses their fuel metering and fuel storage technology and subsystems development. In Lake Forest, CA, about 20 minutes away, they work on vehicle design concepts and power train controls. Quantum also has a site in Sterling Heights, Michigan, which serves as a focal point for their OEM customers. They also manufacture light systems in Mexico. They have an Advanced Research and Production Development Division and an Automotive OEM Division.

The Advanced R&D group is involved in the development of gas mass sensors, medium pressure regulators, gaseous fuel injectors, in-tank high-pressure regulators, and "Tri-Shield" composite hydrogen and natural gas storage tanks.

Quantum develops all of their electronics in-house.

As a Tier 1 (or "Tier 0.5") supplier to the automotive industry, Quantum has a platform focus. It includes development, production, servicing, certification, and validation. Quantum is responsible for the emission warranty for the life of the vehicle.

Quantum does not get into fuel cells themselves, or ICEs for that matter, but they are part of the support mechanism for these components, and help with their integration.

The R&D group also is involved with advanced compression, bi-directional mass flow sensors with concentration detectors, leak detectors, and of course, tanks. The group has contracts directly with the Department of Energy as well as Lawrence Livermore National Laboratory (LLNL) and Sandia National Laboratories (SNL), and with the Southern California Air Quality Management District. They also have an exclusive technical license with Thiokol. Quantum believes that their relationship with Thiokol is of mutual benefit due to differing goals. Thiokol is "very technical" but is not interested in commercialization the way that Quantum is.

III Initial Discussion:

Fuel Storage:

Dr. Sirosh led the discussion on fuel storage. The composite direction for IMPCO/Quantum is fairly new. They entered the automotive storage area via a contract with GM in 1993. Earlier, they were involved with industrial gas tanks.

Quantum develops materials and designs systems and processes. They buy uncured resin/fiber composite (*sometimes called "tow"*) from Thiokol, but wind and cure it in-house. Quantum does the test engineering and analysis in-house including hydrostatic testing, fatigue pressure cycling, thermal cycling, and corrosion testing. They sell the overall storage system.

Currently, Quantum has the capacity to produce 3,000–10,000 tanks per year. We're talking about CNG tanks primarily – not the high-pressure hydrogen tanks being developed for this Program. They sell about 3,000 per year to GM.

The tank design that Quantum uses is referred to as Tri-Shield Tanks. This comes from the three layers of containment and protection provided. There is the inner liner layer, the composite (carbon fiber/resin) layer, and a tough, protective shell on the outside. The outer shell is largely to protect against impact. For some of their CNG tanks, it may just be a glass fiber/resin system, but for some of their newer designs it is made of a proprietary fiber/resin system. *I guessed the identity of the fiber, but I will not reveal it* *here. Suffice to say that it is indeed a tough fiber*. These tanks are meant for both NG and hydrogen, and have been endorsed by GM.

In the gaseous fuels market, says Dr. Sirosh, if you are designing for bigger vehicles, you need bigger tanks. If the tanks are larger, composite design has an advantage. They are 70% lighter than steel (which raises hydrogen embrittlement issues anyway), can hold more fuel than aluminum (which has to be designed more thickly); and for larger diameters they are cost-competitive with steel as well. Their burst pressure (for similar configurations) is 40% higher, and they are corrosion, damage, and leak resistant. There is also very little fatigue (no creep issues) on recycling for carbon-fiber systems as compared to steel. Because the composite tank is lighter, the brackets necessary to hold it in place can also be lighter – another weight saver.

The difficult part is to attach the metallic hardware to the plastic liner, but Quantum has developed a reliable redundant seal system.

For hydrogen systems, they design the tanks using the assumption that most people will over-fill a tank with hydrogen due to the reverse Joule-Thompson effect. *Unlike other gases, hydrogen (and helium) gets hotter when expanded into an empty volume. This results in a higher pressurization during a fast fill.*

Quantum designs their 5,000 psi hydrogen tanks to mostly the same conditions as they design their CNG tanks. This includes a 15-year service life, 15,000 cycles, and –40°C to 82°C service temperature. The allowed leak rate at the fittings is 200 cc/hour, again, the same as CNG. Hydrogen permeation rate is allowed to be no more than 0.50 cc/hr/liter capacity. (At this rate, a vehicle left in a hermetically sealed 1-car garage (36.25 m3) would not leak enough hydrogen to reach the explosive limit until after 3 years.) Moisture in the hydrogen is not as big a problem for composite tanks as it is for metal tanks.

Much of the impetus for a 10,000 psi system comes from Europe and Japan. The major impetus for the higher pressure is volume efficiency (energy density). You really don't get much of a weight efficiency benefit because of the need for thicker tanks as well as compressibility losses. In fact, Dr. Sirosh indicated that the "final number" might be about 7,000 psi. (*It's a different way of thinking than a lot of other ideas I have heard – optimizing the pressure rather than optimizing at a pressure. It appears to make a lot of sense.*)

The DOE Project:

Mr. Fregeau led the discussion on the DOE project itself. This involves, in eight separate phases (that I would call tasks), the development and delivery of a series of hydrogen tanks at 5,000 and 10,000 psi, including in some cases, in-tank regulators.

The regulator group is separate from the tank group and was not at this meeting. Developing and delivering the in-tank regulator (some installed and some spare) is part of the current project. The patented in-tank regulator is an important safety feature of the tank.

Tanks have been and will be delivered to LLNL, and to the Universities of Virginia and Texas. The University tanks will be part of the Future Truck Program. Some of the LLNL tanks are for testing, and some are for the Nevada Bus. The Nevada Bus tanks will have manual valves as part of a Quantum manifold, and will be equipped with external regulators rather than the in-tank kind.

The number of tanks delivered has been modified, *and in some cases the numbers were hard to follow*, but suffice to say that it involves about 90 tanks of varying lengths (48, 69, and 93 inches) and diameters (18 inches for the 48-inch tanks and 11 inches for the longer tanks).Also, some are 5,000 psi and some are 10,000 psi. The earlier designs involved tanks of 18-inch diameter (these were the Nevada Bus tanks), while the later ones, including all 10,000 psi tanks have 11-inch diameters.

IV Tour:

As mentioned earlier, I was shown the facilities both in Irvine and in Lake Forest. Much of the Irvine tank manufacturing facility is making CNG tanks. However, it can also be used for hydrogen tanks and is adaptable.

The liner is molded in a two-axis rotomold machine. About 4–5 liners can be processed at once. In the same step, the polar boss is molded to the liner. The liner (and subsequently the tank) only has one opening. This design prevents tank collapse. The liner is visually inspected by shining a light through it.

Since a good surface is needed to install the in-tank regulator, the internal lip of the hole in the liner is “finished”.

In winding the carbon/epoxy layer over the liner, the liner is bonded to the composite. *In other projects that I have seen, the liner was not chemically bonded to the composite. It was felt that if a bondline became part of the design, and the two became partially unbonded, it could lead to a failure. Thus, the liner was allowed to be only physically constrained by the composite, and held in place by that constraint and the internal pressure. I can see the value of the non-bonded liner design, but would not dissuade Quantum from their design either. I would, however, recommend that the load on that bond be looked at, and that cases that have been destructively tested have that bond examined.*

Winding is done with fiber that comes as a pre-impregnated (*and apparently partially cured either at Thiokol or by natural processes over time*) tow from Thiokol, or with fiber that is impregnated at Quantum. The Quantum (or “wet”) material has to be partially cured (the term is ‘B-staged”) on site. (Ultimately, Quantum will want to use the “dry” wind with the tow whenever cost effective. The overwrap (outer shell) is then wound on top. A full oven cure follows. The cured tanks are then subject to volumetric and leak testing.

Corrosion testing is performed in a cyclic corrosion chamber, where the tank is subjected to battery acids, road salts, etc. A dry air tester subjects the tank to a very harsh environment that accelerates the wear process. Other testing locales include thermal shock chambers and environmental test chambers that can simulate velocity, temperature, and vibration conditions.

These facilities can be used to test components and subsystems. It is where accelerated aging tests can be performed.

One very important point that I took away from my visit is the very strong commitment to quality control, with a very detailed paper trail, that exists at Quantum.

I also saw a series of burst pits where cycling and burst tests are run. The tank is filled with inert gas or hydraulic fluid for these tests. Hydrogen burst tests are done at Thiokol.

Barrier (crash) testing is done by an independent laboratory or by Quantum's customer. Quantum is responsible for crash worthiness. The criterion is that there should be no leaking after a 33 mph crash simulation. They do 50 mph tests as well.

I was also taken to Quantum's Lake Forest, CA, Vehicle Concept Center. Most of what I saw was proprietary, but I did see an impressive collection of computers that could break a vehicle down to any degree of detail, interchanging components with a mouse click, and a "printer" that printed three dimensional components from a computer program.

V Questions and Answers:

I sent Quantum a set of discussion questions prior to my arrival. The questions were answered by various team members. In addition, I was given a written set of answers for the questions. These are reproduced below.

1. **Please discuss the designs to which you are building (5,000 psi @ 7.5 % H_2, 5,000 psi @ 8.5%, 10,000 psi). Address what the key differences are in the three designs. Include lengths, diameters, tank weights, tank volumes.**

Data are summarized in Exhibit 1, using a Table provided by Quantum.

Because the tank domes are the thickest part of the tank, the longer you make the tank, the higher the weight % of hydrogen that you can get at a given pressure. All you are adding is length, so you are increasing the amount of thinner side wall and leaving the thicker domes alone.

The polymeric liner has been optimized to thickness and weight. Metallic components (polar bosses and seals) are optimized to limit hydrogen embrittlement.

The external shell will stop a bullet. Quantum does not feel that it will be necessary to modify the outer shell for 10,000 psi applications.

Quantum does not think that they will be able to achieve 8.5 weight % for the shorter (11 inch x 46 inch) tank design at 5,000 psi. *Probably this is a thick dome to thin side wall ratio issue.*

We have used the data in Exhibit 1 to calculate some weight of hydrogen and energy density numbers. The results are shown in Exhibit 2. These data show some energy densities that are higher than those reported by Thiokol (see the Thiokol report), especially at 10,000 psi. The weight percent hydrogen is also higher here than in the Thiokol design, either conformable or cylindrical.

2. What liner material is being used?

"The liner material being used is an advanced cross-linked Polymer, highly resistant to Hydrogen permeation and to temperature extremes."

This is not the same liner that is being developed by LLNL, which is a variable thickness liner. Quantum is using one that they developed themselves; it is something that they can use commercially. They are aware of, but have not used coated liners as LLNL has spoken of. *(See my FY 2000 report on LLNL lightweight tank and liner development.)* Quantum, however, is very interested in coated liners as a means of reducing thickness.

3. What fiber/resin system is being used?

"The fiber being used is a commercially available intermediate modulus, high strength carbon fiber. The resin system is a 250°F cure Epoxy."

Although the fiber is commercially available, Quantum would prefer to keep its identity proprietary at this time.

4. What safety tests have been/will be performed on the tanks?

Tests are summarized in Exhibit 3, provided by Quantum.

The tests that Quantum performs satisfy NGV-2 2000, and the tests also often satisfy more stringent criteria. For instance, they will usually pressure cycle (they use hydraulic fluid) well past the required 11,250 cycles up to about 45,000 cycles. Some tanks have been found to leak after that many cycles, but they do not rupture.

Environmental testing materials include acids, bases, battery fluids, road salts and gasoline – the typical materials that on-board tanks might be exposed to.

For the accelerated stress-rupture test (*see #8 in Exhibit 3)*, Quantum has found that the burst pressure does not drop at all, although a drop to 75% of the original burst pressure is allowable.

Quantum is running gas cycling tests using hydrogen at Thiokol. Having Thiokol as a partner opens up many testing opportunities. Direct hydrogen testing is one of them.

The problem as I see it is that when testing involving hydrogen has to be done in remote bunkers as occurred at LLNL last year, or at specific tests sites at Thiokol as Quantum is now doing, or even when other materials (hydraulic fluid, inert gases) are used in lieu of hydrogen this information is interpreted by the public as 'hydrogen is dangerous' rather than 'we'll be limited until all the standards are in place'. How do we get from there to a hydrogen tank on every car?

5. In tests such as drop tests, burst pressure tests, penetration tests, what were the results, the failure modes?

Test results are summarized in Exhibit 4, provided by Quantum. Some clarifications: "Fatigue" tests refer to fatigue/cycling. TÜV is a third party product certification agency from Germany. The TÜV inspector visits the NGV-2 test site.

We had heard that within the past few months, a "catastrophic" failure had occurred during the testing of a Quantum tank by another laboratory. The Quantum team stated that while this did indeed occur, it was not during a "real" test. It involved the striking of the side of a narrow tank, pressurized to 5,000 psi (*with nitrogen, I believe)*, with a two-inch diameter rod. Quantum was unaware as to the rationale for this test. Quantum stated that it is not a standard test, and that this particular tank was not designed for such a test. *Nevertheless, it still creates an issue of uncertainty. Why was the test run; who authorized it; was it run properly; why was Quantum not really in the "loop"? (Note that this is NOT a hydrogen problem; it is a solvable tank issue.)*

6. What cycling studies have been performed?

"Cycle fatigue test on a plastic liner, composite overwrap tank:

Tank A
- 450 – 4,500 psi
- 170-liter tank (AQMD)
- 103,500 cycles
- 2 proof tests
- Burst 9,800 psi (11,250 virgin burst)

Tank B
- 300-4,500 psi
- 250-liter tank, 20 gallon Tank (gas equivalent)
- No cycle test
- Burst 15,000 psi (mid cylinder failure)"

Proof tests go to 1.5X service pressure. Tank A shows a typical cycling test. Tank B exhibited a leak failure mode at the metal seal end during testing. *The subsequent burst test resulted in an acceptable failure mode.*

7. **Have any aging/accelerated aging tests been performed on the tanks or components of tanks? If so, please discuss the results. If not, please discuss what aging tests are anticipated. Do the aging tests (completed or planned) include cycling?**

A) "Yes. GM Draft 6 testing has been performed on a plastic-lined composite CNG tank. The test was a complete success.

B) "Aging test anticipated on the DOE hydrogen tanks include:

   a. Accelerated stress rupture.
   b. Fatigue cycle test.
   c. Environmental exposure.
   d. Cycle test using H_2.

C) "Yes. The GM Draft 6 test, fatigue cycle test, environmental exposure test, and the gas cycle test (using H_2), include cycling."

Also, there were TÜV tests performed on NECAR 2 tank material in 1996. In addition, Allied Signal examined the chemistry of the liner under exposure to hydrogen in 1996. No chemical changes were detected.

It is good to see that aging tests including aging in the presence of hydrogen have been done and are planned. In too many of the materials-based hydrogen projects aging studies are delayed or ignored.

8. **What steps have been taken to ensure the integrity of "non-continuous" components? That is, portions of the tank that would be manufactured separately from the general case winding (e.g., stability rings, dome closures, filling/dispensing connectors, etc.).**

"Components being manufactured separately from the general case winding, and steps taken to ensure integrity are:

"A) Dome protective encapsulation (end protectors):

   a. Have been tested extensively.
   b. Manufactured by an outside vendor to strict QA requirements.
   c. Receiving inspection performed prior to use by Quantum QA inspection."

The end protectors are made of polyurethane. It would be too expensive to change the dome winding design. The end caps are adequate protection.

"B) Metallic boss and seal assembly:

a. Has been designed using FEA.
b. Prior history exists for testing same configuration.

"C) Plastic liner:

a. Extensive testing history exists for this configuration.
b. Manufactured by Quantum personnel in-house and subjected to rigorous QA inspection prior to release for use."

There are no stability rings.

9. How much of the testing is performed with the tank filled with hydrogen as opposed to an inert gas? How about aging in conjunction with hydrogen?

A) "Testing performed with the tank filled with Hydrogen includes:

a. H_2 aging test
b. Fast-fill test with H_2
c. H_2 bonfire
d. H_2 fatigue cycle test

B). Aging in conjunction with Hydrogen has been performed on a tank of similar configuration. In the test performed, a plastic-lined cylinder was filled to 2,700 psi and conditioned to 80°C for 200 hours to simulate the effects of environmental aging. The effects were evaluated by cycling the conditioned cylinder to 5,000 pressure cycles from 0 to 3,600 psig and subsequently burst at 9,750 psig (minimum burst 8,100). The average ultimate tensile strength of the liner material after test was 2,977 psi, exceeding the minimum requirement of 2,326 psi. Elongation was greater than 81%, exceeding the minimum requirement of 68% for molded plastic liners."

Test "B" above does not represent a test on a DOE tank, but has been performed many times on tanks similar to the DOE tanks. The aging tests on the DOE design will be performed "very soon."

More direct hydrogen testing. This is encouraging.

10. Are the tanks that are currently being built using the same composite components that is anticipated for large scale production?" (This question is based on interviews that have been held with other contractors, for other hydrogen projects. On occasion I have heard 'We're using XYZ, but when we go into production we'll switch to ABC because it's more cost effective'.)

"Yes. The same exact configuration used in tank development/validation will be used in production. Quantum internal QA/QS regulations prohibit any changes to be made to the tested/validation configuration."

Quantum validates their material and stick with it. *Perhaps this is the difference between a laboratory and a manufacturing company. Regardless, it is the right way to go.*

11. How will safety be ensured when tanks are being mass produced? What NDE quality assurance will be used?

“A) Quantum adheres to an inspection process flow chart for each tank configuration produced. A specific flow chart exists for Type IV tanks. All process/inspection steps are strictly adhered to.

“B) Production batch testing is performed, as mandated by the governing specification, in this case, NGV2 – 2000. The NDE testing performed is as follows:

a. NDE so that flaws in the liner to not exceed the allowable defect size.
b. Verification that the critical dimensions and parameters specified in the part drawings are within design tolerance.
c. Hydrostatic proof test (expansion).
d. Leak test.”

In addition, a burst test is run on a random tank in each production batch.

12. Please explain (to whatever level allowable) the relationships for compressed hydrogen tank development between IMPCO, DOE, Lawrence Livermore National Laboratory, and Thiokol.

“Quantum has developed a partnership agreement with Thiokol Propulsion for access to their considerable technical resources in materials, processes, testing and hydrogen gas management.

“Thiokol Propulsion developed high storage cylindrical hydrogen tanks for the Department of Energy (DOE), Lawrence Livermore National Laboratory (LLNL), under contract B503790. This contracted effort has successfully designed, fabricated, and delivered an 18 inch diameter, 48 inch long cylindrical tank that stores 12% hydrogen by weight at 5,000 psig.

“The Quantum-Thiokol partnership offers the technical depth and breadth of experience to successfully develop hydrogen storage tanks that meet the DOE specifications identified in this current contract.

“Thiokol is pleased to offer Quantum access to both the technical staff and tank design experience that exists within Thiokol’s Science and Engineering organization to insure the success of the effort outlined in this current contract.”

Quantum makes use of Thiokol’s talents through a Time and Materials contract, using Thiokol as an extension of Quantum’s own testing capabilities. Quantum also has an exclusive license to produce Thiokol’s conformable tanks.

The Quantum/Thiokol relationship is non-competitive says Dr. Sirosh. Quantum has a repeatable/commercial flavor to their work, while Thiokol’s is more maintenance and improvement oriented.

Exhibit 1. Quantum Hydrogen Pressure Tank Parameters

Wt. % Hydrogen	Tank Pressure	Tank Dimensions	Further Description
7.5%	5,000 psi	• 18” x 48”: 91 lbs, 144 liters • 18” x 28”: 55 lbs, 70.5 liters	• Optimized polymer liner. • Optimized metallic components (H_2 compatible). • Seal system optimization for Hydrogen service at 5,000 psi. • Optimized composite carbon/epoxy shell (lightweight and capable of passing NGV_2 – 2000 requirements). • Developed external damage tolerant shell.
8.5%	5,000 psi	• 11” x 83”: 69 lbs, 89 liters • 11” x 46”: 36.8 lbs, 42 liters	• Further liner weight optimization. • Further composite shell optimization.
8.5%	10,000 psi	• 11” x 83”: 145.2 lbs, 89.6 liters • 11” x 46”: 73.6 lbs, 42 liters	• Liner material and weight optimization for 10,000 psi service pressure. • Optimization of metallic components for 10,000 psi Hydrogen service (H_2 compatible). • Optimization of composite carbon/epoxy shell (reduced weight/higher performance). • Optimization of the external damage-tolerant shell.

Exhibit 2. Capacities and Energy Densities of Quantum's Tank Design (Calculated From Data in Exhibit 1)

% Hydrogen	Tank Pressure (psi)	Tank Dimensions	Wt. Hydrogen (lbs)	Energy Density (Wh/liter)
7.5	5,000	18" x 48" 91 lbs,	7.38	550
7.5	5,000	18" x 28" 55 lbs	4.46	570
8.5	5,000	11" x 83'' 69 lbs	6.41	740
8.5	5,000	11" x 46" 36.8 lbs	3.42	712
8.5	10,000	11" x 83" 145.2 lbs	13.49	1557
8.5	10,000	11" x 46" 73.6 lbs	6.84	1425

Weight of hydrogen based on the fact that the weight of the tank does not include the weight of hydrogen.

Energy density calculated from external tank cylinder volume, and using the fact that one pound of hydrogen is equivalent to 14,920 Wh (lower heating value).

Exhibit 3. List of Tests for Tank Certification

No.	Test	Testing Procedure	Test Pass Criterion
1	Hydrostatic Burst	Tanks to be hydrostatically pressurized to failure.	Min. burst pressure shall be greater than 225% of the service pressure.
2	Ambient Cycling	Pressure cycle with non-corrosive fluid at ambient temperature.	Min. of 11,250 cycles before rupture.
3	Environmental	Pressure cycle for 3,000 cycles. Expose tank areas to corrosive/environmental fluids. Pressurize to 125% of service pressure for 48 hrs.	Tanks shall not leak or rupture.
4	Extreme Temperature Cycling	Pressure cycle for 4,000 cycles at 180°F and -40°F each.	Tanks shall not leak or rupture
5	Composite Flaw Tolerance	Uncoated tank to have two flaws in the longitudinal direction cut into composite sidewall. Pressure cycled to 125% of service pressure.	Min. of 11,250 cycles before rupture.
6	Drop test	Horizontal, vertical and oblique (45°) drop. Pressure cycled to 125% of service pressure.	Min. of 11,250 cycles before rupture.
7	Bonfire	Subject pressurized tank complete with pressure relief device to a uniform fire source.	The tank shall vent through a pressure relief device without bursting.
8	Accelerated Stress Rupture	Pressurize tank to 125% of service pressure at a temperature of 149°F for 1,000 hours. Follow this with a hydrostatic burst test.	Hydrostatic burst pressure shall be greater than 75% of minimum burst pressure of test #1.
9	Penetration	A pressurized tank containing air or N_2 to be shot with a 30-caliber bullet. The bullet is required to pass through at least one sidewall of the tank.	The tank shall not rupture.
10	Permeation	Tank filled with CNG or He/N_2 mixture at service pressure to be placed in an enclosed sealed container at ambient temperature to monitor gas leakage.	Steady state permeation rate shall be less than 0.432 $in^3/hr/ft^3$.
11	Gas Cycling	Tank to be pressure cycled between 10 and 100% of service pressure for 1,000 cycles. After cycling, the tank will be subjected to leak test as in test # 10.	Sectioned tank shall not show any deterioration or damage in liner and liner/boss interface.

Exhibit 4. Tank Testing History

No.	Dimensions (in)	Internal Volume (L)	Pressure (bar)	Testing	Certification
1	11.5 x 23.0	24	350	Burst, Cycling Fire	DOT
2	13.75 x 35.5	62	250	Burst, Cycling	-
3	16.5 x 33.0	72	250	Fatigue, Burst, Flaw tolerance, Drop, Bonfire, Penetration, GM Durability	NGV2-1998 (TÜV), & DOT
4	22.0 x 61.0	250	250	Fatigue, Environmental, Burst, Flaw Tolerance, Drop, Bonfire, Stress Rupture, Penetration, Permeation, Cycling, GM Durability	NGV2-1998 (TÜV), & DOT
5	12.6 x 38.0	52	250	None (Tooling is Available)	-
6	16.5 x 50.0	118	250	None (Tooling is Available)	-
7	15.75 x 74.5	180	250	Burst, Penetration, Bonfire	NGV2-1998 (TÜV) & DOT
8	18.0 x 33.0	72	350	Burst, Cycling, Fire, Stress Rupture	DOT
9	18.0 x 26.0	144	350	Burst, Cycling, Gun Fire Stress Rupture	NGV2-1998 (TÜV) in progress Completion 02/01
10	18.0 x 26.0	67	350	None (Under Development)	Target: NGV2-1998 (TÜV) 04/01
11	11.0 x 44.0	52	350	None (Under Development)	Target: NGV2-1998 (TÜV) 04/01
12	11.0 x 81.0	99	350	None (Under Development)	Target: NGV2-1998 (TÜV) 04/01
13	12.6 x 23.0	24	700	Burst	-
14	11.0 x 44.0	53	700	None (Under Development)	Target: 12/01

Technical Evaluation Report
Project: PEM Fuel Cell Stack Project
Company: Los Alamos National Laboratory, Los Alamos, NM
P.I.: Dr. Mahlon Wilson
Date of Visit: January 26, 2000
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

This R&D project at Los Alamos National Laboratory (LANL) deals with the development of components for small (3-5 kW) PEM fuel cells for home use. The components of interest are the bipolar plates, CO resistant anodes, and humidification devices. Much of what is being done on this project is in conjunction with LANL's CRADA partner, Plug Power.

The bipolar plates work appears to be the centerpiece at this time. It is a two-pronged effort that involves looking at both molded composite plates and plates based on metal alloy foils as alternatives to expensive, machined graphite plates.

The humidification work also seems to be progressing well, centered on the use of wicking threads to get water to the membrane. The status of the CO tolerant anode is less clear.

Project Strengths:

- The identification of PEMFC needs is very sound. The cost of the bipolar plates has long been considered to be a major obstacle to inexpensive fuel cells. Anode tolerance to CO is essential for hydrocarbon-based feedstock. An efficient humidification process is necessary to optimize membrane performance, especially at low pressure.

- Working with a respected CRADA partner lends credibility to the process. Plug Power provides that aspect. (A similar situation exists with LANL's other project, the fuel cell "battery", where the CRADA partner is DCH Technologies.)

- The entire bipolar plates effort seems well thought out, and covers sufficient options to maximize chances of success. A coated aluminum option seems particularly interesting. The humidification/near-ambient operation effort also addresses real system issues, and appears to be headed in the right direction.

- Materials handling and testing facilities and capabilities appear to be first-rate.

Issues that should be Addressed:

- There needs to be more of an understanding as to what the operating pH of the system will be under a variety of conditions, feedstocks, membrane types, etc. If metal alloy foils or coatings are going to be used for the bipolar plates, their corrosion testing conditions should be based on well understood, real-world scenarios. For instance, we would not want to see a potential inexpensive, effective alloy be eliminated because it showed poor corrosion conditions at a pH that a system would never see.

- The state of the CO tolerant anode work (or at least the manner in which it was presented to me) is somewhat uncertain. There is a plan to look at both anodes that will work with an air-bleed (lower tolerance) and without an air-bleed (higher tolerance necessary). It is not at all clear, however, as to what has actually being done, and what needs to be done.

Overall, the pluses far outweigh the minuses. This is a good project, headway is being made, and it looks like significant improvements to the PEM fuel cell will be realized.

II Introduction and Background:

I visited LANL on January 26, 2000 to assess the small PEM Fuel Cell Stack project. LANL is also working on a small PEM fuel cell "battery" for portable devices. I met with **Dr. Mahlon Wilson**, the team leader for the two Hydrogen Program projects at LANL, and with **Ms. Christine Zawodzinski**, who is a technician on the project. (LANL considers any technical person without a Ph.D., a "technician". Ms. Zawodzinski possesses a Master's degree in chemistry.) We spent nearly an entire day discussing the project and touring the Group's facilities.

The CRADA that LANL has with Plug Power has just recently been signed. The tasks were written two years ago, however, and LANL is trying to "push" Plug toward steam methane reforming and membrane separation as opposed to partial oxidation (as was indicated in the initial task statements). They are currently in dialog.

Project Components:

Bipolar Plates

Bipolar plates are viewed as one of the most expensive fuel cell components. This is largely true because standard bipolar plates are made of intricately machined graphite. The machining is particularly cost intensive due to the incorporation of flow fields (paths for the reaction gases) in the graphite. LANL's work on bipolar plates includes development of both composite and metal alloy replacements for the machined graphite plates.

Composite plates generally involve a thermoset or thermoplastic material with graphite filler to provide the conductive element. The thermoplastic version is more expensive, primarily because processing includes cooling in the mold under pressure to avoid void formation. The material of choice is polyvinyl difluoride (PVDF), a very good barrier plastic that tends to be stable right up to its melt temperature. LANL is no longer working in this area, having handed the work off to a producer, SGL. Plug power's work with composite bipolar plates at this time, largely involves PVDF.

Thermosets that have been evaluated have been based on epoxies or vinyl esters. Epoxies are cheaper, but have poor elongation properties and need incorporation of plasticizers to improve this parameter. Vinyl esters, while having about the same tensile strength as epoxies, have inherent elongation capabilities of about ten percent. The vinyl ester plates also show greater tensile strength than thermoplastic plates. The thermoplastic plates are likely to break if they are dropped; the vinyl esters won't break.

The composite bipolar plate is about 1/8 inch thick, and weighs about 200 grams. Since the cost of raw material is a few dollars per pound, LANL has been looking for an alternative type of plate as well. They are focusing on a plate made of a thin metal alloy foil mounted on an inert polycarbonate backing. The foil, being only about two thousandths of an inch thick, adds little to the raw material cost of the plate.

LANL metal alloy work currently uses thicker samples, just to make it easier. Once a material is identified, they will look at having foils made. One method of getting foils that they are looking into is through a company called "Metal Samples." This company procures, processes, and provides samples of other companies' metals. Eventually, the plan would be to simply stamp flow-fields into the foil. For 2-mil thick foils, this should be quite easy to do. The real question may be whether the foils can stand up to clamping pressures of 700 psi. (The polycarbonate backing should help sustain the pressure.)

The alloy of choice for LANL right now is Ebrite 26-1 – an iron/chromium/molybdenum alloy that is showing very low corrosion amounts. The company that makes it, Allegheny Ludlum does not make it in foil form yet.

LANL is also looking at another metal option – coatings. For example, one could coat cast-aluminum with a bipolar coating. Dr. Wilson is excited about this idea, but recognizes several potential problems such as pinhole formation, adhesion, and conductivity anomalies. LANL is working with a company that develops these types of coatings, but wishes to keep the information proprietary at this time.

Coated cast-aluminum could ultimately be cheaper than (or at least as cheap as) foil with backing. Since aluminum would be more thermally conductive, this type of design might be good for stacks that require better temperature control. Better electrical conductivity would also be likely; this could lead to higher efficiency or more power. Finally, this type of design would eliminate the clamping pressure concerns of foils.

CO Tolerant Anodes

A major issue with all PEM fuel cells is the effect of carbon monoxide on the anode (hydrogen side) of the cell. CO presence lowers fuel cell performance and reduces the lifetime of the anode. Since much of LANL's work, especially with Plug Power, involves using mixed-fuel streams as well as hydrogen formed via partial oxidation processes, a high content of CO in the product stream is likely. There are three ways of dealing with this problem. One involves using a pre oxidation (PROX) step to reduce the CO content prior to feeding the mixture into the fuel cell. A shift reactor should reduce CO down to at least 1%. This product is fed into the PROX reactor, mixed with air, and run over a precious metal (such as platinum) catalyst bed. This process will bring the CO level down to less than 100 ppm, but reduces the overall efficiency of the process.

The second approach involves the use of an air bleed into the hydrogen stream. This reduces the effect of CO on the anode. It also causes a reduction in overall efficiency (about one percent efficiency reduction for each percent of air bled in) and also increases the safety risk should the hydrogen ignition limits be accidentally reached.

The third approach is the development of the CO tolerant anodes. The tolerance level is variable, based on whether the system has an air bleed or not. One CO tolerant anode system that LANL is looking at, which is proprietary, is to be used in a non-air-bleeding mode. While the system will work on up to 100 ppm CO, there are some aging problems with the anode alloy catalysts. At this time, they only have lifetimes of hundreds of hours.

If on the other hand air bleeds are allowed, you can get by without using a PROX reactor. Under these conditions, you would want an anode that could handle thousands of ppms of CO. Dr. Wilson does not believe that this can be done easily, but he says that LANL does have some catalysts that can handle 1000 ppm of CO for hundreds of hours.

The overall CO tolerant anode work is being performed in Dr. Tom Zawodzinski's "shop". There are three task leaders within this fuel cell group, one is Mahlon Wilson, a second is Tom Zawodzinski, and the third is Dr. Shimshon Gottesfeld. Dr. Gottesfeld is concentrating on direct methanol fuel cells these days.

Unfortunately, I was unable to meet with Dr. Zawodzinski for any length of time, and did not get a good feeling for the CO work.

Humidification

It is necessary to keep the membrane wet to ensure good membrane performance. The standard process is reactive humidification, that is, letting some of the water formed in the fuel cell recycle into the fuel feed stream. But this water is in vapor form, and the membrane's uptake of water vapor is limited. To get enough water vapor from the reaction to the membrane would mean running at a very high current density. LANL therefore believes that there are advantages to using liquid water to hydrate the membrane.

The LANL process involves distributing the water over the entire anode side of the plate, and then using porous, hollow wicks to transport the water to the membrane. This type of approach also allows for near ambient operation of the fuel cell, which results in a lower cost system, and one that is more efficient (fewer parasitic losses.)

III Tour:

Dr. Wilson and Ms. Zawodzinski took me on a tour of their facility. Most of their equipment is in one laboratory that they call the “Stack Lab”. The equipment in the lab includes:

- A computer-controlled positioning table/milling machine
  An interesting little story here: They were not authorized to buy a “real” milling machine. But they could buy a positioning table, and mounted a hand-held mill on it.

- A computer-controlled embroidering machine. Accurate to 0.1 mm; used to incorporate the wicking threads.

- A 50-ton parallel plate press

- Three fuel cell test stations. A test station controls fuel cell temperature, supplies reactants to the cell, and monitors voltage and current. It contains two humidification bottles, pressure regulators, rotometers, cartridge heaters, and an HP 6060 load box. You enter a voltage, and the load box maintains it. You can measure cell resistance under load; you measure voltage and current to calculate resistance. You can tell if a cell is drying out.

- Two smaller stations (maximum of 60 amps and 300 watts) are currently being used for corrosion testing. One large station is used for large cells or stacks (up to 8 kW and “several hundred” amps). One can use this station to measure overall stack resistance.

- Several complete and partial fuel cells and stacks.

- A few small (10-50 W) fuel cell “battery” systems (the other LANL hydrogen project) for which they have a CRADA with DCH Technologies. One of the small cells was powering a radio.

I also saw the CO tolerance lab briefly. There were several fuel cell test stations here, perhaps six, but I saw no ongoing work. Dr. Wilson did mention that the ambient pressure work had not yet started.

The set-up for the direct methanol fuel cell laboratory is very similar to that of the “Stack Lab”.

The diagnostic equipment for the group is quite impressive. Among other equipment I saw an X-ray Fluorometer, SEM/EDAX, X-ray Diffraction system, sputtering chambers, an Instron tensile tester, FTIR, UV/Vis spectrophotometer, environmental chamber, GC/MS and an Atomic Force Microscope.

IV Questions and Answers:

I sent Dr. Wilson a set of questions that then became the basis for a major part of our discussion. These are shown, and discussed, below:

1. **Is there any thought being given to direct hydrogen systems, where hydrogen is made from non-hydrocarbon sources? How would the LANL system be modified under those conditions? In what ways could the system be simplified? What, if any, additional problems might be incurred?**

Dr. Wilson repeated often that direct hydrogen is his preferred method of operation. It's "easier", he said. All of his work except the anode task is based on neat hydrogen. His ideal system uses steam reforming and membrane separation prior to use in a fuel cell (ala Northwest Power). He prefers the higher efficiency of this process to the Plug Power method of partial oxidation and stream clean up. *Despite LANL's alliance with Plug.* Dr. Wilson does not particularly like processes that are going to result in more CO formation, and require a higher air-bleed to preserve the anode. These processes result in higher parasitic losses and lower efficiency.

Interestingly, Dr. Wilson did not even consider "non-hydrocarbon sources" as the question stated. He looks at reforming as the clean system. The discussion continued, however.

Processing other species that contained a sulfur compound would likely be a problem (sulfuric acid would form, lowering the pH and potentially corroding the bipolar plates). Trying to make hydrogen from ammonia would create a special problem. The proton, rather than reaching the membrane, would react with ammonia, forming the ammonium ion:

$$H^+ + NH_3 \rightarrow NH_4^+$$

The ammonium ion would clog the membrane, but it would eventually unclog, according to Dr. Wilson.

The concept of the membrane clogging, but eventually unclogging came up several times, especially in conversations about metal bipolar plates. I don't believe that an answer that the membrane will eventually unclog is a good answer. It likely won't unclog if it is in constant service, and periodic cycling means either down time, or increased material cost.

2. **Roughly, what are the comparative costs associated with bipolar plates made from machined graphite vs. 316 Stainless Steel vs. "metal alloys more noble than 316SS," both from an absolute dollars and a life cycle standpoint?**

Overall, one could consider the cost of metal plates to be about 50 cents each. If the alloy were high in Ni, Mo or Ti, it would be a "little higher." Composite plates would cost about $1-2 each, with thermosetting vinyl ester-based composites being less expensive, and thermoplastic PVDF plates being more expensive. Machined graphite plates are 1-2 orders of magnitude more expensive than PVDF plates.

Graphite plates would last the longest, but the composite plates have considerably long lives as well. Graphite plates would be virtually unaffected by the fuel cell process. The only concern would be that a "dirty" graphite could reduce membrane lifetime.

With composite plates, the major concern would be the effect of water. Quite a lot of water could permeate the plates over ten or 20 thousand hours. The question is what effect will it have on the tensile properties of the plates? LANL is addressing that issue via a series of accelerated wetting tests. These tests are being done with methanol rather than water. Methanol wets out the plates quicker than water does, so one would expect to see any adverse effect sooner. Plates have been tested with methanol for 1000 hours to date, and no tensile changes could be seen. Testing continues.

Metal plates have not been tested in fuel cells to any great degree as yet. It is known, however, that they last for "years" in similar electrochemical environments. The membrane's life, however, is somewhat compromised by the presence of metal ions from the metal plates. Life of the membrane can be extended if it is flushed, but some stagnant areas will remain clogged.

3. **How long a lifetime would you expect for a membrane exposed to 316SS bipolar plates?**

Dr. Wilson and Ms. Zawodzinski feel that a membrane exposed to 316 SS would be fine for a transportation application, where total usage would likely be under 2000 hours, but that it probably would not survive a 20,000 hour stationary power supply application. Other alloys such as the aforementioned E-Brite 26-1 looks particularly promising. Membranes exposed to this alloy have been tested for 1000 hours at 0.5 volts and 1000 hours open circuit, and appear to be still clean.

Dr. Wilson estimates a goal for the FC system to be 40,000 hours, but Plug Power touts 15 years as possible. Aside from contamination from metal bipolar plates (or "dirty" graphite plates, for that matter) a serious contamination source could be humidification water. The presence of calcium is the chief concern. Calcium could clog membrane functional sites at, perhaps, one percent per year.

4. If a membrane retains metal ions, can it be "recharged", or does it need to be permanently replaced?

Theoretically, a membrane could be recharged by pumping nitric acid through it, and ion-exchanging out the clogging metals. The nitric acid, however, would likely passivate the metal bipolar plate surface. The LANL group is not seriously considering recharging of membranes.

5. You say that the 316SS plates are essentially corrosion free, yet the membrane picks up metal ions. Are you looking at corrosion in a "macro" sense as opposed to a micro (metal ions) sense, or could the ions be coming from another source?

Yes, it is a macro vs. micro situation. Corrosion effects reduce plate thickness by less than ½ micron per year (and thus the plate is visibly corrosion-free) but metal ions can be seen in the membrane using x-ray fluorescence.

Seeing that the presence of metallic ions in the membrane is the key parameter, it is probably misleading to emphasize the visible condition of the plate.

6. Is there any correlation between metal ions in the membrane and the source of hydrogen?

There may be a correlation if the reformate stream contained a large amount of CO_2, say 30%. This could result in the formation of carbonic acid, which would lower the pH and thus contribute to an increase in corrosion. Dr. Wilson feels that a pH of 4 would be enough to cause a problem. It is pH that causes corrosion problems far more than the nature of the input gas.

No effect on corrosion was seen on SS 316 when exposed to the chloride ion.

LANL are also aware of potential problems with exposure to hydrogen itself. They have found that nickel alloys resist corrosion from exposure to hydrogen better than stainless steel alloys, while the latter do better on exposure to air.

Dr. Wilson thinks that he may want to look at different foils for the anode and cathode sides, – say SS 316 for the cathode (air) side, and E-Brite 26-1 for the anode (hydrogen) side.

(As I write, I wonder why he said E-Brite 26-1. This is an iron-based non-nickel alloy (see equestion 7). As such, based on the above comment, I would think it would be more subject to attack from hydrogen.

7. In Table 1 of your FY1999 Annual Review Report, can we assume that the balance of material for E-Brite 26-1 is Fe – that is, no Ni?

The sum of the elements presented for this material only added up to 27% -- 26% Cr and 1 % Mo. All other materials listed in the table showed complete compositions.

Correct. The balance is iron; there is no nickel present in E-Brite 26-1.

Minor point: I realize that LANL simply reported the assay as provided by Allegheny-Ludlum, the manufacturer, but an effort should have been made to identify the remaining elements and report it in the paper.

8. **Is the pH range of 2-6 what is to be expected as the typical operating parameters of the fuel cell?**

LANL has not ever seen pH=2 water coming out of their own stacks, but have seen reports that others observed these conditions. Dr. Wilson speculates that the acidic pH may stem from the presence of sulfuric acid-based species in the effluent. Under normal conditions, however, the pH shouldn't be any lower than about 6.

One exception may be found when Gore membranes (as opposed to DuPont membranes are used in the PEMFC. Gore impregnates their Gore-Tex membranes with liquid Nafion (which they buy from DuPont), and the liquid could leach out of the membrane and lower the pH. If the water is stagnant in spots, localized areas could see higher Nafion concentrations, and conceivably a pH of 2. *If this is the case, a better question might be: why use Gore membranes?*

Based on these reports and theories, LANL feels that pH=2 is one logical point at which to test.

I think that it is important not to overstate the likelihood of an acidic environment. While testing at pH=2 should continue in order to bracket likely conditions, it should not be used as a basis for eliminating alloy candidates that are "winners" under all other conditions.

9. **You refer to the use of composite bipolar plates (in conjunction with Plug Power) as being a short-term solution. Why are they only a short-term solution? How do they compare cost-wise with the metal plates?**

The composite hardware task is winding down simply because it has gone as far as LANL can take it. The "compounders" (two Midwestern companies – "Premix" and "Bulk Molding Compounds" [BMC]) are working the problem now. Plug Power likes the composite option, but presently they are using machined graphite plates. The composite option is considered short-term because composites, while the price will come down when mass-produced, will never be as cheap as metal foil plates.

This assumes that metal foil plates will give the type of lifetime needed for stationary fuel cells.

10. How would composite bipolar plates "age"? Are there plans to do any testing in this area following the identification of a system?

A number of polymer systems would be affected by long-term exposure to water. If hydrolysis took place, tensile properties could be affected. Actually, this may not be a serious problem *per se*. The plates must have good tensile properties during assembly, but compression strength is the key during long-term operation. However, if hydrolysis causes the plates to start leaking, this is a serious problem.

LANL is currently running accelerated aging tests. Since methanol wets out the polymeric binder more quickly than does water, and the hydrolysis mechanism is similar, they can get a more rapid approximation of the effect of long-term exposure to water. They are also running tests at pH=2 to test the effect under these conditions.

11. What is your goal for CO tolerant anodes?

The goal is constantly moving because fuel processing is improving. It is probably better to consider two goals – one if air is being bled into the hydrogen, and one if it is not. It is desirable not to use an air bleed. Using an air bleed causes a decrease in overall efficiency by about one percent for each percent of air added, and also presents a potential safety issue if too much air is injected, the upper ignition limit is reached, and an explosive mixture leaks out. In addition, an air-handling system increases the overall system cost.

Fuel processing is getting more sophisticated. Using a Prox process, fuel cell feedstock gas can be supplied with an average CO content of about 20 ppm, with spikes up to 100 ppm. Thus, the goal is to have an anode that is tolerant to 100 ppm of CO without the need of an air bleed.

Recall that I did not talk to Dr. Zawodzinski at any length. Based on the conversation with Dr. Wilson, however, it seems that the major effort is to go away from an air bleed. This apparently will lock them into a Prox reactor mode. Dr. Wilson does not hold out much hope for the alternative system (no Prox with an air bleed).

12. Please explain the reconfigured anode. What is it made of? How is it reconfigured?

The reconfigured anode includes a backing – a gas diffusion layer. This modification improves CO tolerance, but its nature is proprietary. Dr. Wilson mentioned that this is a "very competitive" topic.

13. What partial pressure of hydrogen is necessary to achieve acceptable anode performance? – Or is the parameter that needs to be monitored the ratio of hydrogen to CO partial pressures?

Dr. Wilson gave the answer based on stoichiometry rather than partial pressure. With about 40% hydrogen in the feed stream (not including water), you want a 1.1-1.2

hydrogen to oxygen stoichiometry. If you have a lower hydrogen content, you would have to flow much faster, that is, use a much higher stoichiometry. The higher stoichiometry improves performance. You need the extra hydrogen to "push the inerts out of the way." But the extra hydrogen could then be used for some other process. *Or presumably, recycled.*

If you had neat hydrogen (membrane separation or hydrogen from water) you wouldn't have these problems. Dr. Wilson is a proponent of membrane separation even though his project does not practice it. He mentioned Northwest Power's diesel reforming project as something that would benefit from membrane separation.

H_2/CO ratios do not affect performance. It's the actual amount of CO that is important.

14. What alternatives to the wicking method for hydrating the membrane were considered?

LANL also considered using tubes molded into the membrane and pumping the water through. The ability to keep the tubes open at high pressure, however, was the chief concern.

LANL is also considering running the water through the hydrogen flow channels on the anode-side plate (rather than over the entire plate), and then wicking over to the membrane.

I am not sure what advantage this last option would have. It appears to me that it would be more difficult to supply sufficient water and would be harder to control.

15. What material is the wicking thread made of?

The thread is a polyester material, specifically "Coolmax." The fiber in the threads have a convoluted geometry that allow more efficient wicking. The thread is 50-denier multifilament and is wound with a thicker co-thread of cotton-polyester.

VI Additional Discussion:

- One of the LANL/Plug tasks is the systems-based humidification effort. Plug, however, seems to be backing away from this task, and apparently is moving toward their own proprietary humidification process.

- During our discussion on using ammonia as a source of hydrogen (see Question 1), Dr. Wilson wondered about the possibility of using ammonia as the fuel, and NH_4^+ as the actual transport ion (an ammonium exchange membrane fuel cell).

This page intentionally left blank.

Technical Evaluation Report

Project: Reversible Solid Oxide Fuel Cells
Company: Technology Management Inc., Highland Heights, OH
P.I.: Drs. Robert Ruhl and Christopher Milliken
Date of Visit: March 20, 2001
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

Technology Management, Inc. (TMI) is developing a reversible solid oxide fuel cell (SOFC) designed primarily for off-grid residential use. It can act as an electrolyzer, utilizing excess renewable resources to make hydrogen. As a fuel cell, it can operate off the stored hydrogen to make electricity. If no hydrogen is available, it can operate from reformed propane.

Phase 1 of the project, completed last year, was a paper study. Phase 2, where TMI is getting into hardware, was just beginning at the time of my visit. Originally, TMI based their paper study on a system in Boulder, CO that used PV as the renewable resource. A summary of the data they presented for this is shown in Exhibit 1. In the later stages of Phase 1, however, they modified their case study, and considered a wind-based system in Colorado Springs, CO. Exhibit 2 summarizes their findings for this system.

Project Strengths:

- SOFCs, due to higher operational temperatures, provide the opportunity for increased efficiency operations. SOFCs have several advantages over Proton Exchange Membrane (PEM) fuel cell systems for stationary applications.
- The TMI project presents a good opportunity for a near-term water-based reversible fuel cell test/demonstration.

Issues that should be Addressed:

- I am not convinced that there is a "middle ground" here for a more complex, expensive system, with some environmental benefits. I think we need to find out.
- The jump from solar to wind, although done for valid reasons, needed to be adequately explained in the formal reporting mechanism. It is not the kind of thing we should have to ask about.
- We need to take care that the propane fuel cell mode does not become the only mode.

II Introduction and Background:

I visited TMI at their facility in Highland Heights, OH, outside of Cleveland, to discuss their rather unique kind of reversible solid oxide fuel cell. Present at the meeting from TMI were **Benson Lee**, President; **Michael Petrik**, Vice President; **Dr. Robert Ruhl**, Vice President, Engineering; and **Dr. Christopher Milliken**, Research Materials Scientist. Dr. Ruhl was the PI for Phase 1; Dr. Milliken is the PI for Phase 2

Mr. Lee provided some background information on his company. TMI was founded in 1990. Its major product is solid oxide systems. Solid oxide fuel cells were originally developed by BP/Sohio, which is also in Cleveland, hence the interest in this field by TMI.

TMI has had many Department of Defense contracts. The focus was on small, lightweight systems running on liquid fuel. The main problem was sulfur contamination. TMI thus focused on making a sulfur-tolerant reformer and a sulfur tolerant SOFC. Dr. Lee indicated that at the time, DOE was not interested in liquid systems. He mentioned that the then Federal Energy Technology Laboratory, now the National Energy Technology Laboratory, was working with SOFCs that ran on clean, natural gas.

It was actually through conversations with people from National Renewable Energy Laboratory that TMI decided to write a proposal to the DOE Hydrogen Program. TMI is not proposing their “mainstream” TMI fuel cells for this project.

III Initial Discussion:

Solid oxide fuel cells generally operate at about 900^{o}C and rely on migrating oxygen ions. All SOFCs are designed in three layer “sandwiches” consisting of a solid electrolyte between two electrodes. The major difference is in configuration. For instance, the Westinghouse SOFC design contains three concentric cylinders. The TMI fuel cell has three discs of roughly two inch diameter (per cell) with holes in them for fuel flow. The porous design cuts down on manifolding.

TMI uses particulates to make their three layers. It is therefore not necessary to co-fire the three layers. (Other manufacturers need to co-fire to avoid cracking.) Therefore, TMI has the capability of testing and substituting new materials easily. In general, however, SOFC electrode and electrolyte materials are similar throughout the industry.

TMI makes 2 ½” diameter cells. They believe that this size will maximize efficiency and lower costs. This will happen through superior cooling and temperature control, ease of manufacturing, and lower pressure drops. Smaller diameter cells give a higher volumetric power density, which translates to lower costs.

Seals have not been a problem as TMI’s designs to date have involved seals in the middle of the discs. However, they are now looking at rim seals as well.

In order to keep costs down, TMI uses low cost manufacturing processes and no precious metals.

Without getting into actual material descriptions at TMI, I can make a comparison with another (European) SOFC manufacturer that I had the opportunity to visit about a year ago. This other company used particulate component starting materials as well, using a yttria zirconia electrolyte sandwiched between a nickel oxide anode and a strontium-doped lanthanum manganite cathode.

The electrolyte was cast onto plastic tapes, after which sintering was used to burn off the plastic. The electrolyte layer is then sandwiched between the green electrodes, which have been made as pastes in organic binders and passed through a sieve before the sandwich is made. The three-layer system is then co-fired. That particular manufacturer mentioned that sulfur poisoning was a problem. TMI's claim is that their system is sulfur tolerant.

TMI is also a systems house; they make their own reformers. Their systems are able to switch between natural gas, propane, and jet fuel (JP8). They have run for 1600 hours continuously on JP8. They have not yet tried diesel, but recognize that diesel would be harder to reform. *As we mention later, their initial proposal included diesel rather than propane.*

TMI has targeted grid independent residences. Without the selling electricity to the grid issues, these are somewhat easier to study. There are about 200,000 of these homes in the United States (about 0.2% of all residences) not including seasonal housing. People who live in these houses are "doomed" to pay higher prices, says Dr. Ruhl.

Dr. Ruhl presented comparative data from their final report of their FY 2000 paper study. This is reproduced in Exhibit 2. (*We discuss these data in more detail in the Questions and Answers section)* For the scenarios including wind power (Cases B, D, and E), TMI used a 3 kW wind turbine. In the "Wind + TMI Fuel Cell" cases (D & E), TMI assumed a battery backup for quick start-up. This was the high cost component of the system. The battery was described as a valve regulated lead acid (VRLA) battery of the glass mat design.

TMI thought that a 3 kW wind turbine would be appropriate for a house; anything much smaller wouldn't provide enough energy. In the case study, the 3 kW wind turbine provides about 71% of the total energy needed. *If we look at the earlier solar case (Exhibit 1), TMI showed cases where 99% of the energy could come from the PV panels. An analogous wind system would have made a good comparison.*

Their "propane only" SOFC system (*this is the "mainstream" system that TMI has been mentioning, Case C)* gets 60% efficiency on a lower heating value level. For the system that they are developing for the Hydrogen Program (Case E), they claim a round trip efficiency of 73% (wind → SOFC, electrolyzer mode → hydrogen storage → SOFC, fuel cell mode → load.) In fact, Dr. Ruhl claims they can likely get up to 80%, but this would be more expensive than the $0.30/kWh they claim in Exhibit 2.

The TMI system is planned to contain four 1 kW modules, which would be running in parallel to ensure reliability (*see also Question 12*). Each module would weigh less than 100 lbs. *Note that Exhibit 2 only assumes 3 modules.*

TMI actually sees their straight-propane fuel cell (*Case D in exhibit 1, and Case C in Exhibit 2*) as the most viable in the short term. *Note that these are also the most inexpensive systems, providing electricity at less than $0.17/kWh.* As renewable energy becomes more desirable, the reversible fuel cell option becomes more attractive. TMI does point out, however, that battery storage makes a pretty good competitor. *It comes down to how long do you want to (or need to) be able to survive in the absence of the wind blowing or the sun shining and how many batteries do you want to own and maintain.*

IV Tour:

I was given a tour of the facility, but was asked not to comment on any specific details of their setup. TMI has moved into this new facility only in the past few months. It is impressive in capability for a small company; TMI has the necessary equipment to manufacture and test SOFC components.

V Questions and Answers:

Dr. Ruhl led the discussion on the questions that I had sent to TMI earlier.

1. **What properties of solid oxide systems make them superior to, say, PEM systems for reversible fuel cells? Please look at both the electrolyzer and fuel cell "halves" of the system to answer the question.**

There are several advantages; some are in one direction, some in both:

a. As both an electrolyzer and a fuel cell, the TMI SOFC can operate at low voltages due to the high operating temperatures (800-900°C). There is very good high temperature kinetics, and there is no activation polarization at high temperatures. Therefore, TMI in fuel cell mode, can operate at about 880 mV/cell, and in electrolyzer mode, they can operate at about 1030 mV/cell. This gives an efficiency of about 85%; Analogous PEM efficiencies would be around 30%. *True if you're operating the PEM in the electrolysis mode at an overvoltage of about 2000 mV, and operating the fuel cell at about 600 mV. I believe we should be able to at least use a higher voltage for the fuel cell — maybe about 800 mV. I'm not sure the comparison here is fair.*

b. The ceramic membrane does not leak; PEM membranes do leak. Again this is an advantage in both directions.

c. In the electrolysis mode, there is more favorable thermodynamics using high temperature steam than liquid water. The free energy is much lower.

d. Also in the electrolysis mode, they can make use of thermal storage. In the fuel cell mode, excess heat is produced, so they let the temperature "float" upwards during fuel cell operation, and then use the heat in the electrolysis mode. In addition, the heat of condensing water during fuel cell operation can be used to vaporize water during electrolysis. *Not on a one-to-one basis, of course.*

Dr. Ruhl also indicated that they have a solid oxide electrolyzer that will operate with about 95% efficiency (if they have only a very small power conditioning factor) and makes 5000-psi hydrogen.

2. **Your FY 2001 Annual Operating Plan contribution speaks of demonstrating the system in "storage battery mode." Does this simply mean storage of hydrogen as opposed to lead acid batteries? How will the hydrogen be stored? Is this part of the project, or will it just be off the shelf.**

It does simply mean storage of hydrogen. TMI's design calls for the hydrogen to be stored as a compressed gas; there are more inefficiency issues with hydrides, especially the need for temperature to remove the hydrogen. *Might not this actually be a good candidate for hydrides seeing the high temperature operation anyway?*

TMI's design also calls for storing the electrolysis-produced oxygen, and use it in the hydrogen/fuel cell mode. They use air in the propane/fuel cell mode. The need for high-pressure oxygen storage helps to justify the use of high-pressure hydrogen storage.

Phase 1 was just a paper study; there is no plan to do any storage development in later phases.

3. **Do you anticipate home units? Would they include hydrogen storage at high pressure?**

TMI's major market thrust is toward non grid-connected residences. Conceptually, hydrogen would be stored as a compressed gas. TMI believes that safety issues in this regard would be handled by others.

4. **In your FY 2000 Annual Review Report you use a hypothetical home in Boulder CO as your test case. What conditions were you meeting by choosing this application? Do you feel that this is a typical application (domestically/ internationally) for your system? What other applications do you see for this type of system?**

TMI recognized that there were a large number of homes in Colorado that were not connected to the grid. In addition, solar data was available for the Boulder area. (Later, they switched to wind as the renewable resource and moved their hypothetical site to Colorado Springs (*See Question 6*)).

The use of Boulder was more "favorable" than typical. The home in the case study does not use air conditioning, but this is not unusual for non grid-connected homes.

5. **Your cost of electricity from what appears to be your most advanced system (labeled "G" in your FY 2000 Annual Review Report is $0.66/kWh. This seems rather high, especially if it is being used as the only source of energy. What (other than the low emissions) will make such a system attractive?**

The data are shown in Exhibit 1. The number has come down. Now using wind resources, TMI is quoting $0.30/kWh (*Exhibit 2 Case E)* for the analogous system. Dr. Ruhl says that they can even beat $0.66 for solar. The other side of the coin is that some people are willing to pay more for renewable power. Granted, it's a small fraction of the people. Dr. Ruhl believes that the price will come down further with improved renewables technology.

Actually, I think Case F in Exhibit 1 (the older, solar-based system) is more analogous to Case E in Exhibit 2. The case that I was actually asking about (Case G in Exhibit 1) is not really represented in Exhibit 2, the newer, wind-based data. Case G is more of an "ideal" set up, where you have adequate renewable energy to take care of most of your needs (99%). It would seem that TMI has abandoned the scenario where the use of the fuel cell in propane mode is only a minor player.

The "small fraction of the people" who are willing to pay more for green energy might have a tendency to occupy these non grid-connected houses. At the same time, however, would they also want to use propane, or would they be more interested in a two-way reversible fuel cell only? It would be more expensive to rely totally on hydrogen storage, but would this market care?

6. **Your Final Report (September 2000) changes the site to Colorado Springs, and changes from solar to wind power. What was the reason(s) for this? (Wind numbers seem more attractive than solar; I assume this is part of the reason.)**

The lower price for wind power is indeed the main reason. The suggestion to move from solar to wind came from Dr. George Thomas (Sandia National Laboratories) *(I later have come to believe that Dr. Ruhl actually meant Dr. Sandy Thomas of Directed Technologies Inc.)* according to Dr. Ruhl. The move from Boulder to Colorado Springs was due to the fact that wind data was available for Colorado Springs.

7. **Do you see this system as more or less attractive in a scenario where grid connection is also a possibility?**

The grid-connected scenario may become attractive when fuel cells “really take off,” but probably not until then. Perhaps it can be attractive in specific scenarios; it’s hard to tell.

It would be too expensive to sell propane-based electricity back to the grid. Natural gas would be another story.

8. **Please discuss heat flows to and from your reversible fuel cell. What is your operating temperature? What is the source of heat? Where does the waste heat go?**

The TMI system runs at 900^{o}C most of the time. When you are in fuel cell mode, you invariably produce more heat than you need. You need to have a cooling system, because you are not always operating in a mode where you can use the heat. So you don’t really have a lot of waste heat.

TMI, however, has looked at using whatever waste heat there is for a domestic hot water system. They thought that this seemed reasonable.

9. **Since efficiencies are generally greater for electrolysis than fuel cell operation, is it necessary for you to oversize your system to maximize your renewable resource input.**

TMI’s system-level study showed that the optimal case may be one in which they may have to “throw away” a little renewable energy. This was economically favorable to oversizing the system.

10. **I assume that to run your system in propane mode, it needs some kind of a reformer. Is this a separate operation? What happens to the byproducts?**

Yes, the propane mode uses a reformer, but it is heated by hot exhaust. It also burns highly depleted fuel and produces no NO_x.

In the propane mode, the waste products are vented. This is primarily CO_2 and a small amount of SO_2, as there is sulfur in propane. *This strikes me as possibly alienating the very people you are trying to market.*

There is also a small VRLA battery in the system. This is used to get fast response during the time the system is switching between modes. A fuel cell will take about four seconds to respond, while the battery is instantaneous.

11. **The reviewer’s comments in answer to your FY 2000 Peer-Reviewed Presentation indicate that you were concentrating on diesel engine backup rather than a propane fuel cell. (They make no mention of propane.) Were you presenting the propane system at the time?**

TMI had spoken of propane during the review. Dr. Ruhl theorizes that the reviewers might have seen a copy of TMI's original proposal, which was keyed to diesel reforming because of the Alaska tie-in.

Recall that TMI mentioned that their reformer was robust enough to handle NG, propane or JP8, but they were unsure about diesel. Yet, they originally proposed diesel.

Dr. Ruhl admits that the system is complicated (*the FY 2000 reviewers found fault in the complexity of the system)*, but it is the most cost effective system.

TMI has looked at two separate systems (electrolyzer and fuel cell), but found that you lose too much heat in this manner. *The need to conserve heat might be a major reason why a company making PEM systems might opt for a two-stack system (ala Proton Energy Systems) while a solid oxide system manufacturer would desire a single stack.*

12. **In your September 2000 report, you show four reversible fuel cell modules for the wind/reversible fuel cell case (system E). Is the plan that all modules will be running on the same fuel at the same time, or might, say a couple be running on hydrogen and a couple on propane? Would it be fair to assume that if you're running in electrolyzer mode, all four modules are in that mode? In system E, will any of the wind-produced DC electricity go directly to AC conversion and the load, or will it all go through the fuel cell?**

When in the wind mode, wind power first goes directly to power conditioning and the load. Excess wind goes to the electrolyzer for conversion to hydrogen and oxygen. When in the fuel cell modes, all of the hydrogen and oxygen is depleted first (hydrogen fuel cell mode). You only switch to propane when you have to. Also, recall that the battery is there for the quick start.

VI Additional Discussion:

The New (Phase 2) Effort:

Dr. Milliken, who is the PI on the newly started hardware-based phase, briefly discussed TMI's plans and technical hurdles. TMI will resolve performance over a full range of conditions. They will concentrate on multi-stack systems (*their later Phase 1 work was based on three modules, and they have said that they envision four modules as a likely scenario)*, and will address life and gas cycling. They are especially concerned with degradation of the system under electrolysis conditions.

TMI is not planning to do much in the way of stack seal development. Recall that the seals are in the center of their discs, but that they will need some rim seals as well. Their contract, however, does not have sufficient funding for seal development.

TMI also plans cost studies in which they will be evaluating stacks over a wide range of conditions.

VII Final Thoughts:

In FY 2000 at the Hydrogen Peer Review, the reviewers showed concern that the proposed process was too complex. At the time, it was in the PV mode. The reviewers felt that more detailed cost breakouts were needed (although presumably, the data we show here in Exhibit 1 and the data backing it up should have been available.) Since that time, TMI basically revamped their study, turning it from a PV-based single module system, heavily reliant on renewable energy in Boulder, to a wind-based three-module system, only partially reliant on renewable energy in Colorado Springs. This was done in what looks like a complete severance from the earlier PV work. The PV portion, which was quite detailed, is not even mentioned in the September 2000 final report. While wind, as it was pointed out is indeed a less expensive system, the solar case studied had some merit, and should not be lost to the ages.

The major question, however, is where does this work fit in? It is heading toward a demonstration of a reversible fuel cell – certainly a worthy goal. The hydrogen community is in need of assessing reversible fuel cells adequately once and for all. On the other hand, is this type of system the right one for such an assessment? The non-grid connected domestic market may be one that is willing to pay more for electricity. But what is its motivation? If it's environmentally based, why does it want a propane reformer and sulfur emissions as opposed to a fully renewable system with perhaps a larger stack and more hydrogen storage (or battery storage, I suppose). If it is not environmentally based, but just needs remote power, why not just the "old" TMI fuel cell (the one-direction, propane fuel cell)? Add to this that the proposed system is a complex system that will require much optimization, and this optimization is not likely to be generic, but might be case by case. Is there a market for a somewhat expensive, somewhat environmentally friendly system?

The comparison I would have liked to see would be the TMI three-way fuel cell system to a TMI two-way reversible SOFC and a diesel generator backup – preferably in the mode where the backup system is rarely used.

Exhibit 1. System Comparison From FY 2000 Annual Review Report, Solar-based Scenario, Boulder, CO

Case	A	B	C	D	E	F	G
Solar Power (%)	0	33	99	0	33	33	99
Primary Fossil Fuel Generation	Propane Engine	Propane Engine	None	Propane Fuel Cell	Propane Fuel Cell	Propane Fuel Cell	None
Backup Fossil Fuel Generation	Diesel Engine	Diesel Engine	Diesel Engine	Propane Fuel Cell	Propane Fuel Cell	Propane Fuel Cell	Propane Fuel Cell
Primary Storage	VRLA	VRLA	VRLA	VRLA	VRLA	Hydrogen	Hydrogen
Pollution	Highest	High	Low	~0	~0	~0	~0
Noise	Highest	High	Low	Very low	Very low	Very low	Very low
Installed Cost ($/kW)	8,000	13,900	27,300	1,800	10,300	8,600	16,800
Fuel Cost ($/kWh)	0.269	0.193	0.002	0.071	0.051	0.049	0.001
Maintenance ($/kWh)	0.329	0.330	0.555	0.046	0.196	0.129	0.215
Cost of Electricity ($/kWh)	0.811	0.895	1.286	0.166	0.521	0.407	0.666
CO_2 Emissions (tons/year)	9.5	6.9	0.07	2.5	1.8	1.7	0.021

A. Engine-Generator
B. Solar + Engine-Generator
C. Solar + Engine backup
D. TMI Fuel Cell
E. Solar + TMI Fuel Cell
F. Solar + TMI Reversible Fuel Cell
G. Solar + TMI Reversible Fuel Cell (TMI Propane Fuel Cell backup only)

Exhibit 2. Comparison Data from TMI Final Report, September 2000. Wind-based scenario, Colorado Springs, CO

System Type	A	B	C	D	E
% Wind Power	0	71	0	71	71
Primary Fossil Fuel Generation	Propane Engine	Propane Engine	Propane Fuel Cell	Propane Fuel Cell	Propane Fuel Cell
Backup Fossil Fuel Generation	Diesel Engine	Diesel Engine	Propane Fuel Cell	Propane Fuel Cell	Propane Fuel Cell
Energy Storage	VRLA	VRLA	None	VRLA	VRLA
Pollution	Highest	Medium	~0	~0	~0
Noise	Highest	High	Very low	Medium	Medium
Total Installed Cost ($/kW)	22,900	33,900	5,500	24,900	18,200
Unit Cost ($/kW)	7,600	11,300	1,800	8,300	6,100
Fuel Cost ($/kWh)	0.279	0.069	0.070	0.021	0.021
Maintenance ($/kWh)	0.365	0.416	0.048	0.265	0.119
Cost of Electricity ($/kWh)	0.826	0.758	0.167	0.486	0.303
CO_2 Emissions (tons/year)	9.8	2.4	2.5	0.7	0.7

A Engine-Generator
B Wind + Engine-Generator
C TMI Fuel Cell
D Wind + TMI Fuel Cell
E Wind + TMI Reversible Fuel Cell

This page intentionally left blank.

Technical Evaluation Report

Project: Hydrogen Internal Combustion Engine Research
Company: Sandia National Laboratories, Livermore, CA
P.I.: Dr. Peter VanBlarigan
Date of Visit: May 3, 2001
Evaluation by: Edward G. Skolnik, Energetics Inc.

I Summary:

Sandia (Livermore) National Laboratories (SNL) is conducting an internal combustion engine (ICE) project that is developing a free piston, two stroke cycle-based engine that can burn hydrogen and/or several other fuels. The energy is then used to run an alternator to generate electricity.

One of the key premises to this work is that if you use a lean, premixed fuel/air mixture in the ICE, you can limit the amount of emissions you get without using a catalyst.

While the initial objectives for this project involved the development of the ICE for vehicular hydrogen combustion, the recent focus has been on the production of electricity in stationary, distributed energy scenarios. They are currently working on a 30 kW prototype system.

Project Strengths:

- As a stationary electricity resource for distributed power, the ICE system has estimated efficiencies reported by SNL to be in the 50% range (likely to be still near the mid-40% even when you include some alternator losses). This makes it competitive with fuel cells and well ahead of microturbines.

- This is one of very few utilization projects that provide an alternative to fuel cells. It's a good thing to keep an ICE option open.

Issues that should be Addressed:

- Hydrogen is just one of many materials being used as fuel. (They're also looking at several alkanes as well as methanol and ammonia.) As a hydrogen project [and they are receiving funding from the Office of Distributed Energy Resources (DER) as well] they need to focus more on hydrogen. Even the ammonia argument (see Question 5 below) is a bit of a stretch.

- The very attractive efficiency numbers appear to be tied (at least in part) to some older data (see Exhibit 1 and Question 7). Some validation of these data is needed to increase confidence.

II Introduction and Background:

I visited the SNL site and met with the PI for the ICE project, **Dr. Peter VanBlarigan**. Dr. VanBlarigan has been involved with the ICE work at Sandia for about five years. coming on-board near the beginning. Originally the project was a multi laboratory project with Lawrence Livermore National Laboratory (LLNL) and Los Alamos National Laboratory (LANL). Dr. VanBlarigan was originally developing the power plant for a vehicle. The goal now is to generate electricity, with stationary systems the main thrust.

Currently, the project is one year into a three year $500K project that is half funded by the Hydrogen Program and half funded by the DER as part of their Reciprocating Engine Program. The project is receiving additional internal funds from SNL. The money is to develop the components and build a 30-kW prototype engine.

Dr. VanBlarigan is currently concentrating on the development of a linear alternator and scavenging (pulling in fresh input and blowing out exhaust) efficiency for the 2-stroke cycle engine – not combustion.

Dr. VanBlarigan took me on a tour of the appropriate facilities, and we also spent a significant amount of time in discussion. This included discussing a series of questions that I had sent him prior to our meeting.

III Tour:

Piston Systems:

The first stop was the 30-kW free piston experimental setup. The chamber is three inches in diameter and contains a long-stroke piston, which displaces 1000cc. The piston is placed at one end, and a premixed fuel/air combination is admitted to the other end of the tube. High-pressure helium is used to push the piston to the other end. The compression ratio is determined by the driver pressure, usually 8,000 – 11,000 psi. They measure the pressure and the displacement. As they already know the fuel/air ratio, they can determine the efficiency. They measure emissions via flame analysis. Kinetics had been performed on the combustion reaction previously by Dr. Charlie Westbrook at LLNL.

A combustion test is “one shot” of the piston down the tube. A test is done in about 20 minutes. A real-life situation would likely encounter a little more turbulence, but Dr. VanBlarigan feels that this is probably not important. They get good reducibility.

SNL also has a smaller piston system. It has a 12mm bore, and is equivalent to a 1-kW sized system. This is a step in a scale-down process that Dr. VanBlarigan is looking for to provide soldier (portable) power (at the ~30 W level).

Alternators:

SNL is evaluating two alternators. One is being developed by SNL; the second was built by Magnequench at no charge to SNL. Power is generated in the alternator by having a series of magnetic rings, which are magnetized radially with alternating polarity. This results in a series of flux loops with adjacent loops going in the opposite direction. This results in electricity being generated. Dr. VanBlarigan referred to the SNL alternator as a brushless DC motor in a linear configuration.

In the SNL design, the pieces are laminated; the Magnequench model uses powdered iron in epoxy to make the iron part.

Dr. VanBlarigan has calculated alternator efficiency at about 95% for the SNL design. Losses are due to eddy currents and heating of the coils.

SNL will be testing the alternators with a different engine – not the prototype. They wanted to use a piston with a little shorter stroke so they could test the alternator under full power conditions.

Flow Bench:

Finally, I saw the system for testing swirl reduction. This was the engine head built by LLNL with shrouded valves. It is discussed below in Question 1.

IV Questions and Answers:

I sent Dr. VanBlarigan a list of questions prior to the site visit. The results of our discussion on these questions follows.

1. **The Hydrogen ICE project, I know, has been ongoing for several years including a period where it was a multi-lab project. Since this is the first time I've reviewed the project, we should spend a little time going over it's history – who was doing what; to what degree and how the goals have changed; what have been the key accomplishments over the years.**

The original concept was to build an ICE that would run on hydrogen in a lean mode to minimize NO_x. They used a quiescent combustion chamber. Five years ago, they had built a new cylinder head designed to minimize swirl.

A German paper written during World War II spoke of an ICE hydrogen engine that could obtain an efficiency of 52 –53%. In the mid 1990s, SNL was getting efficiencies of 42-43%. They therefore switched from an Onan Engine to a Perkins Engine with a modified cylinder head. They introduced a shrouded valve to try to reduce swirl and tumble. The result was that they were still in the low 40s in efficiency, but had reduced NO_x emissions to 2-4 ppm at an equivalence ratio of 0.4.

The project was a 3-lab project at the time, with LANL and LLNL basically providing modeling services and SNL developing the engine. In 1997, the project got downsized due to a report from the President's Council of Advisors for Science and Technology (PCAST) that, in evaluating renewable energy options, advised against demonstrations of hydrogen-based ICEs. It has since been an SNL project only.

One of the major changes that has occurred is that the ICE project is no longer specific to vehicles. It has become a project in which the main goal is to produce high efficiency electricity using equipment that is less complex (*and more familiar*) than a fuel cell.

Dr. VanBlarigan identified the demonstration of a high efficiency, low emissions combustion system as the key accomplishment to date. The next key objective is to design an alternator that will work at a good power density and a high efficiency. Following this, focus will move to the scavenging system in the combustor. SNL want s to have a uniflow scavenging system that will have an 80% scavenging efficiency (that is, 80% of the old, spent, gases will go out the exhaust with each stroke, but none of the new flow goes with it.

This project has had its share of ups and downs due to the politics of ICEs being "in" or "out" as a vehicular hydrogen technology. The fact that Dr. VanBlarigan and his group were able to move to a non-vehicular application and keep the work going is commendable in itself.

2. **During your FY 2001 presentation you spoke of both vehicular and stationary applications for your ICE, converting the hydrogen to electricity. What stationary applications do you have in mind?**

The unit currently being developed is a 30 kW unit. This is the right size for distributed applications; its high efficiency make it very attractive competing with other distributed energy generators. Reported microturbine efficiencies are around 28%; the piston provides about twice that efficiency.

As we stated above, the DER focus seems like a smart fit. The efficiency (if we are indeed comparing apples with apples here) of the ICE system makes it potentially attractive here, as does the possibility of using locally available fuels. (The latter fact may not be best for the furthering of the Hydrogen Economy, however) Continuing an effort to develop a system that does not rely on a fuel cell also makes sense.

My apples with apples comment stems from making a comparison with a 28% efficient microturbine. The DOE microturbine efficiency goal of 40% might be a better number to compare the ICE system with, if the ICE system is using projected 50% efficiency numbers.

3. **What benefits do you obtain from this engine design that makes it more attractive to other designs? Is fuel versatility a large part of it? What parameters do you vary to optimize the engine to the various fuels?**

The design leads to a high efficiency, low emissions system that has multi-fuel capability without hardware changes. SNL arrives at optimization for different fuels by varying the compression ratio. The present design works very well at 30 kW. Dr. VanBlarigan believes that you could use the same design up to, say, 200 kW, but he is not really addressing large applications.

4. **What is the status of the linear alternator (both designs)? What criteria will be/has been used to quantify the performance of the designs?**

They are nearly ready to test the Magnequench alternator. The SNL design still requires some minor design changes, primarily to allow easier assembly.

The main criterion for the alternators is efficiency. SNL will test both alternators, obtaining load vs. time and power vs. time data, and calculate efficiency. Then they'll do a down-select, or if necessary, design a new alternator.

5. **Please discuss the combustion of ammonia. How does this process fit into the overall scheme of hydrogen research? (I assume you are not making hydrogen from ammonia.) What are the overall advantages of burning ammonia in this scheme?**

Dr. VanBlarigan reiterated that the SNL ICE is not limited to burning hydrogen – or hydrogen blends, for that matter. It is a multi-fuel device. In the case of ammonia however, he stated that there is a strong hydrogen connection. You can make ammonia from hydrogen (*Haber Process:* $3H_2 + N_2 \rightarrow 2NH_3$), and if the hydrogen comes from a renewable resource, so does the ammonia. This is why they are using ammonia. (They have also looked at biogas as part of the renewable effort.)

In addition, an infrastrucure for ammonia exists today, especially in the farming industry. The distribution network is already there, and ammonia also stores easily. One good early application would therefore be the running of farm equipment.

It's a bit of a stretch to use that kind of argument to consider ammonia renewable hydrogen unless there is an effort to tie ammonia to hydrogen storage. But maybe doing just that is not that bad an idea.

6. **How efficiently does passing NO_x over ammonia reduce NO_x emissions? How much of an energy penalty does one pay for this?**

It turns out that both NO_x and NH_3 are already in the exhaust gas stream at about the same level – about 600 ppm. Therefore, all you need is the catalyst. If the numbers weren't the same, you might have to add a little ammonia. *The amount of ammonia you would lose in this manner is not enough to indicate any significant energy penalty.*

7. **You presented some efficiency data for several fuels in your FY 1999 Annual Review report (Exhibit 1). Is there any update on these data?**

Exhibit 1 (*which is attached)* included extremes and "maybe shouldn't have been used. – Some data was questionable." SNL has not been working on the combustion efficiency since then. They would like to do some tests in which they vary the piston speed to study its effect on efficiency, but they haven't the time or the money.

If the data are questionable, and SNL has not been working on efficiency matters since then, it would be good to have something to back up the high efficiency claims.

8. In the same table, you show non-zero CO and hydrocarbon emissions for hydrogen fuel. What is the emission source?

The emission source is likely an external contaminant, possibly from a lubricant. It could also be a decomposition product of the piston rings.

9. How do emissions in general compare for the current engine design compared to more standard ICEs?

Emissions are about equivalent to what could be done with a spark-ignition engine and a three-way catalyst, but the efficiency is much higher. Compared to a diesel engine, however, the current design is far superior in emissions, and also has some efficiency advantage. Compared to a turbine, emissions are about the same (perhaps a little lower NO_x), but with much better efficiency.

If the projected efficiency and emissions results are borne out at the end of the final year, I would think that the project would be successful. It appears that the ICE could compete favorably in the distributed energy market.

10. Are there any plans to address systems issues?

Next year's plan will be focused on selecting the alternator, and working on the control system and doing the design layout of the overall system. The following year (the final year of the current program) they will be building the overall prototype. They also have to determine "how to start the thing." Dr. VanBlarigan is considering using the alternator, although for the prototype, perhaps he'll just use compressed gas to start it.

SNL's goal is to operate the prototype system under one set of conditions as part of that final year effort.

Dr. VanBlarigan is considering, as a way to control the system, a NO_x feedback loop. That is, if the NO_x level starts going up, it will send a signal to drop the equivalence ratio or the compression ratio.

V Additional Discussion:

- SNL decided to work with the free piston concept. With the Otto cycle you have constant volume combustion, but as you get to a higher compression ratio you deviate from this condition as the burn slows down. You want a fast burn.

  One way to increase the burning rate is to premix the fuel and air. This has the additional advantage of reducing both NO_x and hydrocarbon emissions. SNL uses homogeneous charge compression ignition (HCCI) as a means to ignite the premixed charge: You compress the mixture to higher temperature and the mixture ignites but, since there is no flame propagation, it remains at constant volume. This is a very fast process, taking about 20 microseconds. (The Otto cycle itself is about two orders of magnitude slower.) The microsecond range is sufficiently rapid so that the piston is effectively not moving during ignition. Furthermore, the process is not held to flammability limits; there is no flame.

The process is controlled by the compression ratio. The alternator, by drawing off electricity, slows down the piston so that the compression ratio is the same at both ends. The free piston system is shown in Exhibit 2. (You can run HCCI in a standard diesel engine, but is difficult to control the compression ratio.)

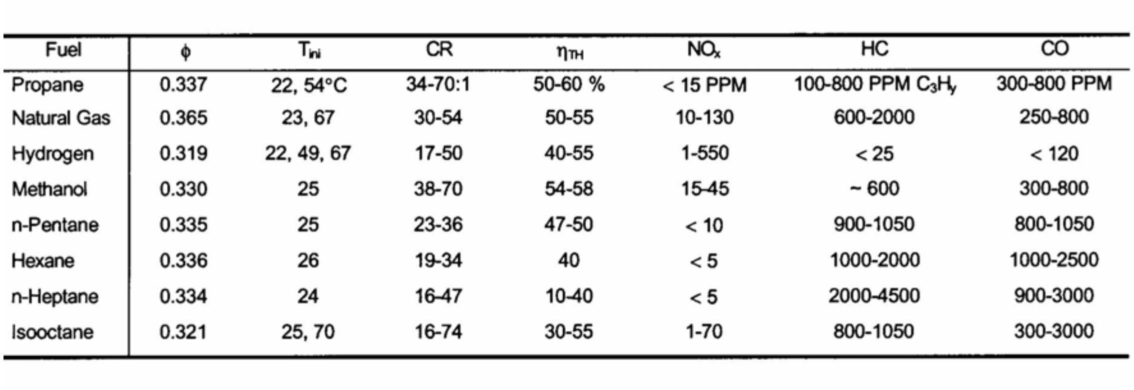
Dr. VanBlarigan has found efficiencies of about 56% with fuels that have higher compression ratios. These include hydrogen, natural gas and propane all of which have compression ratios in the 30-40 range. Materials with lower compression ratios (higher alkanes, for instance, with compression ratios under 20) have lower efficiencies. With some of these higher alkenes (e.g., hexane, heptane), they don't get complete combustion; with others they find the combustion mechanism to have two steps.

- Aside from the tie-in with Magnequench, SNL has received interest from Caterpillar, Unique Mobility (a power conditioner manufacturer), and Delphi (a valve manufacturer).

- This project is having the same kind of problems as is common for other projects: feast or famine. At times, the budget is constrained too tightly to work effectively, and at other times, they have the money, but they can't get the staff (who have moved over to other projects during the lean times) to support the level of effort they need.

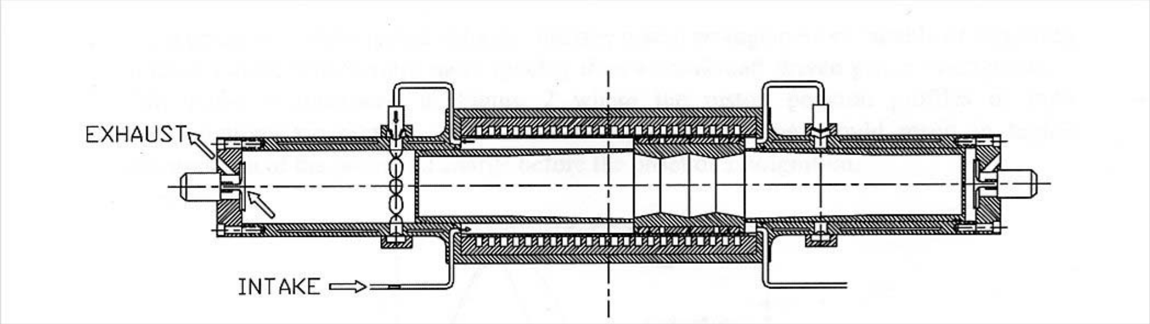
- The current DOE project has two more years left to run. After that, Dr. VanBlarigan is not sure. He mentioned that perhaps at that point, they won't need DOE support.

Exhibit 1. Table from 1999 Hydrogen Annual Review Paper "Homogeneous Charge Compression Ignition with a Free Piston: A New Approach to Ideal Otto Cycle Performance" P. VanBlarigan



Fuel	ϕ	T_{ini}	CR	η_{TH}	NO_x	HC	CO
Propane	0.337	22, 54°C	34-70:1	50-60 %	< 15 PPM	100-800 PPM C_3H_y	300-800 PPM
Natural Gas	0.365	23, 67	30-54	50-55	10-130	600-2000	250-800
Hydrogen	0.319	22, 49, 67	17-50	40-55	1-550	< 25	< 120
Methanol	0.330	25	38-70	54-58	15-45	~ 600	300-800
n-Pentane	0.335	25	23-36	47-50	< 10	900-1050	800-1050
Hexane	0.336	26	19-34	40	< 5	1000-2000	1000-2500
n-Heptane	0.334	24	16-47	10-40	< 5	2000-4500	900-3000
Isooctane	0.321	25, 70	16-74	30-55	1-70	800-1050	300-3000

Exhibit 2. The 2-stroke Free Piston/Linear Alternator System. Combustion occurs alternately at each end. (From same reference)



Afterward

Although a few of the projects reviewed have since ended, most are still funded, either under the original concept or in a somewhat new direction. Others reached completion, and a follow-on project was funded. The comments below address the status of some of these projects (mainly the ones evaluated more than two years ago) and some of the personnel who participated in the site-visits.

Dr. Jonathan Woodward, whose project was the very first visited, recently (Spring 2002) left ORNL. A project that evolved from that first one, moving toward producing hydrogen from glucose, is currently being funded by DOE. Dr. Barbara Evans, who was a post-doc during the 1996 visit, has recently become the PI. In this new project, ORNL is generating enzymes from different bacteria, and is able to collect all of the hydrogen from the glucose molecule. The review of the latest version of this project is scheduled for August of 2002.

Carbon storage (nanotubes and nanofibers) has been, over the past few years, the subject of as much controversy as any hydrogen-related technology. At this point, most people do not believe that nanofibers can store huge quantities of hydrogen, and may not be able to store any at all. The community is still split on nanotubes. The nanofiber project at Northeastern University was funded by DOE for about a year. More funding was supplied by private industry. The researchers formed a private company, which I believe still exists. No announcements of breakthroughs have come recently. Dr. Mike Heben at NREL continues to make progress with nanotubes, but is likely still far from a commercial product. The number of carbon nanotube projects in the Hydrogen Program, however, has increased from one to three over the past two years.

The division of Tecogen/Thermo Power/ThermoTechnologies under which the hydrolysis hydride slurry work was performed no longer exists. Mr. Andy McClaine has left the company, and formed his own business. He is reportedly still interested in hydride slurries, and is looking for funding.

ECD turned their metal hydride work and alloying capabilities into a project in which they have developed a hydrogen-powered scooter. The Hydrogen Program provided some of the funding for this development. ECD is also still pursuing metal hydride storage research and development, but not for the Hydrogen Program.

Dr. Salvador Aceves at LLNL is still developing cryogenic storage tanks, and is now also considering both 5000 psi tanks and hydrogen storage at liquid nitrogen temperatures (77^{o}K). These efforts are aimed at increasing the energy density for on-board storage.

Dr. Fred Mitlitsky left the employ of LLNL shortly after our meeting, leaving the storage vessel project in the hands of Dr. Andrew Weisberg. Dr. Mitlitsky moved to Proton Energy Systems and was actually part of the team that I visited at Proton later that same year.

SNL is still involved with hydride storage work, transitioning from magnesium-based hydrides to alanates. Dr. George Thomas has recently retired. Sadly, his associate, Mr. Steve Guthrie passed away in August 1999.

On another sad note, Dr. Myung Lee of SRTC and the membrane separation project, passed away in December 1999. The project is now under the direction of Dr. Kit Hueng, and is still being funded by DOE.

One big success story of a project moving from the laboratory to the field has been the biomass pyrolysis/reforming work at NREL, which was started by Dr. Esteban Chornet and Dr. Stefan Czernik. While process improvement and related projects continue at NREL, a group at Clark Atlanta University led by Dr. Yaw Yeboah has been pursuing the use of peanut shells as a feedstock for this process with a goal of producing a fuel for urban transportation.

Acknowledgement

I would like to express my appreciation to all of the PIs and researchers that I have visited, and about whose projects I have written. The evaluations could not have been performed, and this compilation could not have been made without their cooperation and help. I also gratefully acknowledge the U.S. Department of Energy Hydrogen Program for their funding.

Ed Skolnik
July 2002