Fossil Fuel Derivatives with Reduced Carbon

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Phase I Final Report

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I. EXECUTIVE SUMMARY

This project involves the simultaneous production of clean fossil fuel derivatives with reduced carbon and sulfur, along with value-added carbon nanofibers. This can be accomplished because the nanofiber production process removes carbon via a catalyzed pyrolysis reaction, which also has the effect of removing 99.9% of the sulfur, which is trapped in the nanofibers. The reaction is mildly endothermic, meaning that net energy production with real reductions in greenhouse emissions are possible.

In Phase I research, the feasibility of generating clean fossil fuel derivatives with reduced carbon was demonstrated by the successful design, construction and operation of a facility capable of utilizing coal as well as natural gas as an inlet feedstock. In the case of coal, for example, reductions in CO₂ emissions can be as much as 70% (normalized according to kilowatts produced), with the majority of carbon safely sequestered in the form of carbon nanofibers or coke. Both of these products are value-added commodities, indicating that low-emission coal fuel can be done at a *profit* rather than a loss as is the case with most clean-up schemes.

The main results of this project were as follows:

1. It was shown that the nanofiber production process produces hydrogen as a byproduct.
2. The hydrogen, or hydrogen-rich hydrocarbon mixture can be consumed with net release of enthalpy.
3. The greenhouse gas emissions from both coal and natural gas are significantly reduced. Because coal consumption also creates coke, the carbon emission can be reduced by 75% per kilowatt-hour of power produced.

II. INTRODUCTION

2.1 Background on the Concept

Fossil fuels can be used in a co-generation cycle in which valuable carbon by-products are formed as well as hydrogen-rich fuel. By fabricating carbon nanofibers from the fossil fuel input, carbon is removed from the fuel cycle. Thus the resultant fuel is hydrogen rich and carbon poor. Accordingly less carbon can be exhausted in the effluent.

The key to this concept is the recent development of nanoscopic highly-ordered carbon fibers with exceptional properties, which are inexpensively produced at our facilities. These fibers have been added to polymers such as polypropylene, rubber, nylon, polyester, silicone and epoxy to greatly improve one or more physical properties including tensile strength, modulus of elasticity, coefficient of thermal expansion, thermal and electrical conductivity.

This fiber, referred to as PYROGRAFTM-III is produced by a catalytic process using hydrocarbon-containing gas (e.g., methane or natural gas). The catalyst functions as a nucleation point for carbon fiber growth, bonding securely in a graphitic bond. Rather than forming a plane, however, the graphitic sheet wraps around itself to form a cylindrical sheath, as depicted very schematically below (for the sake of simplicity, only a few atoms are shown. Actually, the dimensions of the catalyst must be on the order of 10^2 to 10^4 carbon atoms in order to promote the formation of a cylindrical sheath).

Thus, the metal catalyst acts as a sieve for pyrolytic carbon atoms, with the result being that carbon fibers are nucleated and grown from the catalyst particle. These fibers can grow up to several mm long.

PYROGRAFTM III is made under a joint development agreement between Applied Sciences, Inc. and General Motors Corporation. This nanofiber is potentially very inexpensive since it is grown using economical natural gas as a feed material. Thus, the carbon source is very inexpensive compared with pitch or polyacrylonitrile (PAN) fibers.

Figure 1. Nucleation of Carbon Nanofiber by Metal Catalyst.

PYROGRAFTM III is a well-ordered highly graphitic material with strength and modulus comparable to other high-quality carbon fibers. It also has an extremely high surface area to volume ratio owing to its submicron diameter. Although the individual fibers are very difficult to characterize, larger fibers (referred to as PYROGRAFTM I) have achieved thermal conductivity of 1950 W/mK, or over four times higher than copper. The highly ordered graphitic lattice results in nearly metallic electrical conductivity. Since the aspect ratio is extremely high (~mm length by ~tens of microns diameter), a highly interconnected network is assured in composites using this fiber.

Figure 2. Scanning Electron Micrograph of As-Grown PyrografTM-III Nanofibers.

Figure 3. Transmission Electron Micrograph of an ASI carbon nanofiber, showing the metal catalyst particle at the end of the nanofiber.

2.2 Implications for the Greenhouse Effect

Over the past few years, many climatologists have questioned the effect of an increasing global burden of several gases such as carbon dioxide on the earth's mean temperature, fearing that carbon dioxide can inhibit the radiation of heat from the earth's surface, thus resulting in a "greenhouse effect."¹

The question of how much carbon dioxide in the atmosphere's gas is "good" and how much is "harmful" is being debated internationally. What is not being debated is that the levels of carbon dioxide are rising, and rising significantly. Measurements taken in Hawaii show concentrations 25% higher than those of just 75 years ago. Carbon dioxide levels are now about 375 parts per million (ppm) compared with calculations of just 300 ppm during other warm periods and around 200 for periods of the ice ages.

Computer models show a net environmental change of from 4 to 6 degrees, at which temperatures the ice caps will be largely melted resulting in the oceans rising approximately 6 to 8 feet. Vast areas of the world will be flooded, mostly low lying coastal regions such as portions of Florida and most of the Netherlands.

President Clinton said in his State of the Union Address on January 27, 1998: "...Our overriding environmental challenge tonight is the worldwide problem of climate change, global warming, the gathering crisis that requires worldwide action."

Of the greenhouse gases, carbon dioxide is of the greatest concern because the combustion of fossil fuels produces large quantities of carbon dioxide, 1.3 billion metric tons in 1990 for the United States alone. The Kyoto Protocol, if implemented, would likely result in the establishment of an international carbon dioxide emissions trading program to provide a mechanism to reduce man-made carbon dioxide emissions.² The Kyoto Protocol would commit the U.S. to reduce its carbon emissions to 7 percent below the 1990 emission level beginning in the year 2008, but growth in the population and economy means that the actual reductions need to be much larger. U.S. carbon emissions have grown by 17 percent above 1990 levels and are expected to be 31 percent above Kyoto Protocol levels by 2010.

Obtaining 30+ percent reductions would be a formidable challenge and would significantly negatively impact the domestic and global economies. It is estimated that the power generation industry would likely need to close most coal fired plants, which have been built over a period of fifty years, and build new gas turbine generation facilities within the next 9 years. This is an impossibility as the infrastructure simply does not exist on that scale.

Alternatives to replacement of existing plants would be to sequester the carbon dioxide as carbonates either at the point of discharge, or to have carbon dioxide air scavengers removing it at a location where the carbonates can be permanently disposed of. A carbon tax of around \$15 is being proposed to discourage the use of fossil fuels and to raise funds for carbon dioxide sequestering.

The future of the Kyoto Protocol is very much in doubt, and we can not take it for granted that these levels will be implemented. The underlying science associated with greenhouse gases and global climate change is still in dispute. Nevertheless, there is clearly an incentive for alternative means for producing energy if the industrialized nations are to maintain their high standard of living. This implies that the nation will seek new means of burning fossil fuels which do not release as much carbon, especially in the form of CO₂ or other greenhouse gases.

For that reason, it makes sense to consider technologies which can produce carbon-based products, thereby sequestering carbon, in addition to producing energy. In this proposal, the basic idea is to produce carbon nanofibers, a high value added product, while also producing carbon-depleted (hence, hydrogen rich) fuel sources. This will result in much less carbon being expelled to the atmosphere.

2.3. The Vision 21 Energyplex

Partially in response to environmental concerns as well as the uncertainty of depending upon old technology for the nation's energy needs, the "Vision 21 EnergyPlex" is a new approach to energy production from fossil fuels. It will integrate higher-efficiency power generation and more effective pollution control using fuel-flexible facilities capable of co-producing electric power, process heat and high value fuels and chemicals.

The concept of using coal to produce carbon nanofibers as well as high hydrogen content fuels is consistent with this vision. Specifically, this technology has the following useful attributes:

a. *Power.* Because the cycles envisioned herein result in cleaner (sulfur-depleted), hydrogen rich fuel mixtures, it becomes possible to consider using fuel cells with coal derived products. This makes it possible to achieve higher efficiency operation. Hydrogenated coal can offer higher energy content than normally achieved.

b. *Combined heat and power.* The process inherently produces a raw material (carbon nanofibers) on site, which can be processed with other materials. Given the presence of "free" waste heat from power production facilities, chemical processing needs (such as cement based materials, polymers, thermoplastics and other low-cost materials) can efficiently use the heat, thus increasing the overall heat utilization.

c. *Environmental.* The environmental aspect is especially noteworthy, since the nanofiber production process removes carbon and sulfur from the fuel stream. As a result, the exhaust is hydrogen rich and largely free of sulfur.

d. *Greenhouse Gas Reduction.* The ability to remove carbon is of particular interest due to greenhouse effect considerations. Currently measured efficiencies are 30% (carbon produced in solid form divided by carbon present in the inlet stream).

e. *Coproducts.* Use of hydrogenation from the nanofiber process, combined with a solvent-extracted coal pitch can lead to a clean transportation quality fuel with a cost comparable to oil. Other coproducts are also possible. The main point is that the nanofiber production process results in a hydrogen rich effluent which can be utilized with other fuels or perhaps burned separately.

In addition, the technology developed for nanofiber production may be generically applicable to fossil fuel cycles. For example, in the area of *chemical catalyst* development, the process currently uses chemical catalysts to produce nanofibers (which simultaneously removes sulfur and traps it in the nanofibers). This effect may be of interest for coal burning in any case, even if no nanofibers are produced, due to the environmental advantages. For example, carbon black or even soot production may be enabled through the use of these catalysts, simply to allow coal products to be burned with less release of carbon.

Because the nanofiber production process uses gas phase pyrolysis, it can dovetail with other efforts involving *coal gasification*. Gasification of biomass products or even waste streams, such as recycled automobile tires, can also form the basis for profitable collaboration.

Finally, *carbon sequestration* is one way that energy strategists are considering coping with greenhouse gas emissions. Obviously, the best way for this to be accomplished would be to lock up the carbon in a form which can be sold for hundreds of dollars per ton or even more. This is exactly the intended result of our carbon nanofiber production/fuel generation cycle.

The derived fuel forms will consist of sulfur-free, hydrogen rich fuels which can be cleanly combusted, easing environmental considerations as well as cost. As noted above, the carbon fiber has a unique affinity for sulfur and extracts virtually 100% percent of the sulfur present in the gas. The applications of PYROGRAFTM III include use as an additive for synthetic rubber, polymers,

epoxy, silicone and other composites. ASI, due to its connection with the automotive industry, is currently interested in expanding the markets for carbon fiber.

Specific applications and enhancements which we have identified include:

a. Electrically conductive plastics and sheet molding compound. Electrostatic spray painting is a very effective way to apply an adherent finish to a surface. This is normally accomplished by holding the paint dispenser at one potential and the target (e.g., sheet molding compound for a automobile body panel) at the opposite polarity. Obviously, this is not possible if the target is electrically insulating. Thus addition of electrical conductivity is important.

b. Static dissipation compounds. Electronic items are often subject to upset from static discharges. For example, it is commonplace to accidentally destroy digital electronics from static discharges from the human body. Materials such as cases for video displays could be improved if they could be made slightly electrically conducting, thus allowing them to be grounded.

c. Thermally conductive plastics. Plastics are in many cases cheaper than metal and easier to tool for. For certain applications such as oil pans and wheel assemblies, the material must not only bear loads, but must also dissipate heat. For example, auto makers and racing teams have experimented with plastic wheels for several years, and have demonstrated very good mechanical performance, but have had problems dissipating heat from brake systems. Plastics made from PYROGRAFTM III have thermal conductivity higher than steel and thus are likely to win acceptance.

d. Use as an additive for synthetic rubber. Because of the high strength and modulus of the fiber, it is possible to produce tires with enhanced wear resistance and traction as well as excellent rolling resistance. Similar arguments apply to polyurethane for in-line skate wheels, as well as the soles of athletic shoes.

e. High temperature electrically conductive silicone. Applications such as solar cell contacts require a compliant electrical contact. Electrically conductive silicone can be made by suspending metal particles in the silicone. However, upon heating, thermal expansion causes the metal particles to become separated, greatly affecting the electrical resistivity. This effect does not occur with carbon fiber. Thus, good electrical properties can be maintained at high temperatures simply by adding a few percent of carbon fiber.

f. Lithium batteries. PYROGRAFTM III is an excellent candidate to replace carbon black in lithium and other batteries, resulting in improved energy and power density.

g. Electrically shielded boxes. The unique electromagnetic absorption properties of carbon nanofibers result in excellent attenuation of electromagnetic signals. This can be used either for isolation of electronic circuits, or for stealth applications.

h. Cement, concrete and asphalt. In addition to adding structural strength and improved modulus to concrete, the addition of electrical conductivity results in decreased galvanic corrosion

of Rebar embedded in the concrete. For practicality, a cost of less than \$1 per pound of carbon fiber is probably required. This is potentially achievable from fiber manufactured from coal, since coal has a cost of \$0.03 per pound or even less.

To illustrate the potential for enhancement of electrical conductivity in selected polymer matrices, the figure below shows the electrical conductivity obtained for Pyrograf-III as an additive at low volume loadings. The conductivity of the medium has been found to be a function of fiber loading, as well as the type of compounding and the type of polymer constituting the matrix material. The following illustration demonstrates the potential for structural reinforcement, where the tensile strength and modulus of 3-D Pyrograf-III/polypropylene composites are compared to polypropylene similarly loaded with glass fiber with a two-dimensional architecture. Even with a three dimensional architecture, the Pyrograf-III composites demonstrate similar strength and modulus, as anticipated for the graphitic reinforcement.

Figure 4. Electrical Conductivity as a Function of Volume Fraction of Pyrograf-III in Polypropylene.

Figure 5. Comparison of Pyrograf-III and Glass Fiber for Tensile Strength and Modulus in Polypropylene.

2.4. Hydrogen Rich Fuel Forms

The hydrogen rich effluent can be used by itself or combined with other fuels to make a more environmentally friendly fuel form.

It is possible to create either small amounts of very hydrogen-rich hydrocarbon gas, or alternatively, to dilute this hydrogen-rich gas in other fuels.

In the case of solid fuels (i.e., such as coal, coal tar pitch, solvent extracted coal pitch or petroleum pitch), the latter approach may be advantageous.

West Virginia University has carried out several experiments which show that the hydrogen content does in fact increase. Typical values are in the range of several percent.

An additional benefit is that the solvent extraction process is more effective with hydrogenated coal than without hydrogenation. In the case of WVGs 13421 Coal, the extraction process yields only 35 wt. % extraction, whereas it is over 80 wt % when the coal is first hydrogenated. In addition the energy content of the hydrogenated material is increased by several percent.

Data are summarized in the table below.

Table I. Atomic Constituents of Coal and Extract.

	Raw Coal	Ash-free extract	Hydrogenated Ash-free Extract
C	86.07	84.24	88.11
H	5.26	5.47	5.83
N	1.51	2.08	2.22
S	0.87	0.77	0.78
O	6.29	7.44	3.06
H/S Ratio	193	227	239
H/C Ratio	0.73	0.78	0.79

Note that since the energy content per unit mass of hydrogenated material is also increased, the amount of pollutants per kilowatt of power is reduced even more than it would appear from the table.

III. EXPERIMENTAL RESULTS

3.1. Facility Design and Construction

A facility was retrofitted for the use of coal. Two methods were used: a gas injection method for use with pulverized coal, and a liquid injection system.

The first method uses coal which has been pulverized to -200 mesh. A coal feeder is used to deliver the coal dust to the furnace, where it is entrained in a puff of inert gas or nitrogen. This process is suitable for laboratory demonstrations, but the cost of inert gas or even nitrogen would be expensive for actual production.

A less expensive method is to use liquid injection. In this case, we initially tried an automotive fuel injector. Pulverized coal was dissolved or suspended in a methanol solvent, along with catalyst. The mixture was pumped under about 50 psig pressure to the fuel injector. However, the fuel injector tended to get easily clogged, probably due to the ash present in the coal. A second method was to simply

Figure 6. Coal-Derived-Nanofiber Furnace.

Figure 7. Furnace for Producing Carbon Nanofibers from Coal Pitch.

Figure 8. Digital Control Room.

IV. RESULTS

4.1 Energy Balances for Fuel Cycles.

Analytic results verified that the nanofiber production furnace can produce hydrogen rich hydrocarbon gas as well as valuable carbon nanofibers, as illustrated in the tables below. These results predict a substantial reduction in CO₂ emissions, even when energy penalties associated with the pyrolytic reactions are accounted for.

In the case of coal, there are two forms of solid carbon produced: nanofibers and coke. Both are equally effective in permanently sequestering carbon so that it can not be released into the atmosphere. As a consequence, the amount of CO₂ released as an effluent is decreased from 63 to 71% depending upon the reaction temperature.

Figure 9. Process Flow Diagram.

Table II. Summarized Results for Natural Gas.

Reaction Temperature (°C)	% of Carbon in feed to Carbon Fibers	% of Carbon in feed to CO ₂	Net Energy without combustion (KJ)	Net Energy with combustion (KJ)	% CO ₂ Reduction on an equal energy basis
1000	20.0	80.0	13.4	-743.4	12.0
1025	25.0	75.0	17.5	-724.0	15.3
1050	30.0	70.0	21.5	-704.7	18.7
1075	35.0	65.0	25.6	-685.3	22.3
1100	40.0	60.0	29.7	-665.9	26.1
1125	45.0	55.0	33.7	-646.5	30.0

Table III. Summarized Results for Coal.

Reaction Temperature (°C)	% of Carbon in feed to Carbon Fibers	% of Carbon in feed to CO ₂	Net Energy without combustion (KJ)	Net Energy with combustion (KJ)	% CO ₂ Reduction on an equal energy basis
1000	3.80	16.3	0.252	-13.7	63.4
1025	4.75	15.4	0.301	-13.5	65.2
1050	5.71	14.4	0.350	-13.2	67.0
1075	6.67	13.5	0.399	-13.0	68.9
1100	7.61	12.5	0.448	-12.7	70.8
1125	8.56	11.6	0.497	-12.5	72.8

The carbon fiber process was modeled using a simplified block flow diagram. The feed is contained in Stream 1. In block one, the feed is heated to reaction temperature by the addition of Q_1 . Q_1 is heat which must be added to the process. Stream 2 contains the feed at reaction temperature. Carbon fiber formation occurs in block two by reacting the feed material. The formation of carbon fibers occurs between the temperatures of 1000 and 1125 °C. Heat, Q_2 , must be added during this reaction to drive the endothermic formation of carbon fibers and to maintain the temperature. Stream 3 is a mixture of product gases and solid carbon fibers. Once the carbon fibers are formed all the reactor effluent is cooled for separation of the fibers. Block three represents this process where the amount of heat removed is Q_3 . Stream 4 contains all cooled reaction products. Block four shows the separation of carbon fibers from the product gases. Stream 5 is the cooled product stream of carbon fibers and Stream 6 represents the unreacted feed material and gases created during carbon fiber formation. Block five shows these combustion of the product gases. The net heat released by this combustion process is given by Q_4 . Stream 7 is the required input of oxygen for complete combustion. Stream 8 contains the products of combustion.

4.1.1. Carbon Nanofiber Process Using a Methane Feed

The temperature for which carbon fiber formation occurs ranges from 1000°C to 1125°C for a methane feed. For methane, the percent of carbon in the feed which is converted to carbon fibers is between 20% to 45%, depending on the reaction temperature. The carbon which does not get converted to carbon fibers remains as methane and is combusted to CO₂, in block five.

The net energy output per CO₂ released increases with an increase in reaction temperature, seen in Figure 2. The reason for this is that as more fibers are produced, less methane appears in the product gas. However, the product gas is enriched in hydrogen which contributes to the fuel value without forming CO₂, upon combustion.

The percent CO₂ reduction is based on an equivalent energy basis. This was calculated by assuming that one mole of feed methane was put into the process. Then the composition of the reactor effluent gases was found. Knowing the composition, the lower heating value of the gas mixture was calculated. The number of moles of the product gas, which would be needed to be combusted to produce the same amount of energy as the combustion of the original one mole of methane feed, was then found. This put the amount of CO₂ formed on an equivalent energy basis between the original feed and the product gases. The percent reduction of CO₂ increases as the reaction temperature increases, (Figure 3) for the same reason as above.

Q₁, Q₂, Q₃, and Q₄ are the energy requirements for the carbon fiber process. Positive Q's mean energy that is put into the process (during heat up and reaction) and negative Q's mean energy that is taken out of the process (during cooling and combustion of the products).

The sum of Q₁, Q₂, and Q₃ is the amount of energy required to make carbon fibers (Net Energy without Combustion). The net energy required to make carbon fibers increases with an increase in reaction temperature, Figure 4. This is primarily because more energy is required to drive the reaction at higher temperature.

The sum of Q₁, Q₂, Q₃, and Q₄ shows the amount of energy that is available after fiber formation and combustion of the product gas (Net Energy Output). The net energy output decreases with an increase in reaction temperature, Figure 5. This is the result of two effects: 1) the reaction requires more energy at higher temperature and 2) the product gas contains much less methane and more hydrogen (the heat of combustion for hydrogen is less than that for methane so the overall energy of combustion decreases).

Figure 10. Carbon Conversion Efficiency for Methane.

Figure 11. Net energy output per mol of CO₂ released from combustion of effluent using a methane feed.

% Reduction of CO₂

Figure 12. Percent reduction of CO₂ on an equivalent energy basis for combustion of reactor fuel effluent from methane compared to conventional combustion of methane.

Figure 13. Net energy required to make nanofibers using a methane feed.

Figure 14. Net energy output including combustion of the reactor effluent for a methane feed.

4.1.2. Carbon Fiber Process Using a Natural Gas Feed

The material and energy balances for carbon fiber production using a natural gas feed was evaluated. The components and composition of natural gas used in this evaluation was taken from a typical make up of natural gas given in Perry's Chemical Engineers' Handbook. Natural gas is comprised primarily of methane, 96.2 mole %. Natural gas contains 0.52 mole % carbon dioxide, 0.46 mole % nitrogen, 1.82 mole % ethane, 0.3 mole % propane, and 0.7 mole % butane.

The temperature for which carbon fiber formation occurs is between 1000°C and 1125 °C for a natural gas feed, Table 2. All data in Table 2 are for a feed of one mole of natural gas feed having the above composition. For natural gas, the carbon present in the feed which was converted to carbon fibers is between 20 % and 45 %, depending on reaction temperature.

Ethane, propane, and butane was assumed to completely decompose before the methane. Therefore, methane is the only hydrocarbon found in the reactor effluent gas. The carbon in methane which does not get converted to carbon fibers remains as methane and is combusted to carbon dioxide in block five.

The net energy output per CO₂ released (for a natural gas feed) increases with an increase in reaction temperature. The reason for this is that as more fibers are produced, less methane appears in the product gas. However, the product gas is enriched in hydrogen which contributes to the fuel value without forming CO₂, upon combustion. For natural gas the net energy output per CO₂ released ranges from 882 -KJ/mole to 1073 -KJ/mole.

The percent CO₂ reduction, Table 2, is based on an equivalent energy basis. This was calculated by assuming that one mole of feed natural gas was put into the process. Then the composition of the reactor effluent gases was found. Knowing the composition, the lower heating value of the gas mixture was calculated. The number of moles of the product gas, which would be needed to be combusted to produce the same amount of energy as the combustion of the original one mole of natural gas feed, was then found. This put the amount of CO₂ formed on an equivalent energy basis between the original feed and the product gases. The percent reduction of CO₂ increases as the reaction temperature increases, (Figure 7) for the same reason as above. On an equal energy basis the % CO₂ reduction for a feed of natural gas is between 12 % and 30 %, depending on reaction temperature.

Q₁, Q₂, Q₃, and Q₄ are the energy requirements for the carbon fiber process. Positive Q's mean energy that is put into the process (during heat up and reaction) and negative Q's mean energy that is taken out of the process (during cooling and combustion of the products).

The sum of Q₁, Q₂, and Q₃ is the amount of energy required to make carbon fibers(Net Energy without Combustion). The net energy required to make carbon fibers increases with an increase in reaction temperature, Figure 8. At 1000°C 13.4 kJ of energy is required to make the carbon fibers from one mole of feed natural gas, while 33.7 kJ of energy is required at 1125°C. This is primarily because more energy is required to drive the reaction at higher temperature and the yield of carbon fibers increases at higher temperatures requiring more energy as the yield increases.

The sum of Q₁, Q₂, Q₃, and Q₄ shows the amount of energy that is available after fiber formation and combustion of the product gas (Net Energy Output). The net energy output

decreases with an increase in reaction temperature, Figure 9. This is the result of two effects: 1) the reaction requires more energy at higher temperature and 2) the product gas contains much less methane and more hydrogen (the heat of combustion for hydrogen is less than that for methane so the overall energy of combustion decreases). For a feed of natural gas the net energy output ranges from -743.4 kJ at 1000°C to -646.5 kJ at 1125 °C. The negative sign meaning this is energy the process plus combustion gives off.

Figure 15. Net energy output per mol of CO₂ released upon combustion of reactor fuel effluent gas for a natural gas feed.

Figure 16. Percent reduction of CO₂ on an equivalent energy basis for combustion of reactor fuel effluent from natural gas compared to conventional combustion of natural gas.

Figure 17. Net energy input required to make nanofibers from a natural gas feed.

Figure 18. Net energy output including combustion of the reactor effluent for a natural gas feed.

4.1.3. Carbon Nanofiber Process Using a Coal Feed

The use of a coal feed to make carbon fibers was modeled. A typical bituminous coal was used for the composition of the coal feed. The composition of the coal was taken as 82.6 weight % carbon, 5.16 weight % hydrogen, 1.26 weight % nitrogen, 2.61 weight % sulfur, and 2.61 weight % oxygen. This coal also contains 37.1 weight % volatile matter.

The coal feed was assumed to vaporize at 400°C, at this temperature 37.1 weight % of the coal is gaseous. The composition of the coal volatiles was taken to be similar to that of coke oven gas. The components of such a gas being carbon dioxide, carbon monoxide, hydrogen, methane, and nitrogen. The remaining 62.9 weight % of coal was considered coke, containing mostly carbon and all of the sulfur in the feed.

The temperature for which carbon fiber formation occurs is between 1000°C and 1125 °C for a coal feed, Table 3. All data in Table 3 are for a feed of one gram of coal feed having the above composition. For coal, the carbon present in the feed which was converted to carbon fibers is between 3.8 % and 8.56 %, depending on reaction temperature.

The carbon in methane which does not get converted to carbon fibers remains as methane and is combusted to carbon dioxide in block five.

The net energy output per CO₂ released (for a coal feed) increases with an increase in reaction temperature, seen in Figure 10. The reason for this is that as more fibers are produced, less methane appears in the product gas. However, the product gas is enriched in hydrogen which

contributes to the fuel value without forming CO_2 , upon combustion. For coal the net energy output per CO_2 released ranges from 1223 -KJ/gram to 1563 -KJ/gram.

The percent CO_2 reduction, Table 3, is based on an equivalent energy basis. This was calculated by assuming that one gram of feed coal was put into the process. Then the composition of the reactor effluent gases was found. Knowing the composition, the lower heating value of the gas mixture was calculated. The number of moles of the product gas, which would be needed to be combusted to produce the same amount of energy as the combustion of the original one gram of coal feed, was then found. This put the amount of CO_2 formed on an equivalent energy basis between the original feed and the product gases. The percent reduction of CO_2 increases as the reaction temperature increases, (Figure 11) for the same reason as above. On an equal energy basis the % CO_2 reduction for a feed of natural gas is between 63.4 % and 72.8 %, depending on reaction temperature.

Q_1 , Q_2 , Q_3 , and Q_4 are the energy requirements for the carbon fiber process. Positive Q 's mean energy that is put into the process (during heat up and reaction) and negative Q 's mean energy that is taken out of the process (during cooling and combustion of the products).

The sum of Q_1 , Q_2 , and Q_3 is the amount of energy required to make carbon fibers (Net Energy without Combustion). The net energy required to make carbon fibers increases with an increase in reaction temperature, Figure 12. At 1000°C 0.252 kJ of energy is required to make the carbon fibers from one gram of feed coal, while 0.497 kJ of energy is required at 1125°C . This is primarily because more energy is required to drive the reaction at higher temperature and the yield of carbon fibers increases at higher temperatures requiring more energy as the yield increases.

The sum of Q_1 , Q_2 , Q_3 , and Q_4 shows the amount of energy that is available after fiber formation and combustion of the product gas (Net Energy Output). The net energy output decreases with an increase in reaction temperature, Figure 13. This is the result of two effects: 1) the reaction requires more energy at higher temperature and 2) the product gas contains much less methane and more hydrogen (the heat of combustion for hydrogen is less than that for methane so the overall energy of combustion decreases). For a feed of coal the net energy output ranges from -13.7 kJ at 1000°C to -12.5 kJ at 1125°C . The negative sign indicates the energy release from the process of combustion.

Figure 19. Net energy output per mol of CO₂ released from a coal feed upon combustion of reactor effluent gas.

Figure 20. Percent reduction of CO₂ on an equivalent energy basis for combustion of reactor fuel effluent from coal compared to conventional combustion of coal.

Figure 21. Net Energy Input Required to make nanofibers from a coal feed.

Figure 22. Net energy output including combustion of the reactor effluent for a coal feed.

4.1.4. Carbon Nanofiber Process Modeling Summary

All feedstocks (methane, natural gas, and coal) show similar trends. The net energy output per CO₂ released increases with an increase in reaction temperature, for all feeds. On an equal energy basis the percent CO₂ reduction increases as the reaction temperature increases, for all feeds. The net energy required to make carbon fibers increases with an increase in reaction temperature, for all feeds. The net energy output decreases with an increase in reaction temperature, for all feeds.

Methane and natural gas feeds convert the most carbon in the feed to carbon fibers but do not give the largest percent CO₂ reduction on an equal energy basis. Coal as the feedstock gives the largest percent CO₂ reduction of any of the feeds. This is mostly due to the large amount of coke that is formed during heating the reactants to reaction temperature. The coal feed also has the smallest percentage of carbon in the feed being converted to carbon fibers.

4.2 Cycle Development

Thermodynamic cycles must be based on optimization according to environmental and overall economy, rather than optimizing fiber quality, as had been the case up to the present time. An unexpected finding was that our process can be highly effective at obtaining energy from coal with tremendous reduction of greenhouse (i.e., mainly CO₂) gas. Note that the reduction can be as high as 60-70%. The reason is that carbon is sequestered not only in the form of carbon nanofibers, but also in the form of coke. The coke is also a valuable product which can be processed, if desired, for steelmaking or carbon product manufacture. In any case, substantial amounts of carbon can be safely sequestered in solid form from combustible coal, while still generating valuable carbon fibers and clean fuel.

Efficient energy recovery requires the separation and collection of hydrogen gas from the furnace effluent. This will be accomplished by the Hydrogen Recovery System (HRS). The major components are as follows:

- a. Inlet feed: Consists of welded vessels, piping, access doors for cleaning and maintenance. Instrumentation to measure temperatures and flow rates is also required.
- b. Computer controllers: This system is used to control the injection of gas and liquid to the furnace. It is available at no charge to the contract, other than minor reprogramming needs.
- c. The fuel inlet guides material such as coal pitch to be hydrogenized. It consists of heavy gauge sheet metal which will be welded or bolted in place.
- d. Fuel injectors: based upon automotive technology. The flow speed will be controlled via computer using liquid pumps.
- e. Furnace: Capable of heating furnace tubes up to 1100 C.

f. A compressor which is capable of compressing combustible furnace gas to 1500 psi or higher. Typically, the volumetric flow handling capability is far in excess of our requirement for 10 m³/hour. It is also usable for hydrogenating coal products, as illustrated below.

g. Furnace tubes: SiC-based tubes are preferred due to economy and performance, especially crack resistance during thermal cycling. In addition, special endcaps used to seal the furnace from the outside air need to be manufactured.

h. A low pressure (atmospheric) manifold system. This will be fabricated using Stainless Steel or possibly aluminum duct hosing.

i. Gas chromatograph mass spectroscopy (GCMS) system. This is used to monitor the chemical content of the exhaust from the furnace.

j. A collection point for bottling the gas. This requires high pressure fittings/couplings and tubes. The pressure requirement means that special care must be taken to avoid leaks. Accordingly, metal o-ring seals are preferred rather than the usual viton or other synthetic rubber seal. Similarly, compression fittings should be avoided when possible, although they are rated for high pressure use.

k. A hydrogen separation system. Candidate systems can include distillation, pressure swing absorption or membrane separators. The demonstration unit will bottle the gas so that hydrogen separation can be done off-site (i.e., at WVU), though eventually economics will dictate the hydrogen separation be done on-site at ASI facilities.

Figure 23. Hydrogen Recovery System.

The hydrogen rich process gas from the nanofiber furnaces can also be used to hydrogenate coal. That is, coal will chemically bond with hydrogen and other hydrocarbons at high temperatures and high pressure, thus creating a more energetic fuel with proportionately lower content of carbon, sulfur and other potential environmental concerns.

The hydrogenation process can add as much as 50% additional chemical enthalpy at relatively low energy cost. The hydrogen rich process gas is an ideal material for this purpose. This is especially true if carbon nanofiber production can be economically self sustaining.

An additional benefit is that hydrogenated coal is a much more suitable feedstock for solvent extraction of coal pitch than is untreated coal. Hydrogenated coal can yield up to 80% of the original mass of the coal, whereas untreated coal is often in the range of 35% mass yield.

The pressure requirement for efficient hydrogenation is 1000 to 1500 psig. The temperature requirement is 400 C to 450 C. This requires a high pressure compressor, which can be the same compressor used in the hydrogen separation task above, a hermetic vessel suitable for withstanding 1500 psig and 450 C.

The major components required are:

- a. Inlet feed: Consists of welded vessels, piping, access doors for cleaning and maintenance. Instrumentation to measure temperatures and flow rates is also required.

b. Computer controllers: This system is used to control the injection of gas and liquid to the furnace. It is available at no charge to the contract, other than minor reprogramming needs.

c. The fuel inlet guides material such as coal pitch to be hydrogenized. It consists of heavy gauge sheet metal which will be welded or bolted in place.

d. Fuel injectors: based upon automotive technology. The flow speed will be controlled via computer using liquid pumps.

e. Furnace: Capable of heating furnace tubes up to 1100 C. This is available on-site at no charge to the contract, but must be refurbished, instrumented and controlled.

f. A compressor which is capable of compressing combustible furnace gas to 1500 psi or higher. Typically, the volumetric flow handling capability is far in excess of our requirement for 10 m³/hour.

g. Furnace tubes: SiC-based tubes are preferred due to economy and performance, especially crack resistance during thermal cycling. In addition, special endcaps used to seal the furnace from the outside air need to be manufactured.

h. A low pressure (atmospheric) manifold system. This will be fabricated using Stainless Steel or possibly aluminum duct hosing.

e. Gas chromatograph mass spectroscopy (GCMS) system.

f. A reinforced Steel cylinder, capable of withstanding 400 C and 1500 psi. The cylinder will be manually filled with coal.

g. A vertical tube furnace and stand used for heating the coal.

h. High pressure capable fittings and tubings must be used throughout.

Figure 24. Coal Product Hydrogenation System (CPHS).

4.3. Effluent Analysis

Experiments were run with natural gas as well as coal to verify that simultaneous production of carbon nanofibers and clean hydrocarbons is achievable. Processes for making carbon fibers from high temperature hydrocarbon pyrolysis were investigated by measuring the composition of gases coming from the pyrolyzer. Specifically, the sponsor was interested in the composition of hydrogen and pyrolysis products of methane, ethane, ethylene, acetylene, propane, propylene and higher hydrocarbons.

Samples were taken from a swagelok sampling port with a connector to the port designed to provide a filtering of the carbon fiber material as the gas sample was taken. The sample was extracted using a 1 liter syringe and transferred to a mylar sampling bag for quantitative analysis of the mixture. The sample was taken during that point in time when the carbon fiber was being produced in the pyrolyzer and gases were being vented from the system.

Several different analytical systems were used in these measurements. Initially, the measurements were performed using a Hewlett Packard 5890 Series II GC equipped with a flame ionization detector and a thermal conductivity detector. The GC included two different injectors and column systems. The first was a purged-packed injector connected to a 5A-MS molecular sieve column (J&W Scientific) to the TCD for hydrogen analysis. The second column was a GS-Q column connected from a split splitless injector to a flame ionization detector to measure the

C1 through C6 gases produced. Two different carrier gas systems were used in these analyses: first, a helium carrier gas was used and then a nitrogen carrier gas.

Other analyses were conducted in order to identify the sulfur containing components in the gas sample. For this analysis, a Hewlett Packard 5890/5970B MSD was employed using a non-polar DB-5 30 meter column with helium carrier gas.

The first sample was marked ANC-70 and was collected in a sampling bag as described above. A second bag sample was taken on the same day as this sample, presumably with a different set of conditions. The bag marked ANC-70 contained the following composition:

Table IV. Constituent Composition from Coal Effluent.

Gas	Composition
Methane	1653 ppm (volume)
Ethylene	22 ppm
Ethane	ND
Acetylene	565 ppm
Benzene	46 ppm
Hydrogen	88000 ppm (volume)
Carbon disulfide	trace

These results were obtained by comparing the area responses for the separated compounds to analytical standards injected at the 1000 ppm level. Hydrogen was determined by TCD analysis with a 4 point calibration curve. This calibration curve was extended to incorporate an 8.8% by volume measurement.

Figure 25. Hydrogen Calibration Curve.

The bag was also found to contain trace carbon disulfide and benzene as measured by the GC-MS. The second bag was found to contain no hydrocarbons or hydrogen. The bag did not appear to be leaking so the sampling procedure must have been plugged due to high levels of particulates in the sampling tube. Thus outside air may have been drawn into the bag. Analysis of the bag was performed at the same conditions as the ANC-70 bag.

Analysis of the hydrogen content was flawed in this sample primarily because helium could not be separated from the hydrogen analysis, and helium was a known reactant in the carbon fiber process. Although samples could be analyzed using helium carrier gas (helium would not be an interferent in this analysis), the hydrogen response would be too low to detect below 0.5 volume %. This high detection limit is due to the small thermal conductivity difference between hydrogen and helium. Therefore, we performed all hydrogen analyses with nitrogen carrier gas and the catalytic make up gas for the carbon fiber process was changed to nitrogen instead of helium. Therefore, no helium would be present in the system and the analysis for hydrogen would be accurately performed.

A bag was taken using the new catalytic gas and the results were provided by telephone. Surprisingly, approximately 8.8 volume percent of the residual gas was again detected as hydrogen. Additional experiments were made to verify that no co-elution of argon or other fixed gas accounted for the response observed. No other interferents could be determined.

In summary, we obtained samples on-site and analyzed several samples for light hydrocarbons and hydrogen during this program. A good deal of method development was performed during the program and results from at least 3 samples were obtained over a period of six months. We have a reasonable approach for measuring these gaseous components and have

performed this measurement for several actual samples. The hydrogen content of this process is probably over 8 volume %. We recommend that sulfiding or catalytic gases be used in a nitrogen carrier whenever possible to preclude the co-elution of helium and hydrogen. We also recommend that a mass balance be conducted about the system to provide a further check on the quantitative measurement of hydrogen.

V. CONCLUSIONS

It has been shown that fossil fuels can be produced greatly reduced emission of greenhouse gas per kilowatt of energy delivered, and that much of the effluent from the process is hydrogen. In the case of coal upwards of 70% of the carbon can be sequestered in the form of carbon nanofibers or coke.

However, for this concept to make a meaningful impact on the total inventory of greenhouse gas released to the atmosphere, it must affect millions of tons of coal production. At present, the production of carbon nanofibers is less than ten tons per year. By the end of 1999, production capacity at ASI is scheduled to be increased to the 250 ton per year level. However, this is orders of magnitude below the level required to influence the total amount of greenhouse gas released to the atmosphere due to the worldwide combustion of fossil fuels.

Moreover, this is only possible if there are markets for carbon nanofibers which allow such large quantities to be sold profitably. Presumably, this in turn would require that nanofiber price must drop to the level of carbon black, so that it can penetrate markets such as reinforcement of cement and asphalt. This is not likely for the near term, although in the long term, there is no reason why the price of carbon nanofibers can not continue to drop, especially if coal is used as the main raw material for the process.

VI. References.

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