Final Report

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Project Objective:

This project spanned two distinct areas of importance to the hydrogen (H₂) energy program. The first involved hydrogen storage and the second involved hydrogen production.

Chemical (Ammonia Borane and Novel Hydride) Hydrogen Storage

The objective of the hydrogen storage work was to develop novel hydrides for onboard hydrogen storage and off-board chemical recycling systems to meet DOE goals for storage capacity. Ammonia borane was used based on the large database for this compound but has challenges related to recycling and toxic products. However, very promising alternate novel chemicals such as ethylenediamine bisborane (BED) emerged in work conducted at Purdue with financial support from General Atomics. The systems laboratory developed in this project can be applied to the novel chemicals.

Anaerobic Biological Hydrogen Production

The objective of the hydrogen production work was to investigate hydrogen generation from waste streams using microbial fermentation. In addition, possible paths for implementation of the technology as a local electric and thermal energy source are being investigated.

Background:

The Hydrogen Systems Laboratory in a unique partnership between Purdue University's main campus in West Lafayette and the Calumet campus was established and its capabilities were enhanced towards technology demonstrators. The laboratory engaged in basic research in hydrogen production and storage and initiated engineering systems research with performance goals established as per the USDOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program.

In the chemical storage and recycling part of the project, we worked towards maximum recycling yield *via* novel chemical selection and novel recycling pathways. With the basic potential of a large hydrogen yield from AB, we used it as an example chemical but have also discovered its limitations. Further, we discovered alternate storage chemicals that appear to have advantages over AB. We improved the slurry hydrolysis approach by using advanced slurry/solution mixing techniques. We demonstrated vehicle scale aqueous and non-aqueous slurry reactors to address various engineering issues in on-board chemical hydrogen storage systems. We measured the thermal properties of raw and spent AB. Further,

we conducted experiments to determine reaction mechanisms and kinetics of hydrothermolysis in hydride-rich solutions and slurries. We also developed a continuous flow reactor and a laboratory scale fuel cell power generation system.

The biological hydrogen production work summarized as Task 4.0 below, included investigating optimal hydrogen production cultures for different substrates, reducing the water content in the substrate, and integrating results from vacuum tube solar collector based pre and post processing tests into an enhanced energy system model. An automated testing device was used to finalize optimal hydrogen production conditions using statistical procedures. A 3 L commercial fermentor (New Brunswick, BioFlo 115) was used to finalize testing of larger samples and to consider issues related to scale up. Efforts continued to explore existing catalytic methods involving nano catalysts for capture of CO₂ from the fermentation process.

Task 1.0 AB and Novel Hydride Based Recycling

Accomplishments

- Developed efficient large-scale synthesis of AB using sodium borohydride and ammonium sulfate in ammoniated THF at optimal temperatures.
- AB thermolysis by-product, polyborazylene, was converted to ammonium borate $[\text{NH}_4\text{B}(\text{OH})_4]$, which was subsequently converted to trimethylborate.
- Trimethylborate was reduced using diethylsilane in the presence of TMEDA to TMEDA-Bisborane complex.
- TMEDA-Bisborane complex was converted to AB *via* transamination in 80% yield.
- Ammonium borate was also reduced to AB using lithium aluminum hydride in the presence of ammonium chloride.
- Developed an efficient large-scale synthesis of ethylenediamine bisborane (BED) *via* transamination of AB with ethylenediamine.

Introduction

The focus of task 1 of the hydrogen storage project was to develop energy efficient procedures to recycle the spent fuel from AB thermolysis and hydrolysis to AB.

Approach

The AB spent fuel, ammonium borate or polyborazylene were to be converted to triacyl- or trialkyl borates, which was to provide molecules with weaker B-O bond. The reduction of trimethyl borate in the presence of TMEDA, followed by the displacement of TMEDA using ammonia was to lead to efficient ammonia borane regeneration. Other amine boranes, such as ethylenediamine bisborane (BED) were examined for hydrogen storage applications. Economical synthetic protocol for BED is being developed.

Results

We have developed the synthesis process for ammonia borane from sodium borohydride and ammonium sulfate under ambient conditions in ammoniated THF, in very high yields (90%) and purity (>98%) (eq. 1.1).

We have achieved the conversion of polyborazylene, obtained *via* the thermolysis of AB, to ammonium tetramethoxyborate $[\text{NH}_4\text{B}(\text{OMe})_4]$ in the presence of methanol, followed by reduction to AB using lithium aluminum hydride and NH_4Cl in 81% yield (eq. 1.2).

In an alternate protocol, ammonium tetramethoxyborate was converted to trimethyl borate in the presence of methanol. The reduction of trimethyl borate in the presence of TMEDA using diethylsilane resulted in the formation of bisamine borane complex in near quantitative yield (90%) (eq. 1.3).

The bisamine borane complex could be readily separated by filtration. The displacement of TMEDA from the amine borane complex was readily achieved using liquid ammonia to obtain 80% yield of AB (eq. 1.4) (Figure 1.1).

Figure 1.1: AB themolysis cycle: recycling of polyborazylene

We have also reported the conversion of ammonium tetrahydroxyborate $[\text{NH}_4\text{B(OH)}_4]$, hydrolysis by-product of AB, to trimethyl borate without the conversion to boric acid. The reduction of trimethyl borate was achieved using either the silane protocol or *via* reduction to sodium borohydride using NaH and subsequent conversion to AB in the presence of ammonium sulfate (Figure 1.2).

Figure 1.2: AB hydrolysis cycle: recycling of ammonium borate

However, our attempted reduction of ammonium borate with silanes in the presence of amine as well as the reduction of boron trisulfate, boron trifluoroacetate and trimethyl borate using a variety of silanes, in a variety of solvents, at various temperatures and in the presence of variety of Lewis bases has not been successful.

Energy calculations

We computed the energetics of the steps involved in the recycling of spent borate to AB using B3LYP/aug-cc-pVDZ level of theory. The results for the reduction of various $B(OR)_3$ (R= methyl, acyl, trifluoromethyl) to BH_3 using Me_3SiH and Bu_3SnH are given below.

- Gas phase esterification of $B(OH)_3$ to $B(OMe)_3$ is endothermic (6.7 kcal/mol).
- The reduction of $B(OCOCF_3)_3$ and $B(OTf)_3$ are thermodynamically favorable reactions.
- Me_3SiH is superior for reduction compared to Bu_3SnH . This has been verified experimentally.
- The reduction of $B(OMe)_3$ to BH_3 is endothermic.

Bisborane-ethylenediamine-complex (BED)

The generation of toxic byproducts, such as ammonia and borazine, during the dehydrogenation of AB is detrimental to fuel cell membrane. This led us to examine other amine boranes for hydrogen storage applications. Methylamine borane complex (11.1% hydrogen), methylenediamine bisborane complex (13.5% hydrogen), and ethylenediamine bisborane complex (BED) (11.4% hydrogen) were considered for this application. We selected BED as a potentially viable alternate hydrogen storage material. We developed two new synthesis protocols for the large-scale preparation of BED.

1. Reaction of ethylenediamine with borane-methylsulfide in dimethylsulfide (eq. 1.5)

2. Transamination of AB with ethylenediamine in THF (eq. 1.6)

Hydrogen generation from BED

BED is not hygroscopic like AB, which has broad benefits related to synthesis, handling and dehydrogenation. It is also environmentally harmless, non-flammable, non-explosive and stable in solid form at room temperature and pressure. Comparison of the DSC plots of AB and BED shows the relative exothermicity of the latter is half that of AB (Figure 1.3).

Figure 1.3: DSC plots of AB (left) and BED (right).

Our preliminary experiments on the thermolysis of BED under neat conditions and in diglyme released four molar equivalents of hydrogen. The main advantage of this material is the low dehydrogenation temperature ($\sim 110^\circ\text{C}$) compared to AB as shown in the TGA ramping profiles of BED in Figure 1.4 under three different conditions ($2^\circ\text{C}/\text{min}$ green line in figure, $5^\circ\text{C}/\text{min}$ blue line in figure, and $10^\circ\text{C}/\text{min}$, red line in figure) displays the release of 4 equivalents of hydrogen within 10 minutes. It was also observed that BED tends to foam less than AB, providing considerable advantages in the operation of the system.

Figure 1.4: TGA temperature ramping profiles of BED.).

Conclusions

We have developed an efficient protocol to prepare AB in large-scale from sodium borohydride and ammonium sulfate. We have developed four protocols to regenerate the spent material; (i) the AB hydrolysis by-product was converted to trimethyl borate and subsequently treated with diethylsilane in the presence of TMEDA to yield TMEDA-Bisborane complex which was converted to AB *via* transamination using ammonia (ii) the trimethyl borate was reduced to sodium borohydride which upon treatment with ammonium sulfate provided AB, (iii) the AB thermolysis by-product was converted to ammonium tetramethoxyborate and subsequently reduced to AB *via* silane protocol and (iv) AB was also regenerated from ammonium tetramethoxyborate in the presence of lithium aluminum hydride. An economically efficient large-scale synthetic protocol for BED has been developed *via* transamination of AB with ethylenediamine. We have shown that the thermolysis of BED releases four equivalents of H₂.

Acronyms

AB	Ammonia borane
THF	Tetrahydrofuran
TMEDA	<i>N</i> ¹ , <i>N</i> ¹ , <i>N</i> ² , <i>N</i> ² -tetramethylethane-1,2-diamine
BED	Bisborane-ethylenediamine-complex

Task 2.0 Dehydrogenation Systems Study

Accomplishments

- Captured the details of fast hydrogen evolution at the initial stage of the AB thermolysis process.
- Analyzed gravimetric and volumetric capacities, hydrogen release rates, and byproduct removal for liquid, solid, and slurry based chemical hydride systems.
- Developed and demonstrated complete hydrogen storage and delivery on demand systems using a club car platform addressing associated scientific and engineering challenges.
- Measured relevant thermal transport properties of powdered and pelletized ammonia borane and its partial thermolysis products.
- Characterized rheological properties of ammonia borane spent fuels.
- Completed system engineering analysis of a baseline full scale AB / ionic liquid slurry hydrogen storage system.

Introduction

The dehydrogenation systems study focused on improving the performance of onboard hydrogen storage systems. The AB slurry dehydrogenation work included measuring engineering properties of onboard hydrogen discharge and fresh/spent fuel transfer. A subscale reactor system was developed to provide a platform for the studies of AB and other hydrogen storage materials. We have developed a systems model to simulate the thermo-chemical process in an AB slurry reactor.

We measured elastic stiffness and viscous damping of AB spent fuels from various reactions including hydrolysis, thermolysis and hydrothermolysis. Smaller stiffness and larger mobility indicate better transportability of the spent fuel. The oscillatory squeeze flow technique was adopted to determine the visco-elastic properties of the materials. The technique uses compression forces and characterizes the properties of an acoustic wave moving through the sample rather than a shear deformation as used in typical rheological measurements.

With the three reactor systems, illustrated on the timeline of Figure 2.1, we built on the experiences gained from each to address scientific and engineering challenges with reactor capacities increasing by more than two orders of magnitude (from 0.1 to 50 grams) and using chemical hydrides such as ammonia borane (AB).

We designed and reported on the results obtained with a milligram scale glass reactor (also referenced in the following as the first reactor). This first reactor involved the use of a small mass, typically ~130 mg, of AB in each experiment, such that the evolved volume of hydrogen could be accommodated in a 250 ml burette. Using this reactor, we recorded hydrogen yield and reaction rate measurements of AB thermolysis in the neat form as well as facilitated by the presence of an ionic solvent, 1-butyl-3-methylimidazolium chloride (bmimCl).

In 2010, we focused our efforts on a scaled AB dehydrogenation batch reactor capable of handling two grams of AB per batch. The process cycle was optimized to ensure highly reproducible and controlled batch reactions. This stainless steel reactor (referenced in the following as the second reactor or the stainless steel reactor) was designed to handle reactions with starting temperatures of about 155°C and a nominal batch reaction time of 10 minutes. Heating filaments were used on the outer wall of the reactor to attain the desired reaction temperature.

In 2011, we applied lessons learned on the multi-gram laboratory scale thermolysis batch reactor to design a cartridge-based, self-sustained, and instrumented reactor system. This reactor system (referenced in the following as the third reactor or the cartridge-based, self-sustained and instrumented reactor) was

used to power a hydrogen internal combustion engine (HICE) on a club car. The system uses four pre-filled cartridges with up to 50 grams of AB each with a modified HICE exhaust system supplying the heat necessary for the dehydrogenation process. The system starts up using buffered hydrogen gas from a commercial gas cylinder and switches to the AB cartridges when the dehydrogenation temperature is achieved. The operation of the system was demonstrated by running the club car on a closed-circuit track in May 2011.

The experience gained through designing and operating these three reactors pointed out a need for reliable thermal and rheological property data. Such data are rarely mentioned in the literature, particularly for ammonia borane in powder form and for its thermolysis products. To address this need, we used a transient plane source technique to measure the thermal transport properties of ammonia borane and polyiminoborane (obtained by AB dehydrogenation at 167°C) at representative packing densities and under ambient conditions.

In this report, we summarize the design approaches and experimental results obtained with all three reactor systems with an emphasis on the second and third reactors. We also report the thermal property data analysis and its applicability to other chemical hydrides of interest to the DoE fuel cell and hydrogen programs.

Figure 2.1: Demonstration of AB thermolysis reactors at multiple scales.

Approach

Glass Milligram Scale Reactor

To facilitate the design of thermal management and spent fuel removal, we investigated neat and ionic-liquid aided AB dehydrogenation kinetics, especially at the initial fast hydrogen evolution stage using a milligram scale reactor.

A glass container (500 ml) was loaded with soybean cooking oil and a stirring bead. The oil bath was seated on a hot-plate magnetic stirrer and the oil was heated to the desired reaction temperature. A c-shaped glass container (2 ml) was pre-loaded with the desired amount of AB. A 50 ml 3-necked reaction flask was pre-loaded with desired amount of bmimCl and stored in a glove box under argon atmosphere. After being taken out of the glove box, the flask was immediately submerged in the pre-heated oil bath and a nitrogen purge was connected at the central neck. An open stopcock was seated on one of the two side-necks of the flask to allow any trapped air (being replaced by the N₂) to flow out of the flask. The other side-neck of the flask was sealed with a rubber septum and a hypodermic type-T thermocouple pierced through it to measure the reaction temperature. When the thermocouple was not used, the side-neck was covered by a glass stopcock. The flask was allowed to attain the oil bath temperature for about

10 minutes and was continuously purged with N_2 during this period of time. After pre-heating of the flask, the open stopcock that was used as the vent was removed and that side-neck was connected to a gas burette using a glass stopcock and tubing. The nitrogen source was removed from the central neck and the AB was gently poured into the reaction flask through the central neck from the c-shaped glass container. The c-shaped container was seated on and clamped to the central neck, and the stopwatch (for time recording) started.

The evolving H_2 was passed through two successive flasks of water that could absorb and condense the trace amounts of gaseous byproducts formed during the thermolysis, such as borazine. Subsequently, the H_2 was collected in the gas burette with a resolution of 1.0 ml. The accumulated H_2 volume in the gas burette was monitored and recorded using a high-density video camcorder.

The hydrogen evolution data, from which the reaction rates were calculated, were acquired by pausing and noting down the volume graduations and corresponding time instants from the recorded video. The amount of collected hydrogen in the burette was calculated using the ideal gas law with the consideration of pressure variation caused by the change of water column height. The experimental apparatus is shown schematically in Figure 2.2.

Figure 2.2: Experimental apparatus for AB thermolysis.

Multi-gram Steel Reactor System Design

The multi-gram steel reactor system is a laboratory scale thermolysis batch reactor. The reactor system, shown schematically in Figure 2.3, is described in detail by Deshpande et al. [1]. In brief, pellets of AB (Aviabor, CAS # 13774-81-7) are introduced into a closed volume, stainless steel reactor which is preheated using an electrical band heater. The reactor pressure and temperature are recorded as a function of time with particular attention to the variations following the introduction of hydrogen producing chemicals such as AB. From the measurements of the temperature and pressure time series, the evolved hydrogen gas yield is estimated using the ideal gas law and neglecting the presence of trace species such as ammonia.

Figure 2.3: Schematic of the steel reactor system.

To verify repeatability of the results, two tests were performed at each reaction temperature using AB pellets. Each pellet was approximately 0.4 cm (0.16 inches) in diameter, 0.5 cm (0.2 inches) in length and weighed 0.05 grams. The experiments at the two lower temperatures were conducted with a total of 20 pellets (total weight of 1 gram) in the reactor and those at 157°C were conducted with 40 pellets (total weight of 2 grams). The results of the experiments were checked to be independent of the number of pellets in this range. The results include reactor set-point temperatures of 100°C, 120°C, and 157°C. These temperatures were selected to study AB decomposition under and above the melting point of AB (112°C). The experiments with the 157°C set point were aimed at the generation of the second hydrogen molecule out of the six hydrogen atoms in AB.

A two dimensional axisymmetric model, shown in Figure 2.4, was developed to simulate the neat AB thermolysis chemical reaction and heat diffusion in the steel reactor system. The model is capable of estimating the initial transient heat-up of the steel reactor system from room temperature to the desired reaction temperature, the rate of neat AB thermolysis reaction as a function of temperature and time and the effects of heat of reaction liberated during the exothermic decomposition of AB.

Transient heat transfer in the reactor system is modeled using the unsteady heat diffusion equation. Neat AB thermolysis is assumed to be governed by a first order, Arrhenius reaction [2]. The heat generated during exothermic decomposition is coupled with the unsteady heat diffusion equation through a source term, and a time dependent solver is used to obtain the solution in COMSOL Multiphysics. Future efforts may include consideration of multiple reaction steps including higher order reactions and allow insights into the nature of the exothermic hydrogen release process.

Figure 2.4: Schematic of two-dimensional axisymmetric model.

Onboard Thermolysis System Design

The design of the onboard thermolysis reactor system uses modules that are pre-filled with the storage chemical before being loaded onto the vehicle. The system was operated with AB but has the flexibility to accommodate slurries and other chemical hydrides. For this effort, the AB was acquired from Aviabor (CAS # 13774-81-7) and synthesized in a Purdue University laboratory [3].

The system was demonstrated with a hydrogen internal combustion engine (HICE) on a Club Car in May 2011. The vehicle platform chosen for the reactor system is a Club Car Carryall 2 (2005 model) commercial vehicle that utilizes a 351 cc Kawasaki single cylinder four stroke cycle engine, which has been modified to operate using hydrogen as the fuel. Figure 2.5 shows the operational schematic of the storage reagent reactor system for the vehicle demonstration platform.

Figure 2.5: Operational schematic of the reactor system for vehicle demonstration

Shown in Figure 2.6, the completed on-board thermolysis reactor system consists of a HICE, four reactor modules, a modified engine exhaust, a buffer tank, and an onboard USB data acquisition system with a LabVIEW virtual interface for real time monitoring.

Figure 2.6: Completed on-board thermolysis reactor system

To supply heat to the reactor modules, the hot exhaust gases of the HICE were diverted to the copper spiral tubing located within to the reactor modules. Aluminum honeycomb in contact with the copper spiral further aids heat transfer to the reagent pellets (Figure 2.7). Successful operation of the entire reactor system as well as lessons learned for future improvements are summarized in the next section.

Figure 2.7: Reactor module with AB pellets

Measurement of Thermal Transport Properties

Thermal transport properties of powdered and pelletized ammonia borane and its partial thermolysis product were necessary for the design of the hydrogen release reactors. We measured the thermal properties using the transient plane source (TPS) technique while accounting for the effects of varying input power, measurement duration, and packing densities on the measurement outcomes.

The thermal property measurements on powders (loose and compressed) were performed using a rectangular stainless steel cup with interior dimensions of 29 x 38 x 16 mm (± 0.5 mm) (Figure 2.8a). The sensor was aligned perpendicular to the x-direction as noted in the figure, providing a maximum probing depth of 8mm for the powder measurements and the ability to vary the powder compression through the use of two opposed compaction screws. When the powder was compressed using the compaction screws, this probing depth was reduced by 1 to 2 mm.

For each measurement the TPS sensor was positioned at the center of the sample holder and secured on a stand. Powder was then added loosely around the sensor. Powder was compressed using equal displacements in the x-direction, typically 1-2 mm, from both compression screws (6.35 mm diameter,

1.1 threads/mm ($\frac{1}{4}$ "-28)) to achieve a volume reduction of approximately 5 to 10%. The top of the container was sealed using metal lids so that no extrusion occurred and compaction was only in the x-direction. The packing density of the material in this configuration was calculated using the measured mass added to the sample holder and the known volume occupied by the sample, which was re-measured for each experimental condition.

Initial thermal property measurements were performed on powders with no compaction beyond that of their own weight, referred to in this study as "loose powder". When the compaction screws were used to apply an external force to the powder bed, the configuration is referred to in this study as a "compressed powder". The compressed powder did not hold its shape upon release of the external force, and was thus not considered a "pellet".

In addition to powder samples, pellets of ammonia borane and polyiminoborane were made with 3 grams of material (± 0.01 g) per pellet pressed in a 25 mm diameter pellet die. The powder was compacted in varying increments to adjust the porosity to different values, and the porosity was calculated using the pellet's mass, final dimensions, and the known solid density [4-5]. Thermal property measurements were performed by sandwiching the sensor between two pellets of identical porosity and composition (Figure 2.8b). The configuration was then secured using a compression spring (spring constant 11.6 N/cm), which applied a constant force of 18 N.

Figure 2.8: a) Sample holder for measurements on loose and compressed powder, with the sensor secured perpendicular to the x-direction and in the volumetric center of the powder sample. b) Sample holder for measurements on pellets and solids, with the sensor compressed between the solid or pellet samples

The sensor wires, embedded in Kapton, provide a smooth finish resulting in effective thermal contact between the sensor and the samples. Additionally, the effect of thermal contact resistance between the sensor and the sample results in a constant offset and does not affect the measured values of thermal properties.

Two pellets of identical packing density were required for each measurement. Care was taken to ensure consistent packing densities by keeping the heights of each pair of pellets within 0.5 mm of each other, with a baseline height of 10-15 mm, and adding the same mass (± 0.01 grams) of powder to the die for both pellets. The packing densities reported in the following sections were calculated from the average height of the two pellets used in the measurement, and have an associated uncertainty of 5% of the calculated value based on the uncertainties in the methods outlined above.

Analysis of AB/Ionic Liquid Slurry Hydrogen Storage System

We analyzed a full scale (for a 80 KW fuel cell) system using AB (80 wt.%) and BmimCl (20 wt.%) as the hydrogen storage medium as an example. Figure 2.9 illustrates the baseline system, which consists

of an AB slurry tank, a slurry pump, a slurry reactor, a hydrogen buffer tank, a recuperator, a gas/liquid separator, a burner, and a heat transfer fluid (HTF) pump. To size these components, we used a one-dimensional model to simulate thermo-chemical processes in the reactor and thermo-fluid processes in the remaining components. The simulation was conducted for a nominal steady state hydrogen flow rate of 1.6g/s. A hydrogen buffer tank was sized to meet dynamic (unsteady state) requirements.

Figure 2.9: On-board AB/ionic liquid slurry hydrogen storage system schematic.

The reactor configuration involves a shell and tube heat exchanger, which is designed to meet 20% of the required 1.6 g/s peak H_2 flow rate ($\dot{m}_g$). With the assumptions of steady state one dimensional flow, negligible diffusion effects and viscous dissipation, constant properties, equilibrium temperature among all phases, and nominally two moles of hydrogen generation from each mole of AB, the conservation of mass, species, momentum and energy equations of the AB slurry reactor are as follows,

$$\frac{d\dot{m}}{dx} = 0 \quad (2.1)$$

$$\frac{d\dot{m}_g}{dx} = 2MW_{H_2}\dot{R}A_c \quad (2.2)$$

$$\frac{d\dot{m}_s}{dx} = -2MW_{H_2}\dot{R}A_c \quad (2.3)$$

$$\dot{m}\frac{du}{A_c dx} = -\frac{dp}{dx} - \frac{\rho u^2 f}{2D} \quad (2.4)$$

$$\left(\dot{m}_l C_{p,l} + \dot{m}_s C_{p,s} + \dot{m}_g\right) \frac{dT}{A_c dx} + 2MW_{H_2}\dot{R}T(C_{p,g} - C_{p,s}) = q_s'' \left(\frac{P}{A_c}\right) + \dot{R}\Delta H_f^0 \quad (2.5)$$

Where, MW_{H_2} is the molecular weight of hydrogen; $\dot{m}$, $\dot{m}_g$, $\dot{m}_s$, $\dot{m}_l$ are mass flow rates of the mixture, the hydrogen gas, the fresh/spend AB mixture, and the ionic liquid, respectively; ρ , u , p , T are the mean density, the mean flow velocity, the flow pressure, and the flow temperature, respectively; D , P , A_c are the diameter, perimeter, and cross-section area of the reactor, respectively. The pressure drop

through the reactor will be determined by the friction coefficient (f) in the momentum equation. The non-Newtonian nature of the slurry flow is being considered. The overall heat transfer rate is determined by the heat flux (q_s'') distribution at the reactor wall, which depends on the reaction kinetics ($\dot{R}$) of the AB slurry. Other thermo-chemical properties such as specific heat for the hydrogen gas, the fresh/spent AB mixture, and the ionic liquid ($C_{p,g}$, $C_{p,s}$, $C_{p,l}$) and heat of reaction (ΔH_f^0) are obtained from the literature

Based on the experimental data of AB/ionic liquid (80/20) slurry thermolysis [6], we developed a 1st-order reaction kinetics model as follows:

$$\frac{dF}{dt} = k_o \exp\left(-\frac{E_a}{RT}\right)(1-F) \quad (2.6)$$

F is the reaction progress variable defined as follows,

$$F = \frac{\left(\frac{n_{H_2}}{n_{AB,o}} @ t\right)}{\left(\frac{n_{H_2}}{n_{AB,o}} @ t_f\right)} \quad (2.7)$$

The kinetics parameters ($k_o = 1.67 \times 10^{14} \text{ s}^{-1}$ and $E_a = 120 \text{ kJ/mol}$) were obtained from Ref. 6.

A modified Lockhart-Martinelli correlation (LMC) was utilized to simulate pressure drops for two-phase flows. The LMC has been proven to accurately estimate pressure drops in two-phase flow, only making basic assumptions of flow distribution [7]. The LMC is based on a separated flow model, using the following correlation to calculate two-phase frictional pressure drop:

$$\left(\frac{dP}{dl}\right)_{TP} = \phi_{slurry}^2 \left(\frac{dP}{dl}\right)_{slurry} \quad (2.8)$$

where $(dP/dl)_{TP}$ is the total pressure drop per unit length, ϕ_{slurry} is the two-phase multiplier based on the slurry phase pressure drop, and $(dP/dl)_{slurry}$ is the slurry phase frictional pressure drop per unit length. The two-phase multiplier was determined by Chisholm [8], and is as follows:

$$\phi_{slurry}^2 = 1 + \frac{C}{X} + \frac{1}{X^2} \quad (2.9)$$

where C is the Chisholm constant, which depends on the regimes of the slurry and gas. The Martinelli parameter, X , is given by

$$X^2 = \frac{\left(\frac{dP}{dl}\right)_{slurry}}{\left(\frac{dP}{dl}\right)_g} \quad (2.10)$$

with:

$$\left(\frac{dP}{dl}\right)_{slurry} = f_{slurry} \frac{2\rho_{slurry} V_{slurry}^2 (1-x)^2}{D_{slurry}} \quad (2.11)$$

and:

$$\left(\frac{dP}{dl} \right)_g = f_g \frac{2\rho_g V_g^2 x^2}{D_g} \quad (2.12)$$

where f_{slurry} , f_g , ρ_{slurry} , ρ_g , x , V_{slurry} , V_g , D_{slurry} , and D_g are the friction factor of the slurry phase, friction factor of the hydrogen gas phase, density of slurry, density of hydrogen gas, mass fraction of gas, velocity of the slurry, velocity of the hydrogen gas, hydraulic diameter of the slurry phase, and hydraulic diameter of the hydrogen gas phase, respectively.

For designing the buffer tank, a drive cycle requiring peak power output for 15 minutes is considered as an example. The temperature of the hydrogen stored in the buffer tank is assumed to be 90 °C to account for heat transfer during the storage process. The hydrogen diverted from the fuel cell back to the hydrogen storage system is not considered as a first step. Utilizing the ASME standard for pressure vessel design, the following relationship for hoop stress was utilized in order to determine the buffer tank's thickness.

$$\frac{\sigma_y}{FOS} = \frac{(P)(R_{buffer})}{b_{buffer}} + 0.6P \quad (2.13)$$

Where, FOS , σ_y , R_{buffer} , and b_{buffer} are the factor of safety, yield stress, radius of and thickness of the buffer tank, respectively. Stainless steel was chosen as the material for the buffer tank as an example.

The purpose of the recuperator is to utilize the heat contained in the hydrogen gas flow stream to increase the temperature of the AB slurry. A tubular-fin compact heat exchanger was designed for heat transfer from the gas to the slurry. The engineering process of sizing a compact heat exchanger involves an iterative process [9, 10].

Results

Glass Milligram Scale Reactor

Reaction kinetics of neat and bmimCl aided AB thermolysis under quasi-isothermal conditions in the temperature range from 85°C to 120°C were measured. The measured hydrogen storage capacity of the 80/20 AB/bmimCl mixture was 11.2 wt.% at 120°C and foaming during AB thermolysis was partially suppressed by the ionic liquid. Hydrogen yield reduction caused by impurity and aging of bmimCl should be further addressed. bmimCl aided thermolysis should be implemented at sufficiently high temperature (> 107°C) to achieve a noticeable gain in the hydrogen storage capacity when comparing to the neat AB thermolysis. This work is detailed in a publication in the Journal of Power Sources [6].

The visco-elastic differences between the spent fuels obtained from the various AB dehydrogenation methods were also quantitatively investigated for the first time. It was demonstrated that spent fuels obtained from AB neat thermolysis and hydrothermolysis are the most transportable, followed by its hydrolysis and ionic liquid-aided thermolysis, respectively. The spent fuels obtained at higher temperatures exhibit improved transportability.

Laboratory Thermolysis System – Experimental Results

Rapid evolution of hydrogen was observed at the start of the reaction in the steel reactor system. This gas evolution was accompanied by temperature increase of 30 K due to the exothermic reaction. A maximum yield of 1.9 ± 0.1 mol of hydrogen per mol of AB was observed after 30 minutes of reaction. This accounts for 12 wt. % of hydrogen. Water was used to sequester ammonia generated during the reaction, due to its selective absorptivity for ammonia. Using this technique, ammonia content in the gas stream was measured by titration of the aqueous solution as 4% by mass.

The hydrogen yield rates defined as moles of hydrogen produced per mol of AB, from the electrically heated steel reactor system, for the three operating temperatures are shown in Figure 2.10. Also shown are yield rates of hydrogen from the glass reactor experiments discussed by Basu et al. [6].

Figure 2.10: Comparison of hydrogen yield rates in the stainless steel (solid lines) and glass reactor (hollow symbols). Temperature labels indicate the heater set point.

As shown in Figure 2.10, the final yield of hydrogen gas generated in both the stainless steel and glass reactor experiments agree within the experimental uncertainty. However, the rate of hydrogen generation was much slower in the glass reactor compared to the stainless steel reactor. These transient differences are likely to be due to differences in reactor scale, heat transfer processes, sample preparation, and recording mechanisms. The differences in the rate of hydrogen yield based on the reactor materials, designs, and heating methods point to the need for transient system models that allow for inclusion of transport properties and processes in future reactor designs.

Visual inspection of the reactor after the experiment showed a layer of byproducts (~0.1" thick) on the inner walls. The significantly larger volume of the reaction byproducts indicated foaming during the thermolysis reactions. The ratio of the volume of reaction byproducts to the volume of fresh AB was estimated to be eleven.

Laboratory Thermolysis System – Modeling Results

In the approximate mathematical model of the laboratory scale thermolysis system, the AB is approximated to remain inactive until the desired reaction temperature of 430 K is reached at the centerline of the reactor. This provision simulates the experimental procedure of addition of AB to the reactor after the reactor system has reached the reaction temperature. The reaction is assumed to start at the same instant when the AB is added to the reactor. The heat diffusion equation and the chemical reaction rate equation are solved for the AB domain from this time onwards. Figure 2.11 shows the system and the heat flows prior to addition of AB.

The heat flows from the heater to the other parts of the reactor system at the time of AB addition are shown as arrows with magnitudes equal to the heat flux and direction matching the local direction of the heat flux. It is seen that energy enters the AB through the heated knife gate and through the inner walls of the reactor. The heat flows through the reactor wall to the bottom flange, resulting in heat loss to the surroundings. This effect can be attributed to the low thermal conductivity of AB compared to that of steel.

Figure 2.11: Heat flux in the laboratory scale thermolysis reactor upon addition of AB.

Figure 2.12 shows the temperature profile inside the system 20 seconds after the start of the AB decomposition reaction. Heat liberated during the exothermic AB decomposition reaction results in increase in the gas phase temperature inside the reactor volume. As estimated by the model, the maximum temperature inside the AB is 540 K.

Figure 2.12: Temperature profile inside the reactor 20 seconds after the start of the AB decomposition reaction.

Figure 2.13 shows a comparison of the experimental temperature measured at the reactor axis with the estimate of the two-dimensional model. The drop in temperature just prior to the reaction is due to the AB's initial temperature of 298 K, which is followed by a temperature increase due to the exothermic dehydrogenation reaction. While the two dimensional model calculates the successive decrease and increase in temperature of the gas phase due to addition of AB and due to exothermic decomposition of AB respectively, it over predicts the magnitude of both temperature excursions. Several limitations inherent to the model can explain this discrepancy:

- The model does not incorporate flow of hydrogen gas out of the reactor volume. The heat diffusion equation does not account for the heat transfer due to advection by hydrogen gas. Hence, the

temperature rise due to exothermic decomposition of AB estimated by the model is higher than that observed during the experiments.

- The neat AB thermolysis reactions were modeled as a global first order reaction based on Arrhenius theory with values of pre-exponential factor and activation energy, respectively 4 1/s ($\pm 0.4 \text{ 1/s}$) and 13000 J/mol-s ($\pm 1050 \text{ J/mol-s}$), derived from curve fits of the experimental data. More complex kinetics and thermochemical models are suggested by the experimental data.

Figure 2.13: Comparison of transient experimental and model temperature at the reactor axis.

The data and the lessons learned with the experiments and modeling results from the first and second reactor systems were used to guide the sizing, design, and construction of an onboard thermolysis reactor for the club car.

Onboard Thermolysis System Results

The data from a drive test of the onboard thermolysis reactor system performed in early May 2011 are shown in Figure 2.14. The test made use of approximately 50 g of AB pellets loaded in one module. The hydrogen buffer tank is first filled to a pressure of approximately 6 bar from a commercial gas cylinder. Next the HICE is operated on the buffered hydrogen and the exhaust is routed away from the reactor modules, allowing for system checks and warm-up. Once proper operation is confirmed, the buffer tank is refilled, and the engine is again operated with the exhaust routed to the first reactor module. The exhaust heat raises the AB temperature until dehydrogenation is achieved. The reaction leads to a sharp increase in the reactor temperature and increased pressure in the reactor module. The generated hydrogen refills the buffer tank and is used to power the HICE. As designed, this process can be repeated with multiple reactor modules, leading to a self-sustained operation.

Figure 2.14: Experimental data recorded during May 2011 drive test with on-board thermolysis reactor system

The vehicle scale reactor system design addressed several engineering concerns with on-board chemical hydrogen storage systems. It is compatible with a wide range of hydrogen storage chemicals in pure or slurry form and can produce hydrogen of sufficient purity for operation with a fuel cell.

Thermal Transport Properties Results

The results of the thermal transport property measurements are summarized in Table 2.1. Twenty-one measurements were taken at each of the condition listed in the table and the standard deviations were less than 5% for all measurement sets. The uncertainties for measured thermal properties and porosities were 10% and 5%, respectively, based on the instrument accuracy reported in the literature and the procedures used to measure porosity. All uncertainties on calculated values were estimated using uncorrelated uncertainty propagation.

Table 2.1: Mean thermal property measurements of ammonia borane and polyiminoborane at various porosities, including an extrapolated value for solid ammonia borane.

Material	Porosity (%)	Physical Form	α (mm ² /s)	l (W/m-K)	c (J/cm ³ -K)
Ammonia Borane (NH ₃ BH ₃)	50 ± 2.5	Loose powder	0.167 ± 0.02	0.189 ± 0.019	1.13 ± 0.16
	48 ± 2.4	Loose powder	0.173 ± 0.02	0.199 ± 0.020	1.15 ± 0.16
	47 ± 2.4	Compressed powder	0.174 ± 0.02	0.278 ± 0.028	1.60 ± 0.23
	33 ± 1.7	Pellet	0.215 ± 0.02	0.365 ± 0.037	1.70 ± 0.24
	22 ± 1.1	Pellet	0.242 ± 0.02	0.439 ± 0.044	1.81 ± 0.26
	0 (extrapolated)	Solid	0.30 ± 0.04	0.58 ± 0.08	1.9 ± 0.4
	0 [11]	Solid	0.26	0.56	2.16
Polyiminoborane ([NHBH] _n)	88 ± 2	Loose powder	0.210 ± 0.02	0.068 ± 0.007	0.32 ± 0.05
	15 ± 10	Pellet	0.119 ± 0.01	0.233 ± 0.02	1.96 ± 0.28

Both thermal diffusivity and thermal conductivity of ammonia borane show decrease with increase in the porosity as shown in Figs. 2.14 and 2.15. On the other hand the thermal diffusivity increases and the thermal conductivity decreases for the polyiminoborane product of the dehydrogenation reaction. The thermal diffusivity of NH_3BH_3 increases by a factor of 1.5 (Figure 2.15) and the thermal conductivity of NH_3BH_3 decreases by more than a factor of two (Figure 2.16) as the porosity decreased from 50% (loose ammonia borane powder) to 22% (ammonia borane pellet). In complete contrast, the thermal diffusivity of $[\text{NHBH}]_n$ decreases by approximately 75% as the porosity is decreased from 90% to 16%. This difference in the changes of thermal diffusivity of the two materials with respect to porosity is related to the differences in the contact surface behavior of the two materials as discussed later.

Figure 2.15: Thermal diffusivity vs. porosity for ammonia borane (NH_3BH_3) and polyiminoborane ($[\text{NHBH}]_n$), compared with the measured value for solid ammonia borane by Andersson *et al.* [11]. Solid lines are linear fits to the current experimental data to illustrate trends.

Figure 2.16: Thermal conductivity vs. porosity for ammonia borane (NH_3BH_3) and polyiminoborane ($[\text{NHBH}]_n$), compared with the measured value for solid ammonia borane by Andersson *et al.* [11]. Solid lines are linear fits to the current experimental data to illustrate trends.

The porosity of a powder can be expressed as a function of the ration of densities of the powder and pellet and of the pellet porosity, as shown in Equation 2.14.

$$\phi_{\text{powder}} = 1 - \frac{\rho_{\text{powder}}}{\rho_{\text{pellet}}} (1 - \phi_{\text{pellet}}) \quad (2.14)$$

The measured density ratio in this case is 0.14. Based on our estimate of the pellet porosity as $15 \pm 10\%$, the powder porosity is approximately $88 \pm 2\%$. The thermal conductivity of polyiminoborane is significantly lower than that of ammonia borane and the rate of increase in thermal conductivity is much lower for $[\text{NHBH}]_n$ than for NH_3BH_3 .

The measured thermal diffusivity and conductivity reported in this work for ammonia borane show good agreement with prior measurements of the solid material [11]. The thermal conductivity of ammonia borane exhibited a sharp increase when its porosity decreased from 48 to 47%. This sharp increase most likely results from the increase in contact surface area and the related decrease in contact resistance as the power is compacted from 48% porosity to 47% porosity. The large increase in contact area is plausible based on the 1-2 mm decrease in thickness of the sample. The applied force did not significantly change the overall porosity, but the force was transmitted through the particle bed via inter-particle contact points, which likely increased the contact area between particles. The thermal properties of ammonia borane powder are sensitive to its packing configuration. Due to the irregular oblate shape of the ammonia borane powder, external compression changes the contact area and therefore the thermal contact resistance within the ammonia borane powder itself, resulting in changes in the thermal conductivity of the powder bed.

The volumetric heat capacity is related to the porosity and the solid and interstitial fluid heat capacities by,

$$c = \phi \cdot c_{\text{fluid}} + (1 - \phi) \cdot c_{\text{solid}} \quad (2.15)$$

Because the heat capacity of air is much less than that of solid ammonia borane, it is expected that heat capacity decreases linearly with porosity (Figure 2.17).

Figure 2.17: Volumetric heat capacity vs. porosity for ammonia borane (NH_3BH_3) compared with Equation 7 (evaluated using air properties from [9] and the solid ammonia borane heat capacity from Table 2), and with the values measured by Wolf et al. [12] and Andersson et al. [11]. Values for the polyiminoborane ($[\text{NHBH}]_n$), are also included for comparison.

The thermal property measurements of polyiminoborane show that as its porosity decreases, its thermal diffusivity decreases and the thermal conductivity increases. The volumetric heat capacity of the powder bed can be expressed as the volume-weighted average of the heat capacities of the materials in the bed (Equation 7). The thermal conductivity of such a bed is typically dominated by heat transfer rates at the interfaces between particles rather than by the properties of the solid materials. This can be illustrated by considering the thermal conductivity of beds of stainless steel and copper spheres, which have significantly different solid conductivities (15 vs. 400 W/m-K), but quite similar effective conductivities as powders [13]. For the two materials being considered here, optical microscopy pictures and qualitative observations of required compaction force and particle cohesion made while generating the pellets suggest that ammonia borane particles are more pliable than polyiminoborane particles. These observations are consistent with the hypothesis that the larger measured change in thermal conductivity observed in ammonia borane powder relative to polyiminoborane powder is due to a relatively large change in inter-particle contact area. Because of the material differences, a much smaller rate of change in the bed conductivity is observed with respect to porosity for the polyiminoborane powder. The difference between this rate of change of conductivity and the rate of compaction (which relates to the rate of change in heat capacity) explains the relative difference in the rate of change of thermal diffusivity measured for the two materials. Such considerations, as well as the absolute differences in powder properties between the two materials, should be addressed when designing hydrogen storage systems.

The volumetric heat capacities of ammonia borane at varying packing densities were calculated from the present thermal diffusivity and conductivity measurements and the results showed reasonable conformance with Equation 7, where the solid ammonia borane properties were taken from the data presented in Table 2.1. The anomalous high measured heat capacity for the porosity values of 48% and 47% are not fully understood and future studies of the thermal properties in the transition between loose and compacted powders may be necessary to elucidate the physical changes.

Analysis of AB/Ionic Liquid Slurry Hydrogen Storage System

The AB slurry reactor operating conditions and geometry were determined using the model discussed above. With a total reactor tubing volume of approximately 30 cm³, the reactor weight is 0.25 kg for a stainless steel one ($\rho = 7.85 \text{ g/cm}^3$). The buffer tank was estimated to store hydrogen up to 1.2 kg with 0.8 m in diameter, 1.0 m long, and 4.7 mm in wall thickness. The AB slurry pump handles high viscosity slurries with approximately 80 percent solids at low flow rates. With proven capabilities of handling solids and slurries within the food and chemical industry, a lobe pump has the potential to meet the requirements of the system. A lobe pump that is efficient at low flow rates and high pressures (~35 bar) is necessary. The volumetric flow rate of the pump is required to be $3.294 \times 10^{-6} \text{ m}^3/\text{s}$ (~0.198 L/min). An AccuLobe pump manufactured by Johnson Pump has the necessary flow rate but is only rated for pressures up to 12 bar. Development of a high pressure slurry pump is identified as a significant challenge to the development of an onboard slurry system. An auxiliary pump currently designed for pumping a AB slurry heating fluid called the HTF pump must be able to handle a flow rate up to 24 L/min at 150°C. The pump selected for the present estimates is a Duralobe® Viking bi-rotor pump, which weighs 16 kg. Table 2.2 shows the breakdown of each component's weight contribution to the total system.

Table 2.2: System Weight Breakdown for Individual Components.

Component	Weight, kg
Fuel, W_{Fuel} (80% AB, 20% IL)	47.5
Fuel Tank, W_{Tank}	1.9
Burner, W_{Burner}	1.7
Heat Transfer Fluid, W_{HTF}	1.3
H ₂ Buffer Tank, W_{Buffer}	0.55
Recuperator, W_{HX}	2.5
Reactor, $W_{Reactor}$	0.25
Slurry Pump, $W_{pump, slurry}$	9.5
HTF Pump, W_{HTF}	16.0
Total	81.2

As shown above, the full scale AB slurry system has an estimated weight of 81.2 kg to store 5.6 kg usable hydrogen. System weight distribution of the slurry system is also illustrated in the Figure 2.18. This yields a system gravimetric hydrogen storage capacity of 6.9 wt.%. Close to 60% of the total weight of the system involves slurry and heat transfer fluid pumps. To achieve the ultimate target on gravimetric hydrogen system storage capacity (7.5 wt.%), light weight pumps must be developed. System innovations that can result in reactor designs that may involve fewer and lower material flows may also help.

Figure 2.18: Weight distribution of a benchmark AB/ionic liquid (80:20) slurry system.

Conclusions and Future Directions

The reactor systems designed and operated under Task 2 addressed several engineering challenges including: heat management, foaming of storage of reagent, hydrogen purity, and spent product management.

A two-dimensional model of a multi-gram scale reactor provided better understanding of the heat fluxes in the reactor before, during, and after AB reaction but over predicted the temperature gradients in the system. A model capable of capturing the effects of melting of AB and fluid flow out of the reactor is required. Further additions to the model such as use of thermal properties as functions of temperatures and use of correlations for accurate estimation of convective coefficients are also recommended.

The difference in conductivity between ammonia borane and its thermolysis product polyiminoborane has significant design implications for heat exchangers. Because the thermolysis product of ammonia borane has a much lower thermal conductivity than the ammonia borane itself, design of storage and hydrogen release devices must account for the possibility of formation of insulating layers around the highest temperature locations, preventing predictable heat transfer to the remaining ammonia borane.

A hydrogen storage capacity of 11.2 wt.% (material) from the 80/20 AB/bmimCl mixture thermolysis, which is within the uncertainty limits of the highest ever reported in the literature, was achieved. The AB/BmimCl (80:20) slurry system can meet the 2015 system gravimetric hydrogen storage capacity target (5.5 wt %) and has the potential to meet the ultimate target of 7.5 wt.% with improved pumps, process designs, and reagents.

References

1. Deshpande, K.A., Voskuilen, T.G., Basu, S., Zheng, Y., Pourpoint, T.L., Gore, J.P., "Design, Construction and Test of a Subscale Ammonia Borane Reactor," *Proceedings of the ASME 2010 International Mechanical Engineering Congress & Exposition IMECE2010*, Nov. 2010, Vancouver, British Columbia, Canada.
2. Sutton, A.D., Burrell, A.K., Dixon, D.A., Garner E.B., Gordon J.C., Nakagawa T., Ott, K.C., Robinson J.P., Vasiliu M., *Regeneration of Ammonia Borane Spent Fuel By Direct Reaction With Hydrazine And Liquid Ammonia*. Science, 2011. **331**: 1426-1429
3. Ramachandran PV, Gagare PD. Preparation of ammonia borane in high yield and purity, methanolysis, and regeneration. *Inorg Chem*. 2007;46:7810-7817
4. Rassat SD, Aardahl CL, Autrey T, Smith RS. Thermal stability of ammonia borane: a case study for exothermic hydrogen storage materials. *Energy Fuels* 2010;24(4):2596–2606
5. Hughes EW. The crystal structure of ammonia-borane, H_3NBH_3 . *J Am Chem Soc* 1956;78(2):502–503
6. Basu, S., Zheng, Y., Gore, J. P., 2011, "An experimental study of neat and ionic-liquid aided ammonia borane thermolysis," *Journal of Power Sources*, 196: 734-740.
7. Chhabra RP, Richardson JF. Non-Newtonian Flow and Applied Rheology. 2nd Ed. IChemE; 2008
8. Chisholm D. A Theoretical Basis for the Lockhart-Martinelli Correlation for Two-Phase Flow. *Int. J. Heat Mass Transf.* 1967: 1767-1778.
9. Incopera FP, Dewitt DP, Bergman TL, Lavine AS. Fundamental of Heat and Mass Transfer. 6th Ed. Wiley & Sons; 2007
10. Kuppan T. Heat Exchanger Design Handbook. Marcel Dekka; 2000.

11. Andersson O, Filinchuk Y, Dmitriev V, Quwar I, Talyzin AV, Sundqvist B. Phase coexistence and hysteresis effects in the pressure-temperature phase diagram of NH_3BH_3 . *Physical Review B* 2011;84:024115
12. Wolf G, van Miltenburg JC, Wolf U. Thermochemical investigations on borazane ($\text{BH}_3\text{-NH}_3$) in the temperature range from 10 to 289 K. *Thermochimica Acta* 1998;317:111-116
13. Gusarov AV, Kovalev EP. Model of thermal conductivity in powder beds. *Physical Review B* 2009;80:024202

Publications/Presentations

Archival Papers

1. Brockman, A., Zheng, Y., Gore, J. P., 2010, "A study of catalytic hydrolysis of concentrated ammonia borane solutions," *International Journal of Hydrogen Energy*, 35: 7350-7356.
2. Basu, S., Diwan, M., Abiad, M. G., Zheng, Y., Campanella, O. H., Varma, A., 2010, "Transport characteristics of dehydrogenated ammonia borane and sodium borohydride spent fuels," *International Journal of Hydrogen Energy*, 35: 2063-2072.
3. Basu, S., Zheng, Y., Varma, A., Delgass, W. N., Gore, J. P., 2010, "Catalytic hydrolysis of ammonia borane: intrinsic parameter estimation and validation," *Journal of Power Sources*, 195: 1957-1963.
4. Basu, S., Zheng, Y., Gore, J. P., 2011, "An experimental study of neat and ionic-liquid aided ammonia borane thermolysis," *Journal of Power Sources*, 196: 734-740.
5. Deshpande, K.A., Voskuilen, T.G., Basu, S., Zheng, Y., Pourpoint, T.L., Gore, J.P., "Design, Construction and Test of a Subscale Ammonia Borane Reactor," *Proceedings of the ASME 2010 International Mechanical Engineering Congress & Exposition IMECE2010*, Nov. 2010, Vancouver, British Columbia, Canada.
6. Determination of the Thermal Transport Properties of Ammonia Borane and its Thermolysis Product (Polyiminoborane) Using the Transient Plane Source Technique, Y. Yang, Y., Voskuilen, T.G., Pourpoint, T.L., Guildenbecher, D.R., Gore, J.P., *Accepted for publication in Int. J. of Hydrogen Energy*, Dec. 2011

Acronyms

AB	Ammonia Borane
bmimCl	1-butyl-3-methylimidazolium chloride
CFD	Computational Fluid Dynamics
HTF	Heat Transfer Fluid

Task 3.0 Investigation of Noncatalytic AB Hydrothermolysis

Accomplishments

- Investigated noncatalytic AB hydrothermolysis near proton exchange membrane fuel cell (PEM FC) operating temperatures over a wide range of AB concentrations and pressure. The maximum hydrogen yield, obtained at 77 wt.% AB and $T_{\text{reactor}} \sim 85^{\circ}\text{C}$ along with rapid kinetics, was 11.6 and 14.3 wt.% at pressure 14.7 and 200 psia, respectively.
- Under effective heat management, high H_2 yield (~ 14 wt.%) was obtained near PEM FC operating temperatures ($\sim 90^{\circ}\text{C}$) along with rapid kinetics for neat AB thermolysis.
- Quantified ammonia formation for AB dehydrogenation processes and developed effective methods for its removal.
- Demonstrated a continuous-flow hydrogen generation system based on AB dehydrogenation.

Introduction

We have proposed and demonstrated a new approach to release hydrogen from heating AB aqueous solutions and slurries. In AB hydrothermolysis process, it was found that the heat generated by hydrolysis initiates thermolysis near PEM FC operating temperature (85°C) along with rapid heat evolution. On the other hand, for neat AB thermolysis, the sharp evolution was not observed at 85°C , indicating that AB-water reaction (hydrolysis) drives the sharp heat evolution resulting in high H_2 yield. We have also demonstrated that, with effective reaction heat management, high H_2 yield can be obtained from neat AB near PEM FC operating temperatures with rapid kinetics. It is known that the release of first and second molar equivalents of hydrogen from AB via thermolysis is exothermic. Thus, it was expected that the heat released during the first decomposition step could drive the second step when the reaction heat is effectively managed. Based on neat AB thermolysis approach, we developed the concept of a continuous-flow system, and a prototype unit for laboratory evaluation was constructed. In this unit, the AB fuel feeding, reaction and spent fuel removal steps are integrated, and the reactor has provision for utilization of waste heat from the PEM FC.

Approach

The AB hydrothermolysis method for H_2 generation was investigated over a wide range of AB concentration in water, pressure, and heating rate. The neat AB thermolysis was also studied near PEM FC operation temperatures. To better understand the reaction exothermicity (heat evolution), we developed a smaller size reactor (70 ml). Apart from the reactor temperature, the sample temperature (T_{sample}) was also measured by inserting a thermocouple inside the sample (Figure 3.1).

The neat AB thermolysis was investigated over a wide range of pressure, heating rate, AB density and insulation amount near PEM FC operating temperatures. For effective reaction heat management, some quartz wool was added at the top of the AB sample, which retains heat of exothermic thermolysis reaction while permitting product H_2 to flow. After cooling the reactor to room temperature at the end of the experiments, NH_3 was measured by various methods including Dräger tubing, mass spectrometry and titration technique.

From the PEM FC vehicle viewpoint, the H_2 purification method should account for operating temperature, safety, and complete NH_3 removal. In this context, water has high capacity to absorb ammonia while adsorbent can be used to remove NH_3 completely. Thus, a combination of the two methods can capture the ammonia effectively from the product gas stream by a sequence of absorption followed by adsorption (Figure 3.2). The proposed approach was tested and optimized using simulations, along with experiments.

A continuous-flow hydrogen generation system was designed, constructed and tested. In this unit, the AB sample was loaded from feeder and delivered to preheated reaction zone which is surrounded with a heating coil. The piston was operated using a pneumatic actuator. It was found that sample was not fully loaded in the first step indicating that the feeder needs a pinch valve or vibrator to load the powder-type fuel properly. After the reaction, the spent fuel was moved by the piston and stored in reservoir. The reactor pressure was monitored throughout the experiments using a transducer and hydrogen generation was calculated using pressure increase during the experiment.

Figure 3.1: Schematic diagram of the experimental set-up.

Figure 3.2: Schematic of the proposed method for NH_3 removal.

Results

AB hydrothermolysis was investigated in a 70 ml stainless steel Parr reactor over a wide range of AB concentration, pressure, and heating rate. The maximum observed hydrogen storage capacity, obtained at 77 wt.% AB concentration and $T_{\text{reactor}} \sim 85^\circ\text{C}$, was 11.6 and 14.3 wt.% at pressure 14.7 and 200 psia, respectively (Figure 3.3). For 200 psia and heating rate $1^\circ\text{C}/\text{min}$, AB converted to NH_3 (NH_3/AB) in the

gaseous product decreased with increasing AB concentration. With increasing initial pressure (up to 200 psia) or heating rate (up to 1°C/min), both H₂ yield and NH₃/AB ratio increased. Further increases, however, did not influence either the H₂ yield or the NH₃/AB ratio.

Figure 3.3: Hydrogen yield as a function of AB concentration, at different hydrothermolysis operating conditions.

We evaluated neat AB thermolysis near PEM FC operating temperature (90°C). For neat AB thermolysis without quartz wool, hydrogen gradually evolved with time and only 5 wt.% H₂ yield was achieved in 90 min as shown in Figure 4a. On the other hand, under effective heat management, hydrogen yield ~14 wt.% was achieved and stabilized quickly after sharp heat evolution (Figure 4b). To our knowledge, this value is higher than by any other method using neat AB at near PEM FC operating temperatures. A key factor is that effective reaction heat management is required to obtain sharp heat evolution, which plays a critical role in providing high H₂ yield. In addition, NH₃ concentration in gaseous product was trace amount (<10 ppm), much less than that observed in neat AB thermolysis (~400 ppm) without heat management. The main solid products of neat AB thermolysis under heat management were found to be polyborazylene-like species (after 2 H₂ release from AB).

Figure 3.4: H₂ yield, temperature profiles for neat AB thermolysis for T_{SP} = 90°C, P₁ = 14.7 psia and heating rate = 1°C/min. (a) without quartz wool (b) with quartz wool.

We demonstrated that NH₃ can be effectively removed by absorption in water, followed by adsorption on impregnated carbon. Our optimization results show that the weight required for the NH₃ removal system can be significantly reduced if water is recycled from the PEM FC. Further, since borazine hydrolyzes readily in water (Eq 3.1), our proposed method not only removes ammonia but also purifies the hydrogen stream from any volatile borazine present.

Figure 3.5 shows the effect of the continuous reactor temperature on H₂ yield. The H₂ yield increases with increasing the temperature up to 120°C, while further increase did not change H₂ yield. For temperatures above 120°C, ~13.5 wt.% H₂ yield (~2.1 H₂ molar equivalent) was obtained along with rapid H₂ evolution. It was also found that with increasing reactor temperature, H₂ release rate increases while induction period decreases. Previously, we reported that high H₂ yield (14-15 wt.%) can be obtained at 90°C with sharp H₂/heat evolution. During the study using the continuous-flow system, however, this sharp evolution did not occur at 90°C and >15 min of induction time to release H₂ was required. Only 1.1 wt.% H₂ yield was obtained at 90°C for even 30 min. The increase of required reaction

temperature, from 90 to 120°C, to rapidly provide high H₂ yield occurs due to heat loss from the reaction zone, and methods to minimize this loss must be investigated in the future.

Figure 3.5: Effect of reactor temperature on H₂ yield with time.

Conclusions and Future Directions

For AB hydrothermolysis, the maximum hydrogen storage capacity, obtained at 77 wt.% AB and $T_{\text{reactor}} \sim 85^\circ\text{C}$ along with rapid kinetics, was 11.6 and 14.3 wt.% at pressure 14.7 and 200 psia, respectively. The kinetics of neat AB thermolysis under various operating conditions were also investigated. Under effective reaction heat management, we obtained high H₂ yield (~ 14 wt.%) from neat AB thermolysis at 14.7 psia and $T_{\text{SP}} 90^\circ\text{C}$ with rapid kinetics, without the use of either catalyst or chemical additives. To our knowledge, this value is higher than by any other method using AB at near PEM FC operating temperatures. We optimized and demonstrated that a sequence of absorption in water and adsorption on impregnated carbon captures ammonia, by-product of AB dehydrogenation, effectively from the product gas stream. Based on neat AB thermolysis, we developed and evaluated a laboratory scale continuous-flow hydrogen generation system. Using this system, ~ 13.5 wt.% H₂ yield was obtained along with rapid H₂ evolution at 120°C. The increase of required reaction temperature, from 90 to 120°C, to rapidly provide high H₂ yield occurs due to heat loss from the reaction zone, and methods to minimize this loss must be investigated in the future.

Publications/Presentations

Archival Papers

1. Diwan, M.; Diakov, V.; Shafirovich, E.; Varma, A., "Noncatalytic hydrothermolysis of ammonia borane" *Int J Hydrogen Energ* 2008, 33, (4), 1135-1141.
2. Hwang, H. T.; Al-Kukhun, A.; Varma, A. "Hydrogen for Vehicle Applications from Hydrothermolysis of Ammonia Borane: Hydrogen Yield, Thermal Characteristics, and Ammonia Formation" *I&EC Research* 2010, 49, (21), 10994-11000.

3. Diwan, M. H.; Hwang, H. T.; Al-Kukhun, A.; Varma, A. "Hydrogen Generation from Noncatalytic Hydrothermolysis of Ammonia Borane for Vehicle Applications" *AIChE Journal* 2011, 57, 259–264.
4. Al-Kukhun, A.; Hwang, H. T.; Varma, A. "A Comparison of Ammonia Borane Dehydrogenation Methods for PEM Fuel Cell Vehicles: Hydrogen Yield, Ammonia Formation and its Removal" *I&EC Research* 2011, 50, 8824–8835.
5. Hwang, H. T.; Al-Kukhun, A.; Varma, A. "High and Rapid Hydrogen Release from Thermolysis of Ammonia Borane near PEM Fuel Cell Operating Temperature" *Int J Hydrogen Energ* (in press, DOI:10.1016/j.ijhydene.2011.10.088).
6. Hwang, H. T.; Al-Kukhun, A.; Varma, A. "High and Rapid Hydrogen Release from Thermolysis of Ammonia Borane near PEM Fuel Cell Operating Temperature: Effect of Quartz Wool" (in review).
7. Al-Kukhun, A.; Hwang, H. T.; Varma, A. "Experimental and DFT Studies of Reaction Pathways for Ammonia Borane Dehydrogenation" (in review).

Presentations

1. Diwan, M.; Diakov, V.; Shafirovich, E.; Varma, A., "Hydrothermolysis of Ammonia Borane: A Novel Method to Generate Hydrogen for Fuel Cells," AIChE Annual Meeting, November 18, 2008, Philadelphia, PA.
2. Varma, A., "New Methods for Hydrogen Generation from Boron Compounds and Water," CNR Rao Distinguished Lecture, Chemcon 2008, December 2008, Chandigarh, India.
3. Varma, A., "New Methods for Hydrogen Generation from Boron Compounds and Water," 8th World Congress of Chemical Engineering, August 2009, Montreal, Canada.
4. Varma, A., "New Methods to Generate Hydrogen for Fuel Cell Applications," Dept. of Chemical Engineering, Lamar University, April 16, 2009, Beaumont, TX.
5. Varma, A., "New Methods to Generate Hydrogen for Fuel Cell Applications," Dept. of Chemical Engineering, University of Texas-Austin, September 29, 2009, Austin, TX.
6. Varma, A., "New Methods to Generate Hydrogen for Fuel Cell Applications," Keynote Talk at the US-China Chemical Engineering Conference, October 15, 2009, Beijing, China.
7. Diwan, M.; Hwang, H. T.; Al-Kukhun, A.; Varma, A. "High Hydrogen Yield from Ammonia Borane Hydrothermolysis for Fuel Cell Based Vehicles" AIChE Annual Meeting, November 10, 2009, Nashville, TN.
8. Varma, A., "New Methods to Generate Hydrogen for Fuel Cell Applications," Engineering Distinguished Lecture, University of Western Ontario, March 29, 2010, London, Ontario, Canada.
9. Al-Kukhun, A.; Hwang, H. T.; Varma, A. "Hydrogen Generation from Noncatalytic Hydrothermolysis of Ammonia Borane for Vehicle Applications" NHA Hydrogen Conference & Expo, May 2010 Long Beach, CA.
10. Hwang, H. T.; Al-Kukhun, A.; Varma, A. "Hydrogen for Vehicle Applications from Ammonia Borane: Hydrogen Yield, Thermal Characteristics, and Ammonia Formation" ISCRE-21 Meeting, June 15, 2010, Philadelphia, PA.
11. Varma, A., "New Methods to Generate Hydrogen from Boron Compounds and Water for Fuel Cell Applications," Invited Dept. of Chemical Engineering Seminar, Columbia University, October 19, 2010, New York, NY.
12. Varma, A., "New Methods to Generate Hydrogen from Boron Compounds and Water for Fuel Cell Applications," Induction Lecture, National Academy of Engineering - Mexico, November 5, 2010, Mexico City, Mexico.

13. Hwang, H. T.; Al-Kukhun, A.; Varma, A. "Hydrogen Generation From Thermolysis of Neat Ammonia Borane for On-Board Vehicle Applications" AIChE Annual Meeting, November 8, 2010, Salt Lake City, UT.
14. Al-Kukhun, A.; Hwang, H. T.; Varma, A. "A Comparison of Ammonia Borane Dehydrogenation Methods for PEM Fuel Cell Vehicles: Hydrogen Yield, Ammonia Formation and its Removal" AIChE Annual Meeting, November 9, 2010, Salt Lake City, UT.
15. Varma, A., "New Methods to Generate Hydrogen from Boron Compounds and Water for Fuel Cell Applications," Invited Dept. of Chemical Engineering Seminar, Georgia Institute of Technology, December 1, 2010, Atlanta, GA.
16. Varma, A., "New Methods to Generate Hydrogen from Boron Compounds and Water for Fuel Cell Applications," Invited Talk, Tactical Power Sources Summit, January 25, 2011, Washington, DC.
17. Varma, A., "New Methods to Generate Hydrogen from Boron Compounds and Water for Fuel Cell Applications," Invited Dept. of Chemical and Biomolecular Engineering Seminar, Vanderbilt University, February 22, 2011, Nashville, TN.
18. Al-Kukhun, A.; Hwang, H. T.; Varma, A. "Molecular Reaction Pathways of Ammonia Borane Dehydrogenation: Experimental and DFT Elucidations" AIChE Annual Meeting, October 17, 2011, Minneapolis, MN.
19. Hwang, H. T.; Al-Kukhun, A.; Varma, A. "High and Rapid Hydrogen Release from Thermolysis of Ammonia Borane near PEM Fuel Cell Operating Temperature" AIChE Annual Meeting, October 17, 2011, Minneapolis, MN.
20. Al-Kukhun, A.; Hwang, H. T.; Varma, A. "The Attractiveness of Ammonia Borane to Generate Hydrogen for PEM Fuel Cell Vehicles" AIChE Annual Meeting, October 19, 2011, Minneapolis, MN.

Acronyms

AB	Ammonia Borane
PEM FC	Proton Exchange Membrane Fuel Cell

Task 4.0 Anaerobic Biological Production of Hydrogen

Accomplishments

- Testing of various combinations of microbial consortia was conducted with organic waste materials to determine parameters that maximize production. It was determined that pH, temperature and waste material concentration had the greatest influence on hydrogen production for the test conditions considered. A Central Composite Design was used to determine operating values that maximize hydrogen production.
- An automated testing system was designed, constructed and used to determine optimal operating parameters. Fourth generation tests were completed.
- Tests of hydrogen production for food waste and Distiller's Grain with various inoculum samples were conducted.
- The initial design of a modular energy system for local energy production and waste treatment was completed and used to optimize value.
- A 3 L batch/continuous fermentor was implemented to enhance testing and consider scale up issues.
- The vacuum tube solar collector system was used for pre and post waste processing and consideration of other ancillary uses such as building heating and production of potable water.
- Steam generator tests demonstrated ability to distill water with maximum solar energy conversion efficiency of ~70%.
- Initial designs were investigated for development of a prototype system with reduced substrate water concentration.
- Decreasing water concentration significantly increases value for the modular energy system design. Water concentration has been decreased from 95% to 75% with minimal loss in hydrogen production rates.
- Significant hydrogen production was demonstrated using a new process developed as part of this research for Distiller's Grain from ethanol production as substrate. Maximized operating procedure has shown significant increase in hydrogen production levels for second generation tests of Distiller's Grain. This process has the potential to increase the energy efficiency of ethanol production by an estimated 14% or more.
- Yearly advisory board meetings were held to continue to gain input from industry. Advisory board members include: Cargill, INEOS Technologies, BP, Advanced Power Technologies, and Ajinomoto Food Ingredients, LLC.
- Research results were published in peer reviewed journal articles and conference proceedings.

Introduction

Methods and designs for a modular waste processing system that will utilize an anaerobic process to produce hydrogen from food, animal, or human waste were developed during this research effort. This hydrogen can be used to produce electricity in a reciprocating engine or fuel cell. A solar energy system was designed and tested to provide heat for pre and post processing of waste and production of potable water. Potentially harmful pathogens from the waste are isolated from the environment and are drastically reduced by a solar thermal process. It is anticipated that a combined waste processing and renewable energy unit would be constructed in a standard shipping container for use in undeveloped and/or remote locations or at disaster sites. Hydrogen has many well established advantages as a clean renewable energy source. The use of microbial organisms to produce hydrogen has many advantages over more

conventional techniques. Remote locations place a premium on the availability of electricity, heat, and potable water. Methane production by biological means is often used for producing electricity. Using microorganisms that produce hydrogen rather than methane significantly reduces greenhouse gas emissions for the overall process. By using this hydrogen in a reciprocating engine or fuel cell the major end products would be electricity, water, and heat. To produce hydrogen rather than methane anaerobically it is necessary to first thermally pretreat the feed material. The developed solar energy system has consistently produced temperatures above 120°C. Typical hydrogen concentrations produced in the fermentation using food waste are 23% after 48 hours. A statistical experimental design was used to determine optimal operating parameters and a preliminary modular energy system design. The next steps in this effort will involve research and development of a bench-top prototype system and subsequently development and testing of a full-scale prototype unit.*

Approach

The effort of the biological hydrogen production work was conducted as Task 4.0. This task included includes investigating optimal hydrogen production cultures for different substrates, reducing the water content in the substrate, and integrating results from the vacuum tube solar collector pre and post processing tests into an enhanced energy system model. An automated testing device developed as part of this effort was used to consider optimal hydrogen production conditions using statistical testing procedures. A 3 L commercial fermentor (New Brunswick, BioFlo 115) was used to test larger samples and consider issues related to scale up. A technology appraisal of opportunities to utilize existing catalytic methods including nano catalysts for capture of CO₂ from the fermentation process was conducted.

A supply of energy in one form or another is essential for all human activities. Without a source of energy, most modern cultural activities cease and life is directly threatened as a result of the inability to deal with many critical issues including waste management. Water and food supplies can be contaminated by waste material if methods to isolate potentially hazardous organic wastes are not available. One way to deal with this situation is to produce energy from various organic waste streams in a process that not only produces energy in the form of electricity and heat but also produces drinking water while at the same time eliminating contamination from the processed waste. This research effort developed a design for a modular distributed energy system based upon the anaerobic fermentation of organic waste to produce hydrogen, thermal energy, potable water and sanitized fertilizer. It is initially intended for use in remote locations and in disaster situations. It is anticipated that the modular energy system will be housed in a conventional shipping container for ease of manufacture, transportation, and installation. One key aspect is the utilization of a renewable solar thermal energy system to produce process heat. By using a high efficiency solar thermal collector system it is possible to greatly reduce the parasitic energy losses and increase overall efficiency.

The modular energy system design involves multiple products and associated values. Value streams include; hydrogen for production of electricity, waste disposal, heat for buildings, drinking water, and possibly a marketable chemical product produced from process carbon dioxide. Once proven, it is anticipated that the technology will be leveraged to larger applications. Preliminary estimates indicate that when all costs and benefits are considered, this technology has advantages over many other alternatives for remote and disaster recovery applications. An overview of the value streams for the modular energy system is depicted in Figure 4.1. The general process flow is depicted in Figure 4.2.

Figure 4.1: Process overview.

Figure 4.2: Process flow.

Evaluation of Inoculum and Operating Conditions

Biological production of hydrogen gas offers a sustainable method for the production of fuel with a concurrent minimization of waste. Hydrogen gas has significant advantages as a clean energy source. Unlike fossil fuels, combustion of hydrogen does not produce carbon dioxide or oxides of nitrogen and sulfur. Hydrogen also has a higher energy yield (120 kJ/g) than hydrocarbons (44 kJ/g, petroleum). There are, however, technical and economic concerns with the production and storage of hydrogen reducing its near term viability. Conventional chemical methods for hydrogen production are energy intensive and therefore not cost effective. Biological hydrogen (biohydrogen) production methods offer a potentially economic and sustainable alternative for producing hydrogen. The use of microbial organisms is currently attracting increasing interest as a means of producing hydrogen. Numerous studies have been conducted using microorganisms to generate hydrogen from fermentation of various substrates [1,2,3]. Some studies used pure culture of bacteria, such as species of *Bacillus*, *Clostridium*, and *Enterobacter* [2, 3], while others used mixed cultures that originated from sludge, animal wastes, sewage, compost, soil, etc. [4, 5, 6, 7]. Substrates that have been used for fermentation include pure carbohydrates, such as glucose [8] sucrose [2, 4], xylose [9], cellulose [10], and starch [11], as well as organic wastes, such as municipal solid waste [12], starch manufacturing wastes [11], food processing wastewaters [6, 12, 13], and food waste [14]. Using organic wastes for bio-production of hydrogen not only has the potential to generate cost effective and renewable energy but also can reduce pollution in the environment and provide a source of fertilizer for growing crops.

The efficiency of hydrogen production from an anaerobic process is directly related to the physical and chemical characteristics of the biological reactor. To obtain the greatest value, it is necessary to optimize the operating characteristics to maximize process yield. The ideal inoculum was selected and the optimum growth conditions for hydrogen production were determined using Statistical Design of Experiment methods [15, 16]. Future efforts will include the development and testing of a bench top bio-reactor apparatus. This device will be utilized to determine the major issues associated with the scale up and optimization of the anaerobic production of hydrogen. This reactor will be equipped with controls to regulate temperature, pH, pressure, water content and flow rate. A key issue to be considered is the amount of water present in the hydrogen producing media. Test results indicate that it is possible to use semi-solid media and still obtain significant hydrogen production. The bench top bio-reactor will allow testing and development of a substrate optimized for functional suitability as well as hydrogen production level.

Biohydrogen production can be accomplished using either photosynthetic or anaerobic microorganisms. Much of the current interest in the biological production of hydrogen focuses on photosynthetic processes. This research focused on the use of anaerobic microorganisms and the utilization of organic waste materials for the production of hydrogen. Anaerobic processes are used extensively in a variety of current commercial processes such as waste treatment. Such processes have also been considered internationally for the production of hydrogen. The widespread use of anaerobic processes in waste treatment will facilitate leveraging the relevant technology for hydrogen production.

Currently, methane produced by biological means is used in many locations globally as a fuel for the local production of electricity by reciprocating engines [17]. In general this involves the use of a mixture of naturally occurring microorganisms to digest animal or human waste. The organisms used in these situations are generally obtained from a mixture of common waste sources. The types of organisms from these waste streams vary widely and consequently there is little consistency in efficiency and production levels. The construction of these systems is often primitive and there is potential for significant leakage of methane which is a very potent greenhouse gas. In addition, oxides of nitrogen, sulfur, and carbon dioxide are released in the combustion process.

Results

Laboratory tests were conducted to consider possible inocula and environments for anaerobic hydrogen production. An automated testing device was designed and constructed to facilitate the determination of optimal operating conditions for hydrogen production. The developed device maintains a constant temperature by means of a water bath. Up to ten 120 mL test bottles can be placed in the apparatus at a time.

Samples of food waste were collected from a cafeteria at Purdue University and were inoculated with various types of seed material to test the viability of hydrogen production by anaerobic means. An analysis of the food waste was also performed to provide a typical nutrient and trace mineral profiles. This data is used as part of the process optimization effort [20]. The analysis of the food waste is depicted in Table 4.1.

Table 4.1: Analysis of Food Waste.

Component	As Sent	Dry wt.
Moisture (%)	06.30	////
Dry Matter (%)	93.70	////
Crude Protein (%)	17.40	18.60
Crude Fat (%)	12.60	13.40
Acid Detergent Fiber (%)	33.20	35.40
Ash (%)	03.35	03.58
Total Digestible Nutrients (%)	81.50	87.00
Net Energy-lactation (Mcal/lb)	00.85	00.91
Net Energy-maint. (Mcal/lb)	00.90	00.96
Net Energy-gain (Mcal/lb)	00.59	00.63
Digestible Energy (Mcal/lb)	01.63	01.74
Metabolizable Energy (Mcal/lb)	01.51	01.61
Sulfur (%)	00.26	00.28
Phosphorus (%)	00.25	00.27
Potassium (%)	00.37	00.40
Magnesium (%)	00.06	00.07
Calcium (%)	00.90	00.96
Sodium (%)	00.50	00.53
Iron (ppm)	66.00	70.00
Manganese (ppm)	09.00	10.00
Copper (ppm)	06.00	06.00
Zinc (ppm)	28.00	30.00

The individual samples for testing were prepared according to standard procedures. Initially, each 120 mL bottle containing various amounts of food waste and phosphate buffer solution at various pH values was sealed with a septa, heated in an autoclave and then inoculated with 0.5 mL of thermally pretreated sludge from a waste water treatment facility. The food waste material was statistically sampled from the entire stock of processed food waste to assure homogeneity. The inoculated substrate samples were heated to 100°C for 10 minutes to inhibit methanogen bioactivity. The solar thermal energy system was used to heat the waste and after hydrogen production. Various combinations of temperature and heating time were considered. It was determined that a temperature of 95°C for 10 minutes was sufficient to eliminate methane production. The initial pH was measured after the bottles were sterilized and prior to incubation. Needles for collecting gas samples and measuring pressure are then inserted into each bottle. Continuous monitoring of pressure is accomplished using pressure transducers.

During fermentation, head space pressure in each of the test bottles was continuously monitored and used to calculate the volume of gas produced. The head space gas was sampled automatically for each bottle over time in conjunction with the pressure measurements. The composition of the gas in the headspace was measured using a gas chromatograph (GC) (CP-4900 Dual Channel Micro-GC; Varian Inc.) equipped with a thermal conductivity detector and a 10 M-5A molecular sieve column with argon as the carrier gas. Carbon dioxide was measured in the headspace using a separate channel on the same GC equipped with a 10 M Poraplot[®] (Varian, Inc.) column with helium as the carrier gas. Automated monitoring of the head space gas composition in the individual vials was accomplished using a multi-position stream selection valve (Valco Instruments Co., Inc.) that feeds directly into the injector of the GC as the valve cycles to the individual vials. The quantity of hydrogen produced was then determined based on the volume of gas produced, as determined from pressure data, and the percent hydrogen was determined from the GC. Controlled and/or measured parameters include temperature, residency time, pressure, and pH. This automated testing process makes it possible to consider a large variety of potential microorganisms and conditions for the production of hydrogen. The flexibility of this device assists in isolating particular microorganisms that have the best characteristics for hydrogen production thereby optimizing efficiency and system stability. The developed device maintains a constant temperature by means of a water bath. The gas collection system for the matrix is shown in Figure 4.3. The multiple testing apparatus is shown in Figure 4.4. Future research should extend these measurements to include multiple pH values during the fermentation process. Typical non optimized data from testing of food waste is shown in Table 4.2.

Figure 4.3: Gas Collection System.

Table 4.2: Typical Non Optimized Food Waste Results.

Temp. (°C)	Initial pH after autoclave	Substrate Concentration (g/25 mL buffer)	Total gas volume / 24 h @ 24h (mL)	Hydrogen gas at 24 h (% V/V)	Total gas volume / 24 h @ 48 hrs (mL)	Hydrogen gas at 48 h (% V/V)
32	6.2	0.75	43	14.21	42	22.23
35	6.8	1.00	69	15.80	35	23.86
35	6.8	0.50	31	11.31	13	12.17
35	6.8	1.00	65	16.92	30	23.87
35	5.5	0.50	17	8.05	36	17.24
35	6.8	0.50	45	13.85	15	12.21
35	5.5	1.00	19	9.03	33	16.03
35	5.5	1.00	20	8.70	33	17.50
35	5.5	0.50	14	7.76	42	17.74
45	6.2	0.75	55	14.46	4	15.34
45	7.0	0.75	58	17.88	23	20.42
45	6.2	0.75	51	13.74	1	16.14
45	5.3	0.75	18	5.64	1	5.69
45	6.2	0.75	48	13.47	3	13.98
45	6.2	0.75	56	13.68	2	14.3
45	6.2	0.42	33	9.59	5	10.53
45	6.2	1.08	48	14.09	9	15.18
45	6.2	0.75	55	13.36	2	14.31
45	6.2	0.75	51	13.53	4	13.46
55	6.8	0.50	1	.29	6	0.02
55	5.5	1.00	1	.28	1	0.14
55	5.5	0.50	.1	0.04	1	1.39
55	5.5	0.50	.1	0.66	1	0.18
55	6.8	1.00	1	0.29	6	0.33
55	5.5	1.00	1	0.19	1	0.17
55	6.8	1.00	1	0.17	4	0.17

Figure 4.4: Multiple Testing Apparatus.

An important aspect of this project was to maximize hydrogen yields by optimization of the process using multivariate analysis and statistical design of experiments [15, 16]. This approach significantly reduces the number of experiments required and thus greatly accelerates the determination of conditions for optimal production of hydrogen. A central composite response surface design was employed with optimal factor selection determined by the Simplex method [21]. Figures 4.5 and 4.6 depict results from the response surface model of representative experimental food waste data optimized for hydrogen concentration and volume after 48 hours of incubation.

As can be observed in Figures 4.5 and 4.6 the choice of operating parameters has considerable influence on the total hydrogen produced. The key factors that regulate the hydrogen production rate were temperature, pH, and substrate concentration. Using an iterative approach, it has been possible to determine combinations of these parameters that maximize hydrogen production. Increasing substrate concentration is important since this value directly influences the size and weight of the bio-reactor and hence its efficiency and practical viability. As can be observed in Figure 4.6, it is possible to increase hydrogen production rate as substrate concentration is increased. Methods were evaluated to utilize substrate concentrations up to 50%. Various methods to support the material during fermentation as well as assuring gas is not trapped in the substrate are being considered. We investigated designs for the substrate containment and support that allow for the removal of heat and efficient temperature control. As can be observed in Figure 4.5, another key consideration is pH. We developed methods to efficiently and inexpensively control the pH during fermentation. A commercial bio-reactor (New Brunswick, BioFlo[®]/CelliGen[®] 115, 3 L) was employed to consider how active pH control influences hydrogen production levels. One approach considered involves the use of an inexpensive sodium hydroxide based additive that would release over time in response to pH changes since conventional buffer materials tend to be too expensive for this application.

Figure 4.5: Food Waste H production – temperature vs initial pH.

Figure 4.6: Food Waste H production – substrate concentration vs initial pH.

System Design

It is anticipated that the optimal parameters determined from the matrix test data and response surface analysis will be used to train a neural network that will then be used to control a prototype bio-reactor. Such an approach will be robust and at the same time will be capable of adapting to changes in substrate composition and environmental conditions. An energy model has been developed to estimate key design

aspects and operating variables for a full sized modular energy system. Current hydrogen production levels indicate that it is possible to house a bio-reactor of size sufficient to produce a quantity of hydrogen to supply a reciprocating engine driven generator with an average output of 2 kW. Using the preliminary figures, the required biomass volume to produce the volume of hydrogen required for a fuel cell [22] has been modeled. A base production volume of biomass per kilowatt is calculated based upon the preliminary hydrogen production levels from Fig. 6. The length of a bio-reactor with a 1.5 meter diameter required to produce the necessary hydrogen at maximum demand of 2 kW would be 8 meters. The hydrogen production levels employed are conservative since there was minimal selection of the microorganisms or waste streams in the preliminary results. The current model assumes a food waste concentration of approximately 5% in the bio-reactor. As described previously, there are indications from the current research and in the literature that this concentration can be significantly increased thereby reducing the size of the bio-reactor. It should thus be possible to obtain significantly higher hydrogen production levels and consequently dramatically reduce the physical size of the reactor vessel.

Preliminary laboratory tests indicate that gas produced by the bio-reactor is approximately 23% hydrogen with the remainder being nitrogen and carbon dioxide. Methods for rapid gas removal and separation are also under investigation. Hydrogen separation using membrane technology has been shown to improve hydrogen yields [23] in dark fermentation systems and the use of these methods will be explored. Preliminary concept studies were conducted to evaluate the potential for removal of carbon dioxide using organometallic reagents and nanocatalysts. The bioreactor design will include a component for hydrogen separation and purification so that purified hydrogen will be available for use in a fuel cell or reciprocating engine to produce electricity locally.

It may be possible to store limited amounts of hydrogen in the bio-reactor by increasing pressure. This could provide a means of providing limited peaking capability. We have, however, observed that hydrogen production levels are decreased as pressure is increased. Methods to minimize this effect while still allowing for limited storage of hydrogen were preliminarily considered.

Initial design options for the modular energy system were developed. In addition to the operating parameters described previously, there are a variety of aspects such as material handling that must also be considered. The influence of these ancillary aspects was considered in conjunction with energy efficiency and rate of hydrogen production for the overall design of the system. The basic design approach is depicted in Figure 4.7.

Figure 4.7: Basic design approach.

Based upon the method of hydrogen production, options for the biological system and the bioreactor type were identified. These involve consideration of the preliminary design of the mass, heat flow system, and general bioreactor system. Preliminary results indicate advantages to a solid-state fermentation (SSF) bioreactor.

A variety of different SSF bioreactor designs were considered. SSF bioreactors can be divided into groups on the basis of how they are mixed and aerated.

Group I: Bioreactor in which the bed is static or mixed only very infrequently and air is circulated around the bed, but not blown forcefully through it.

Group II: Bioreactors in which the bed is static or mixed only very infrequently and the air is blown forcefully through the bed.

Group III: Bioreactors in which the bed is continuously mixed or mixed intermittently with a frequency of minutes to hours, and the air is circulated around the bed, but not blown forcefully through it.

Group IV: Bioreactors in which the bed is agitated and air is blown forcefully through the bed.

It is anticipated that the total reaction will be in the anaerobic environment and the reactant will be static on the bed. The anticipated total reaction hour is 24 to 48 hours and the temperature will be on the order of 37°C. Initially it appears that Group I bioreactors satisfy the criteria stated previously. These types of bioreactors are often referred as tray bioreactor. Once the bioreactor design has been determined, it is necessary to consider the design of the internal structure. Figure 4.8 depicts a preliminary bed design for the reactor. We investigated initial methods to continuously move waste material through the beds with minimum expenditure of energy.

Figure 4.8: Preliminary bed concept for reactor.

This type of tray bioreactor consists of a chamber containing a large number of individual trays, stacked one above the other with a gap in between. A 75% packing density is anticipated. The atmosphere of the reactor is controlled and circulates around the trays. The trays themselves may be constructed of wood, bamboo, metal or plastic.

The control of heat flow is a significant issue as indicated by the process temperature sensitivity indicated in the testing program. To consider the heat balance for the entire reactor, a system boundary can be drawn around the bioreactor. Several mass and energy phenomena occur within the substrate bed for the static substrate bed.

- Conduction: This occurs in response to temperature gradients, with energy flowing from warmer regions to cooler regions.
- Metabolic heat production: The bed is the site of microbial growth, and therefore the site of metabolic heat production.

Issues within the headspace must also be considered. Typically the head space gases are flowing, since, even in the bioreactor which the bed itself is not aerated; gas is typically circulated through the bioreactor such that it moves transversely across the bed surface. Heat transfer across the walls of the reactor must also be considered. Heat will be transferred across the bioreactor wall by conduction if there is a temperature gradient across it. Depending on the temperature gradient, conduction does not necessarily occur directly from the inside to the outside. Because that the conduction may occur from a warmer region of the bioreactor wall in contact with the substrate bed to the cooler region of the bioreactor wall in contact with the headspace gas. The distribution of temperature in SSF bioreactor walls and its influence on conduction has previously received minimal consideration. Figure 4.9 depicts the general heat flow for the reactor that has been considered for the preliminary design.

Figure 4.9: Preliminary heat flows for reactor.

Quantities considered in design depicted in Figure 4.3 include:

1. Entry mass and energy
2. Biogas flow within the headspace
3. Exit of mass and energy in the
4. Mass and energy transfer from the bed to the headspace
5. Heat transfer from bed to wall
6. Conduction and mass transport within the bed
7. Heat conduction within the wall
8. Heat transfer from wall to headspace

The developed modular energy system will provide a variety of benefits for use in remote and disaster situations that include production of electricity, heat, sanitized fertilizer and limited amounts of potable water as well as reducing environmental contamination of water and food resources. After the waste material has produced hydrogen in the bio reactor it is removed and heated to sanitize it for use as fertilizer. By heating it is possible to eliminate the majority of potentially harmful organisms left in the digested material. To experimentally verify this, substrate was removed from several bottles after they had produced hydrogen and was plated on a standard nutrient plant and then incubated for 48 hours at 60°C. These plates show considerable growth of organisms remaining in the digested waste. The same bottles were then heated to 95°C for 30 minutes in the solar thermal system described previously. Samples of the heat treated digested waste were plated onto the same type of nutrient plates used previously. After treatment no growth was observed. Figure 4.10 shows a comparison of before and after results for the aerobic solar heat treating of the digested waste material.

Figure 4.10: Growth before and after solar thermal treatment.

In Figure 4.10, the top plates were inoculated with food waste after producing hydrogen in the biological hydrogen reactor. Prior to hydrogen production this material was thermally treated and inoculated with sewage sludge. The bottom plates are for the same material after being aerobically heat treated in the solar collector system. The processing of waste material depends on the availability of heat from the solar thermal system which depends on the availability and intensity of sunlight. Methods to store thermal energy are being developed to reduce the effect of times when there is little or no sun light. In addition to variation through the day, the output from the solar thermal system depends on factors such as the time of the year, weather, and geographic location. The availability of solar energy influences the system energy balance and hence the amount of energy available for ancillary purposes such as production of potable water [19]. The thermal storage options being considered assist in reducing the influence of variations in sunlight. The production of hydrogen from the bio-reactor itself is influenced to a much lesser degree by variations in sunlight since it is anticipated that the residency time for the waste material in the reactor will be on the order of 48 hours and it will be possible to store limited quantities of preprocessed waste material prior to introduction into the bio-reactor itself. The possibility of varying the pressure in the bio-reactor as described previously also reduces the influence of solar energy variations when considering the energy balance for the entire modular energy system.

Ancillary aspects such as the value of waste isolation, potable water, and heat are also being considered as part of the overall design process. A next phase of this research would involve the construction of a bench top reactor based on these designs that will operate with dryer waste material and use solid material handling techniques. It is anticipated that the hydrogen produced from fermenting waste can be used to generate electricity locally in addition to other valuable products produced by the previously described modular energy system. Value streams include; hydrogen for production of electricity, waste disposal, heat for buildings, drinking water, and possibly a marketable chemical product produced from process carbon dioxide. Once proven, it is anticipated that the technology will be leveraged to larger applications. Preliminary estimates indicate that when all costs and benefits are considered, this technology has advantages over many other alternatives for remote and disaster recovery applications.

Other common organic waste substrates were also investigated for the production of hydrogen. As a result of these efforts, a new process was developed for the production of hydrogen from a waste product of ethanol production from grain referred to as Dry Distillers Grain Plus Solubles (DDGS) by fermentation with yeast. This process has the potential to increase ethanol production efficiency.

Distiller's Grains are the material remaining after the production of ethanol from grain. Results indicate that DDGS can be used to produce hydrogen by the process developed by this effort. Due to the increasing amount of ethanol being produced for use as a transportation fuel, there is currently an excess of Distiller's Grains beyond that which can be used for cattle feed and similar applications. The

developed process is robust and is tolerant to variations in DDGS concentration and limited oxygen levels. It has the potential to significantly increase the efficiency of ethanol production from corn and possibly other substrates. We have only used DDGS which is different than DG.

Large quantities of ethanol are currently produced by fermentation of grain and other organic materials as a source of transportation fuel. When grain is used in this process the material left after ethanol production is referred to as DDGS. It has been possible to produce significant quantities of hydrogen by fermentation using a process discovered and developed as part of this research. Initial optimal operating parameters for production of hydrogen from DDGS were obtained from tests conducted with the automated testing device previously described. These tests indicated a significant increase in hydrogen production as compared to food waste. Initial results indicate that yeast remaining in the DDGS after fermentation is able to robustly produce hydrogen under anaerobic conditions.

Figures 4.11 and 4.12 show results from the response surface model of experimental data for DDGS produced from the automated testing device previously described. The production was optimized for hydrogen concentration and volume after 48 hours of incubation using the Simplex method [19]. As can be observed in Figures 7 and 8 the choice of operating parameters has significant influence on total hydrogen production from DDGS. The key factors considered that regulate the hydrogen production rate are temperature, pH, and to a lesser degree substrate concentration. Combinations of these parameters that maximize hydrogen production were determined by using an iterative approach. Increasing substrate concentration is important since this value directly influences the size and weight of the bio-reactor and hence its efficiency and practical viability. As can be observed in Figure 4.11, it is possible to maintain hydrogen production rate as substrate concentration is increased.

Figure 4.11: DDGS Hydrogen Production – Concentration vs. Initial pH.

Figure 4.12: DDGS Hydrogen Production – Temperature vs. Initial pH.

To better understand how this process could be used in an industrial setting, tests of hydrogen production from DDGS were done in a commercial fermentor (New Brunswick, BioFlo®/CelliGen® 115, 3 L). The fermentor is shown in operation in Figure 4.13. Hydrogen production levels are currently approximately 30% greater than for the matrix bottles. This is attributed primarily to continuous stirring. We also have observed that there is less sensitivity to oxygen levels in the fermentor with DDGS. After an initial small concentration of oxygen in the head space that is believed to be associated with the addition of the DDGS to the system, the dissolved oxygen levels remain at essentially zero throughout the production period.

Figure 4.13: Fermentor with DDGS.

Initially 1.0 L of demineralized water was added to the sealed 3.0 L reactor vessel. It was then purged with nitrogen prior to the start of operation. Oxygen levels were monitored with the Gas Chromatograph during the purge process. DDGS was then added and purging of the fermentor continues until oxygen levels in the reactor drop to less than less than 0.25%. Vessel ports were then closed and gas production

monitoring is started. Temperature, stirring, and pH are automatically controlled and recorded by the control system of the fermentor during gas production.

The flow of gas from the fermentor was measured with a mass flow meter (Aalborg XFX mass flow meter). The fermentor was operated at atmospheric pressure. Pressure was continuously measured with a pressure transducer (Omega PX139) and recorded. Gas composition in the reactor head space was determined and recorded every 2 hours with the Gas Chromatograph.

The fermentor has options to control temperature and pH at set levels. Based upon optimal values determined from the test matrix, temperature was maintained at 37°C and pH was maintained at 5.5. A 0.75M solution of sodium hydroxide was added by a pump controlled by the fermentor to maintain the pH at a constant value. Additional work was performed to consider the influence of substrate concentration on hydrogen production rates. As the concentration of the substrate increases, the efficiency and cost effectiveness of the modular energy system increases since the hydrogen produced per unit volume of the bio reactor increases. This allows for decreased mass, size, and cost.

A method to determine both the hydrogen and carbon dioxide concentration and respective volumes of the gas as it is released in the fermentor as a function of time has been developed. These values utilize and are correlated with the mass flow rate from the Aalborg mass flow meter. A Matlab (Mathworks, Inc.) computer program has been developed to automate the calculation process. Values for CO₂ concentration are calculated and are correlated with pH and production levels, however, H₂/g substrate values decreased slightly as substrate concentration increases. Test results for the concentration of hydrogen in the gas produced from 80.0 g of DDGS in the fermentor as a function of time is shown in Figure 4.14. The production rate per gram of substrate was maintained as the substrate concentration was increased to 120 g per L with a 20% increase in stirring speed to 130 rpm.

Figure 4.14: Fermentor test results for DDGS.

Initial tests indicated a plateau in the production level occurring approximately at 12 hours after addition of the DDGS to the reactor and a second plateau at 32 hours. This plateau has been reduced in size for cases with pH control. Control at constant lower pH values seems to reduce the plateau the most. It is believed that this is attributable to a dual enzyme phenomenon and the equilibrium of CO₂ produced through fermentation as a function of pH. We will continue to investigate this further in the next quarter.

By increasing the agitation it has been possible to decrease the time to first hydrogen production. This is important since decreased production time results in reduced system size and cost. This is, however, not as important for DDGS as it is for food waste since the DDGS production would be associated with an industrial system. Tests were conducted to characterize the relation between continuous pH control and production levels for DDGS. Current production rates are 3.0 L of hydrogen from 80.0 g of DDGS in 1 L of buffered demineralized water in 48 hours.

It has been found that increased hydrogen content is obtained by controlling pH below 6.0. At higher pH values increased gas production is observed, but hydrogen concentration decreases slightly. This may be due to the interaction of CO₂ concentration and pH. We observed approximately equal concentrations of hydrogen and CO₂ in the head space of the reactor at 48 hours.

Currently more DDGS is produced in ethanol production from grain than can be used for cattle feed or related purposes. The process developed as part of this research provides a means of using DDGS to produce hydrogen and thereby add additional value to ethanol production. It is anticipated that the produced hydrogen could be used at the ethanol plant directly as an energy source either directly for heat production, as fuel for a reciprocating or turbine electric generator, or as a process enhancement.

The high heating value of ethanol is 12,830 BTU/lb and for hydrogen is 59,806 BTU/lb [20]. The current conversion rate for corn to ethanol is approximately 2.60 gal/bu with one gallon of ethanol having a high heating value of 83,961 BTU per gallon. One tonne (1000 kg) of corn produces approximately 378L of ethanol and 309 kg of DDGS.

For the DDGS hydrogen production process developed by this research, currently 37.5 mL of hydrogen at STP is produced in 48 hours for each gram of substrate in the bioreactor. For comparison purposes, it can be assumed that the hydrogen produced from the DDGS is combusted with high heating value to produce heat. This results in a 14% increase in the heat produced by the combustion of the associated ethanol alone. Other uses for the produced hydrogen have the potential to further increase the efficiency improvement. It is anticipated that the infrastructure associated with the production of DDGS will be relatively small in comparison with total plant cost and hence it can be assumed that this process has the potential to increase ethanol efficiency by at least 10%.

Evaluation of methods to reduce the water concentration

One key factor in sizing the unit is the concentration of waste material in the bio-reactor. Initial tests were performed at a 0.98 mass ratio of water to substrate. Recent optimization efforts have decreased this to 0.75 thereby significantly reducing the size and mass of the bio-reactor. Recent test results also indicate that it has been possible to significantly increase the hydrogen production amounts per gram of substrate beyond initial values as a result of the optimization of operating parameters. Test results for consideration of the influence of solid matter content on gas production are depicted in Figs. 4.15, 4.16, and 4.17.

Figure 4.15: Influence of maximum gas volume production vs. DM%.

Figure 4.16: Influence of maximum hydrogen volume production/ g substrate vs. DM%.

Figure 4.17: Influence of maximum gas volume production/ g substrate vs. time.

Methods to decrease water content in both conceptual designs for a bench top and commercial modular energy system were considered. Methods for potential handling of dry food waste were investigated. Two designs are currently being considered for the orientation of the biological reactor, one with the axis of the reactor vertical and one with it horizontal. We are now testing different methods to support the waste material. Issues involved include pH control, physical support, process flow of the waste material, and gas evolution rates. Use of the new matrix optimized operating parameter values has produced an increase in the substrate concentration levels by +20 %. Tests were conducted to investigate the influence of solid matter content on hydrogen production by placing samples with various water contents in large test tubes and rotating these tubes so as to partially or completely cover the inner of the tubes as they are rotated during the fermentation process. Operating parameter values and physical configurations that result in increased hydrogen production levels for reduced water levels were investigated.

Utilize Vacuum Tube Solar Collector to Process Waste Streams

If the microbial fermentation produces hydrogen rather than methane, emissions can be significantly reduced. By using this hydrogen in a fuel cell or a reciprocating engine, the major end products would be electricity, water, and heat. To produce hydrogen rather than methane by an anaerobic process it is necessary to first pretreat the feed material. Previous efforts by others have shown that heating the feed

material from a municipal sewage treatment plant to 100°C for 45 minutes inhibits bioactivity of methanogens [18]. In our laboratories current test results indicate that a majority of the benefits can be obtained with a temperature of 90°C for 30 minutes. Experimental results and computer simulations have demonstrated that sufficient heat can be produced from a solar collector located on the top of the proposed modular system to sanitize the waste material before and after the production of biohydrogen as well as providing limited additional heat for purposes such as producing potable water by distillation and heating buildings. A prototype solar thermal system developed as part of this research routinely obtains temperatures above 120°C [19]. The solar thermal energy system employs vacuum tube solar collector technology (Apricus Solar Co., Ltd, 20 and 22 tube vacuum tube solar collectors in series).

The vacuum tube thermal solar system was tested for pre and post processing of waste material. Performance and efficiency testing was done for different times of the year. An automated data acquisition system was used to acquire operating information from the solar collector system and was used to continuously generating data during testing. The coolant in the solar system is composed of propylene glycol and glycerin. This has increased the maximum operating temperature of the coolant to 180°C. As a result the efficiency of the dump heat exchanger was increased and problems with temperature drift on sunny summer days were reduced.

It has been possible to distill water using this system and thereby produce limited quantities of potable water. Such an application can be of considerable value in remote locations or in disaster situations. The process for the solar collector is depicted in Figure 4.18. The solar collector system is shown in Figure 4.19.

Figure 4.18: Solar thermal system.

Figure 4.19: Solar collector system.

To better understand how operating conditions influence the performance of the modular energy system, as shown in Figure 3, a computer model of the energy system was developed. Figure 4.20 depicts the temperature of the treated waste as a function of time for a typical day in June with the solar collector located in Hammond Indiana. This case also indicates that sufficient solar thermal energy will be available to treat the material from the biological reactor after hydrogen generation as well as providing limited building heating through the use of a thermal storage system.

Figure 4.20: Feed material temperature vs. time.

The thermal energy flows associated with the process are depicted in Figure 4.21. The solar values are from the solar collector. The process values assume a portion of the solar heat is used for other processes, and the external values assume additional heat from phase change thermal storage. The external values provide flexibility in cases where a quick start up is desired.

Figure 4.21: Thermal energy flows.

Using the preliminary figures, the required biomass volume to produce the volume of hydrogen required for the fuel cell [22] was modeled. A base production volume of biomass per kilowatt is calculated based upon the preliminary hydrogen production levels from Figure 6. The length of a bio-reactor with a 1.5 meter diameter required to produce the necessary hydrogen at maximum demand of 2 kW would be 9 meters. The hydrogen production levels employed are conservative since there was minimal selection of the microorganisms or waste streams in the preliminary results. This model assumed a food waste concentration of approximately 5% in the bio-reactor. Current research results indicate that the substrate concentration can be increased to 25% with minimal loss of production. This would significantly reduce the size of the bio-reactor required for the specified electrical output.

Conclusion

A source of energy is essential for maintaining or developing almost all human activities. This research is developing a modular distributed energy source that processes food, animal, or human waste to produce hydrogen for production of electricity locally as well as additional ancillary energy. This approach utilizes a renewable solar energy system to produce process heat. Excess energy from the solar system can be used for limited building heated and production of potable water. The developed system will process food, animal and human waste streams that potentially can produce health issues and thereby reduce or eliminate many associated concerns. The system produces hydrogen which has value for production of electricity locally in a fuel cell or reciprocating engine, but also leverages the other associated value streams to produce additional benefit. Due to the modular design and size of the system, the electric production efficiency will not be as great as many other more conventional sources that rely on energy produced from fuels such as petroleum based fuels. But, when all the direct and ancillary benefits are considered, this approach offers many advantages over conventional approaches. The basic feed stock for the system is local waste material and hence does not have issues with the logistics of fuel transportation as do most other conventional energy sources. The use of solar thermal energy leverages value and provides an opportunity for enhancing the value of renewable energy production locally. We consider this process to have significant value for waste processing and heat production as well as local electric production.

A second phase of the research developed a new process to increase ethanol production efficiency by anaerobically processing DDGS from grain based ethanol production. This newly developed process produces significant amounts of hydrogen from DDGS. Initial estimates indicate that it can increase ethanol production efficiency by 14% or more depending on the details of the implementation.

Publications / Presentations:

1. Kramer, R., Pelter, L., Patterson, J., Kmiotek, K., “Modular Energy Production From Waste”, proceedings World Energy Engineering Congress, 2011.
2. Kramer, R., Pelter, L., Patterson, J., Kmiotek, K., Ting, E., “Modular Waste/Renewable Energy System for Production of Electricity, Heat, and Potable Water in Remote Locations”, proceedings IEEE Global Humanitarian Technology Conference, 2011.
3. Kramer, R., Pelter, L., Liu, W., Branch, R., Martin, R., Kmiotek, K., “Utilization of Solar Heat for Processing Organic Wastes for Biological Hydrogen Production”, *Energy Engineering*, 108, 3, 2011.
4. Brockman, A., Basu, S., Gagare, P., Diwan, M., Shafirovich, E., Zheng, Y., Ramachandran, P., Varma, A., Gore, J., Kramer, R., Patterson, J., Ting, B., Pelter, L., and Maness, P., “Purdue Hydrogen Systems Laboratory,” *2010 Annual Merit Review & Peer Evaluation*, Washington, D.C
5. Brockman, A., Basu, S., Gagare, P., Diwan, M., Shafirovich, E., Zheng, Y., Ramachandran, P., Varma, A., Gore, J., Kramer, R., Patterson, J., Ting, B., Pelter, L., and Maness, P., “Purdue Hydrogen Systems Laboratory,” *2009 Annual Merit Review & Peer Evaluation*, Washington, D.C
6. Kramer, R., “Demonstration of Biological Waste Processing System for Hydrogen Production and Local Energy Production”, Lugar-Visclosky Energy Forum and Expo, October 2008.
7. Kramer, R., Pelter, L., Patterson, J., Ting, E., “Anaerobic Biological Hydrogen Production”, Fifth Annual World Congress on Industrial Biotechnology & Bioprocessing, Chicago Illinois, April 2008.
8. Kramer, R., Patterson, J., Pelter, L., Ting, E., “Biological Production of Hydrogen from Waste”. Seventh Annual BioCycle Conference on Renewable Energy from Organics Recycling, Indianapolis, Indiana, October 2007.

References

1. K. Kapdan, F. Kargi, “Bio-hydrogen production from waste materials,” *Enzyme Microbial Technology*, 38(5), pp. 569-582, 2006.
2. C.C. Chen, C. Y. Lin., “Using sucrose as a substrate in an anaerobic hydrogen-producing reactor”, *Adv. Environ Res* 7, 2003, pp. 695-699.
3. APHA. 1992. Standard methods for the examination of water and wastewater, 18th ed., Washington DC: American Public Health Association.
4. S. K. Han, H. S. Shin, “Biohydrogen production by anaerobic fermentation of food waste”, *Int. J. Hydrogen Energy*, 29, pp. 569-577, 2004.
5. F. R. Hawkes, R. Dinsdale, D. L. Hawkes and I. Hussy, “Sustainable fermentative hydrogen production: challenges for process optimization”, *Int. J. Hydrogen Energy*, 27, pp. 1339-1347, 2002.
6. S. Oh, B.E. Logan, “Hydrogen and electricity production from a food processing wastewater using fermentation and microbial fuel cell technologies”, *Water Res.*, 39, pp. 4675-4682, 2005.
7. S. Van Ginkel, S. E. Oh and B. E. Logan, “Biohydrogen gas production from food processing and domestic wastewaters”, *Int. J. Hydrogen Energy* (in press), 2004

8. O. Mizuno, R. Dinsdale, F. R. Hawkes, D. L. Hawkes and T. Noike,. "Enhancement of hydrogen production from glucose by nitrogen gas sparging", *Bioresource Technol.*, 73, pp. 59-65, 2000.
 9. F. N. Taguchi, T. Mizukami, Saito Taki, K. Hasegawa, "H₂ production from continuous fermentation of xylose during growth of *Clostridium* sp. Strain No.2.", *Can. J. Microbiol*, 41, pp. 526-540, 1995.
 10. J.-J. Lay, "Biohydrogen generation by mesophilic anaerobic fermentation of microcrystalline cellulose", *Biotechnol Bioeng.*, 74, pp. 280-287, 2001.
 11. H. Yokoi, A. Saitsu, H. Uchida, J. Hirose, S. Hayashi, and Y. Takasaki. "Microbial hydrogen production form sweet potato starch residue", *J. Biosci Bioeng*, 91, pp. 58-63, 2001.
 12. J. J. Lay, Y. J. Lee, T. Noike, "Feasibility of biological hydrogen production from organic fraction of municipal solid waste", *Water Res.*, 33, pp. 2579-2586, 1999.
 13. Y. Ueno, S. Haruta, M. Ishii, and Y. Igarashi, " Microbial community in anaerobic hydrogen-producing microflora enriched from sludge compost", *Appl. Microbial Biotechnol.* , 57, pp. 555-562, 2001.
 14. I.Hussy, F. R. Hawkes, R. Dinsdale, and D. L. Hawkes "Continuous fermentative hydrogen production from sucrose and sugar beet", *Int. J. Hydrogen Energy*, 30(5), pp. 471-483, 2005.
 15. G. Box, W. Hunter, J. Hunter, *Statistics for Experimenters*, Wiley, New York, 1978, pp. 291-432.
 16. G. Box, N. Draper, , *Emperical Model Building and Response Surfaces*, Wiley, New York, 1987, pp. 105-316.
 17. C. Lin, C. Lay, "Carbon/nitrogen-ratio effect on fermentative hydrogen production by mixed microflora", *Int. J. Hydrogen Energy*, 29, pp. 41-45, 2004.
 18. C. Lin, C. Lay, "Carbon/nitrogen-ratio effect on fermentative hydrogen production by mixed microflora", *Int. J. Hydrogen Energy*, 29, pp. 41-45, 2004.
 19. R. Kramer, L. Pelter, W. Liu, R. Branch, R. Martin, K. Kmiotek, "Utilization of Solar Heat for Processing Organic Wastes for Biological Hydrogen Production", *Energy Engineering*, 108, 3, pp. 51-64, 2011.
 20. Midwest Laboratories, Inc., 13611 B Street Omaha, NE, report number 07-211-5088.
 21. Design Expert, Version 8.0.5, Stat-Ease, Inc., Minneapolis, MN.
 22. Fuel Cell Handbook, 6ed., U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, DOE/NETL-2002/1179, 2002.
 23. D. B. Levin, L. Pitt, M. Love, "Biohydrogen production: prospects and limitations to practical application", *Int. J. Hydrogen Energy*, 29, pp.173-185, 2004.
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