

## PROCESS ANALYSIS WORK FOR THE DOE HYDROGEN PROGRAM - 2001

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### Abstract

In 2001, process analysis work conducted at the National Renewable Energy Laboratory for the Department of Energy's Hydrogen Program focused mainly on research projects. The goal of this work is to provide direction, focus, and support to the development and introduction of renewable hydrogen through evaluation of the technical, economic, and environmental aspects of hydrogen production and storage technologies. The advantages of performing analyses of this type within a research environment are several fold. First, the economic competitiveness of a project can be assessed by evaluating the costs of a given process compared to the current technology. These analyses can therefore be useful in determining which projects have the highest potential for near-, mid-, and long-term success. Second, the results of a technoeconomic analysis are useful in directing research toward areas in which improvements will result in the largest cost reductions. Finally, as the economics of a process are evaluated throughout the life of the project, advancement toward the final goal of commercialization can be measured.

This paper presents summary results from three studies: 1) hydrogen production via natural gas splitting with a solar reactor, 2) biological water gas shift for hydrogen production, and 3) assessment of the mass production of carbon nanotubes. The first study covers a project that is considered applicable in the mid-term, while the second study assesses the feasibility of a nearer-term application of the biological conversion of synthesis gas. The third study is on an advanced, long-term hydrogen storage technology.

In 2001, NREL's process analysis task helped to define the conversion processes for these research projects, such that their economic potential could be better understood. Overall, this type of analysis helps the Hydrogen Program to methodically assess the applied research portfolio, in order to focus on those projects that have the potential to significantly contribute to affordable and clean hydrogen systems. Results from the economic studies help researchers concentrate their efforts on those areas that have the greatest impact on cost, such that novel technologies can be commercialized more quickly.

### Hydrogen Production via Natural Gas Splitting with a Solar Reactor

This study analyzed hydrogen production via thermal decomposition of methane using a solar reactor for two different applications: (1) a fueling station and (2) power production. The fueling station application was examined as a stand-alone system. However, because storage limits the amount of hydrogen production and results in a substantial capital cost, the system was also examined as one that could supply hydrogen to a pipeline network. For the power production scenario, the hydrogen is co-fired in a turbine at a natural gas combined-cycle (NGCC) plant.

Material balances were obtained from an entrained flow reactor model developed by the University of Colorado. Energy balances were determined using Aspen Plus® and radiant heat loss calculations based on the size of the reactor. The material and energy balances along with hourly solar data from Phoenix, Arizona were used to determine how much hydrogen could be produced by the system. Reactor designs for converting 95% of the methane were initially examined, but the analysis determined that higher net hydrogen production rates could be achieved at 70% conversion for a given reactor size. Three hydrogen production rates were evaluated by varying the size of the heliostat field for a set reactor size. First, the size of the heliostat field was set so that the reactor operating temperature at the highest hourly solar irradiance did not exceed 2,273 K. This temperature was chosen as a practical limit. Next, the heliostat field was doubled, which meant that more hydrogen could be produced at lower light intensities, but at high light intensities, part of the heliostat field must be taken offline to avoid overheating the reactor. Finally, the size of the heliostat field was cut in half. This was done to reduce the capital costs. For the fueling station application, doubling the size of the heliostat field resulted in the lowest cost hydrogen. However, for the power production application the smallest heliostat field was the most economic option.

Table 1 gives the resulting hydrogen production and storage for the stand-alone fueling station application. For storage amounts of 800 kg, 1,400 kg, and 2,300 kg for the three heliostat field areas, the daily demand that could be supplied by each refueling station is 250 kg/day, 450 kg/day, and 750 kg/day of hydrogen, respectively. At 4 kg/car, this means that roughly 63, 113, and 188 cars are fueled each day for the different heliostat field sizes. There are many times when the storage capacity is reached and the hydrogen production system must be shutdown. For this reason, only 54%-66% of the total possible hydrogen production was actually produced. Increasing the size of the hydrogen storage did not significantly increase the amount of hydrogen that could be supplied for fuel. This small increase in useable hydrogen did not outweigh the large cost associated with storing the hydrogen.

**Table 1: Fueling Station - H<sub>2</sub> Production, Storage, and Demand for Stand-Alone System**

Heliostat size (m <sup>2</sup> )	H <sub>2</sub> produced without storage limit (tonne/yr)	H <sub>2</sub> storage capacity (kg)	Daily H <sub>2</sub> demand (kg/day)	H <sub>2</sub> produced with storage limit (tonne/yr)	% produced (with storage limit) of total possible
2,188	169	800	250	91	54%
4,375	301	1,400	450	164	55%
8,750	416	2,300	750	273	66%

The carbon that is produced from the solar process is assumed to be sold in the carbon black market. The base case uses a carbon black price of \$0.66/kg, which is the price for carbon black in the tire industry. This is the largest market, accounting for 70% of the worldwide carbon black market. Table 2 gives the hydrogen selling price for the stand-alone fueling station application.

**Table 2: Fueling Station - H<sub>2</sub> Selling Price for Stand-Alone System (HHV basis)**

Heliostat size (m <sup>2</sup> )	H <sub>2</sub> selling price		Cost to fill fuel tank with 4 kg of H <sub>2</sub> (\$)
	(\$/GJ)	(\$/kg)	
2,188	\$87	\$12	\$49
4,375	\$73	\$10	\$42
8,750	\$57	\$8	\$32

Hydrogen storage was the largest capital cost item, accounting for 32% of the total capital for the 8,750 m<sup>2</sup> heliostat field size. This was followed by the cost of the heliostat field (21%) and hydrogen compression (19%). However, it is important to remember that any competing system (renewable or non-renewable) will also require some amount of storage as well as hydrogen compression for a stand-alone fueling station.

Because of the large costs for storage and compression, along with the fact that the storage limitation prevents maximum hydrogen production, this system was examined as one where the hydrogen could be sent directly to a pipeline network. For this scenario, the pipeline was assumed to already be in place, therefore, the expense of the pipeline was not included in the analysis. Table 3 shows the resulting economics for the largest heliostat size. The reduction in the hydrogen selling price is 68% from the stand-alone case (\$18/GJ compared to \$57/GJ). Note that this scenario is able to maximize hydrogen production, instead of utilizing only 54%-66% of the total possible hydrogen production like the stand-alone case.

**Table 3: Fueling Station - H<sub>2</sub> Selling Price when Supplied to Pipeline (HHV basis)**

Heliostat size (m <sup>2</sup> )	H <sub>2</sub> produced from solar process (tonne/yr)	H <sub>2</sub> selling price	
		(\$/GJ)	(\$/kg)
8,750	416	\$18	\$3

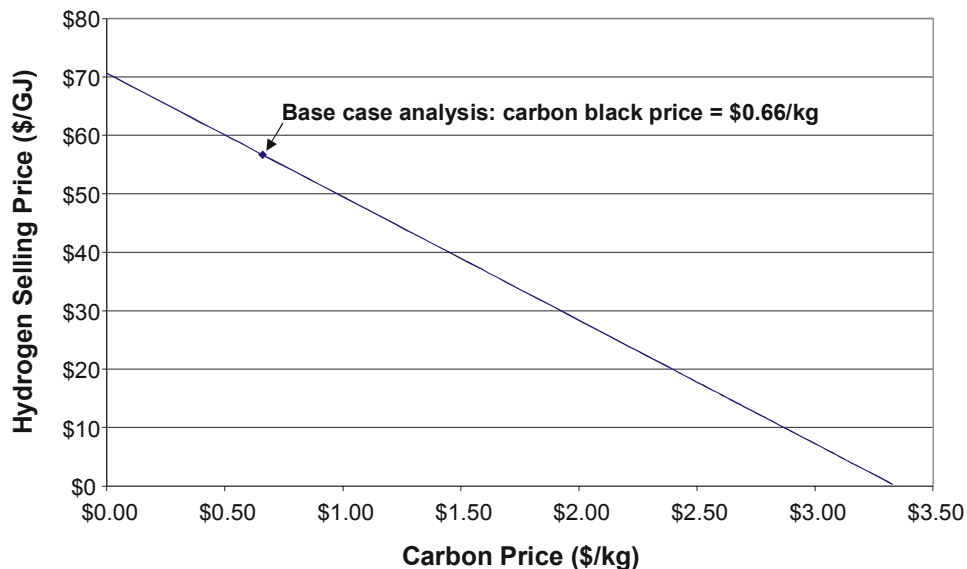
One other option that was examined to help the productivity of the solar process was adding a small electric heater that can be turned on when the hydrogen supply gets low to provide heat to the solar reactor. Two scenarios using an electric heater were examined: one where the storage was kept constant and the daily demand was increased and one where the demand was kept constant and the hydrogen storage was decreased. For the constant storage case, if the daily demand is increased by 40% and only 5% of the hydrogen comes from the electric heater, then the amount of hydrogen produced from the sun increases from 66% to 88% of the total possible. More hydrogen comes from the sun because the backup equipment (i.e., the electric heater) supplies hydrogen during periods of clouds or inclement weather. For the constant demand case, using the electric heater to account for 5% of the hydrogen production decreased the storage requirements by a factor of 3. See Table 4, below for details. The hydrogen selling price with the supplemental electric heater is considerably less than the stand-alone base case at \$42/GJ and \$46/GJ for the constant storage and constant demand cases, respectively, compared to \$57/GJ.

**Table 4: Fueling Station - H<sub>2</sub> Production, Storage, and Demand with Supplemental Electric Heater**

Heliostat size (m <sup>2</sup> )	H <sub>2</sub> produced from solar without storage limit (tonne/yr)	Scenario	H <sub>2</sub> storage capacity (kg)	Daily H <sub>2</sub> demand (kg/day)	H <sub>2</sub> produced from solar energy input		H <sub>2</sub> produced from electric heater	
					(tonne/yr)	% of total possible from solar	(tonne/yr)	% of total produced
8,750	416	base case	2,300	750	273	66%	N/A	N/A
		constant storage	2,300	1,050	365	88%	17	4.5%
		constant demand	750	750	260	62%	14	5.2%

For the power production application, two options were examined: (1) selling the carbon black and (2) burning the carbon to produce more power. Because of its value, it is more profitable to sell the carbon instead of burning it. However, in order for the electricity produced from the hydrogen to be less than the base electricity production cost of the NGCC plant, the price of the carbon must be greater than \$0.80/kg. Even though the reactor and heliostat field sizes were increased compared to the fueling station application, the amount of power produced from the hydrogen is small compared to the size of the natural gas plant. For a 500 MW NGCC plant, the electricity generated from the solar process only accounts for about 0.2% to 1.1% of the total output from the power plant. Therefore, even if the power produced from the hydrogen is more than the base power production price, overall, it would not significantly increase the price of electricity generation from the NGCC power plant and a small portion of the electricity from the power plant would be renewable. However, it should be noted that not all of the power from the hydrogen is renewable because the feedstock to the solar plant is natural gas. Only the heat input from the solar process is renewable. For the scenario where both the hydrogen and carbon are burned, only about 9% of the electricity produced from these feedstocks is renewable. This means that less than 0.1% of the total output from the power plant is renewable electricity.

The specialty markets for carbon black are smaller than the tire industry, but the price of the carbon in these markets is usually higher because of the more stringent carbon quality specifications. A sensitivity analysis was performed on several variables (carbon selling price, heliostat cost, price of natural gas, and greenhouse gas credit) but the price of the carbon black had the greatest effect on the economics. Figure 1 shows the sensitivity in the price of hydrogen for different carbon prices for the fueling station application. Higher value carbon markets should definitely be pursued and currently, tests are being performed to examine the compatibility of the carbon black produced from the solar reactor to the different grades and types of carbon black that are marketed today.



**Figure 1: Hydrogen Selling Price vs. Carbon Price (15% IRR) for Fueling Station Application and heliostat Size of 8,750 m<sup>2</sup>**

Although, the solar process for the fueling station and power production application use natural gas as a feedstock, the net greenhouse gas emissions and overall fossil energy consumption is lower for the solar process than for the conventional fossil system. It was evident that there is a significant environmental benefit from carbon black production via the solar route than from its conventional route. Figure 2 shows the greenhouse gas and energy balance for the fueling station application.

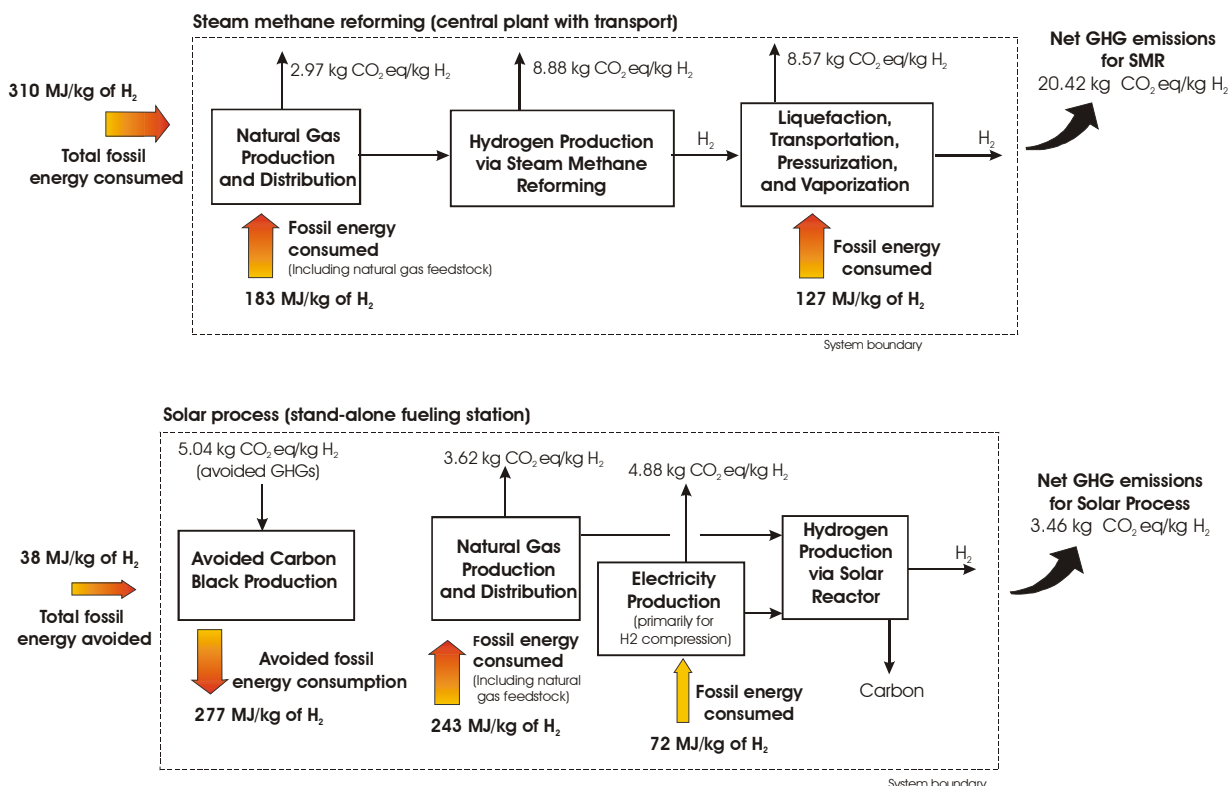


Figure 2: Greenhouse Gas and Energy Balance - Fueling Station Application

A more detailed report about this analysis titled *Assessment of Natural Gas Splitting with a Concentrating Solar Reactor for Hydrogen Production* can be found at the following website: <http://www.nrel.gov/docs/fy02osti/31949.pdf>.

### Biological Water-Gas Shift for Hydrogen Production

The most common route of hydrogen production involves steam methane reforming of natural gas, followed by water-gas shift (WGS) and pressure swing adsorption (PSA). The reforming reaction is carried out at 800-870°C (1,470-1,600°F), 20-27 atm pressure, with a molar steam-to-carbon ratio of 2-5. The reforming reaction produces a mixture of hydrogen (H<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO) and residual methane. Because a nickel catalyst is used for the reforming reactor, sulfur must be removed from the natural gas before entering the reactor. The WGS reaction then converts the CO leaving the reformer into H<sub>2</sub> through a reaction with water (H<sub>2</sub>O). The WGS reaction is  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$ .

This reaction is endothermic, which means high conversions of CO are only possible by dropping the reaction temperature. However, the reaction is normally carried out at a high

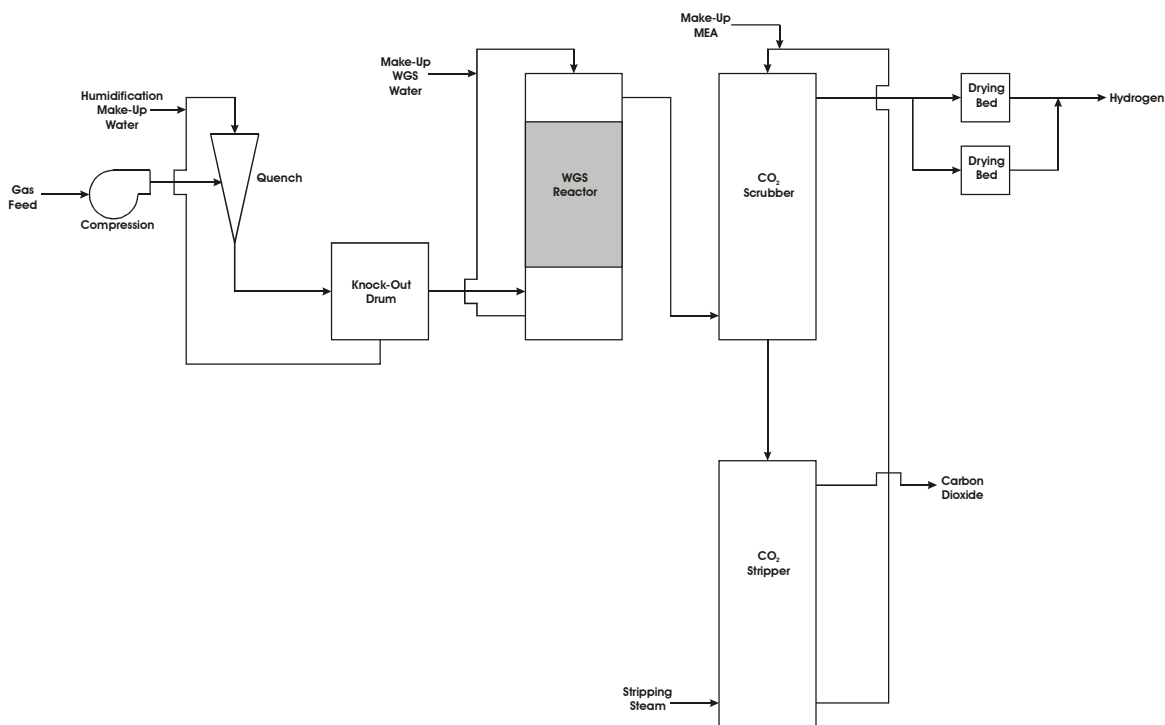
temperature initially (350-370°C, 660-700°F) to increase the reaction rate and minimize the reactor size. If high conversions are desired, the high-temperature shift (HTS) can be followed by a low-temperature shift (LTS) reactor operating at 200-220°C (390-430°F). Any residual CO can either be removed through a methanation reaction, or the entire stream can be purified using a PSA unit.

The biological water-gas shift reaction uses photosynthetic bacteria to ferment CO into CO<sub>2</sub> and H<sub>2</sub>, the same way as in the catalytic WGS reaction. While light is used to initially grow the bacteria culture, the biological WGS reaction is a dark-phase reaction—no light is required and a conventional closed reactor can be used. The bacteria get energy from the fermentation reaction, but because the reaction provides only a small amount of energy, the growth rate is very low and very little excess cell mass is produced. An additional benefit of the biological WGS reaction is that the by-product CO<sub>2</sub> is used as the carbon source. In many common fermentation processes—such as ethanol production—a significant portion of the feed stock is diverted as a carbon source to produce cells, reducing the product yield.

The biological WGS is carried out at ambient temperature, with an optimum shift rate at 43-49°C (110-120°F). Above this temperature, the cells die. The operating pressure can be atmospheric, but as long as the pH of the solution can be controlled, the reaction will work at higher pressures. Because of the low operating temperature of the reaction, high conversions of CO to H<sub>2</sub> are theoretically possible. However, because the mass transfer rate from the bulk gas into the liquid containing the bacteria is a first-order process, the required reactor volume increases in a logarithmic fashion: the additional reactor volume needed to go from 99% conversion to 99.9% conversion is the same volume required to go from 90% conversion to 99% conversion. The target conversion will be set based upon an economic trade-off between the reactor cost and the downstream purification cost. The equilibrium concentration is not, however, limiting as in the HTS reactor.

After successful proof-of-concept tests showed that high biological water-gas shift rates were possible, the next step for the laboratory researchers was to collect reliable kinetic data for the biological WGS process. Because maximizing mass transfer was an important consideration, a trickling filter reactor design was used. Tests were conducted at various CO conversions using two reactor sizes and a number of packing materials. The experiments showed good repeatability for the same packing, a linear scale-up from a 1-liter to a 5-liter reactor, and the expected correlation of surface areas versus reaction rate for different sizes of the same type of packing. A short series of tests were also conducted using biomass producer gas as a feed to a biological WGS reactor and no inhibition of the WGS reaction was observed.

With this laboratory kinetic data available, a preliminary process design could be proposed for shifting the CO from a biomass gasification process into hydrogen. A gas composition of 33.3% H<sub>2</sub>, 33.3% CO and 33.3% CO<sub>2</sub> was assumed. The gas processing steps are shown in Figure 3. The producer gas is first pressurized to 300 psig (2,200 kPa) and then quenched with an excess of water to humidify the gas and control the temperature. Using an excess of water ensures that the temperature limit of the bacteria is not exceeded during process upsets. The gas then passes through a trickling filter/packed column reactor containing a film of the biological WGS bacteria. After leaving the shift reactor, the CO<sub>2</sub> is removed and recovered using a standard MEA process and then any excess water is removed before the hydrogen is sent to storage. In this case, it was assumed that the WGS reactor was operated at high conversions, sufficient to meet a 100 ppm CO standard with no further purification required.



**Figure 3 – Flowsheet for Biological Water-Gas Shift**

The capital and operating costs were estimated for such a system and the results are shown in Table 5. Note that this is an incremental cost of converting the producer gas into hydrogen, it does not include the cost of the producer gas itself. The incremental price does include a 15% internal rate of return.

**Table 5 – Cost of Biological Water-Gas Shift to Produce Hydrogen**

Plant Size (MM scf/d)	Capital Cost (\$)	Annual Operating Cost (\$/year)	Incremental Price of Hydrogen (\$/GJ)
2.5	\$16.9 million	\$3.1 million	\$23.86/GJ
10.0	\$60.0 million	\$10.5 million	\$20.70/GJ

The cost analysis showed that the WGS reactor was a significant cost; nearly \$3 million in the case of the small facility and over \$10 million for the larger facility. Knowing this, several changes were made to the process to reduce the reactor costs. Because a portion of this work was done under a Work-for-Others Agreement, several of the process changes are currently protected by confidentiality statements while patents are pending. However, the costs were cut nearly in half by redesigning the system. Two important conclusions came out of the economic analysis:

1. The system must be operated under pressure to be economical. Pressurizing the system reduces the size of the WGS reactor, thereby reducing the capital cost of the system.

2. A large increase in shift rate is not needed. An increase in shift rate by a factor of 2 decreases the reactor size enough that the reactor then becomes a relatively small cost compared to the balance of plant costs. Increasing the shift rate beyond this point has diminishing returns.

These two results have shifted the course of the laboratory research. Rather than concentrating on getting large improvements in the shift rate, the researchers have designed a high-pressure reactor for testing the biological WGS reaction at pressures up to 400 psig (2,900 kPa). If the process cannot be operated at high pressures, an incremental improvement in rate by itself won't significantly reduce the hydrogen production costs.

### Assessment of the Mass Production of Carbon Nanotubes

The US DOE Hydrogen Program is funding research to improve methods to store hydrogen as part of its mission for making hydrogen a cost effective energy carrier. Carbon nanotube systems for hydrogen storage are at a very early stage of development. Currently, research quantities of various grades of carbon nanotubes are commercially available at \$50-2000 per gram depending upon type and purity.

Neoterics International was contracted by NREL to assess the mass production of carbon nanotubes for hydrogen storage applications. This summary presents order-of-magnitude project level economics for mass production of single wall carbon nanotubes.

The technology base for this analysis is the single wall nanotubes (SWNT) Extrusion concept being developed by Dr. Mike Heben's group at NREL. Carbon nanotubes are produced using methane decomposition chemistry. The design basis is a grassroots facility producing 75,000 metric tons per year of active material. This production rate would satisfy the needs of about 5% of the annual U.S. production of cars and trucks. Hydrogen is also produced as a coproduct from this manufacturing facility.

Table 6 summarizes the results of the study. The high conversion cases assumed a per-pass conversion of 44.48%, which corresponds to thermodynamic equilibrium at the reactor outlet. The low conversion cases assumed a per pass conversion of 30% to account for the possibility that mass transfer or other mechanisms could limit the reaction. Lab experiments to date have only been able to demonstrate 7% per pass conversion, but these experiments were designed to demonstrate catalyst activity rather than high per pass conversion. The experiments were conducted under conditions that were severely mass transfer limited. The high and low levels assumed for selectivity were 100% and 80%, respectively. This reflects that fact that very high selectivity has already been demonstrated in the lab. Higher per pass conversion will also need to be demonstrated.

**Table 6: Summary of Results**

Case	Per Pass Conversion	Per Pass Selectivity	Per Pass Yield	Overall Yield	Fixed Capital (\$MM)	Revenue from CNanotubes (\$MM/yr)	Revenue from Hydrogen (\$MM/yr)	C Nanotube Selling Price (\$/kg)
1	44.5%	100	44.5%	77.7%	164.1	61.8	32.0	0.8
2	44.5%	80	35.6%	62.3%	179.1	65.3	40.0	0.9
3	30.0%	100	30.0%	73.0%	189.0	74.7	32.0	1.0
4	30.0%	80	24.0%	58.5%	208.2	80.6	40.0	1.1



The recovery scheme uses pressure swing adsorption (PSA) to recover hydrogen. One conclusion from this study is that per pass conversions less than 30% will require alternate technology for hydrogen recovery, such as cryogenic processing, since the off gas is too dilute for PSA operation when the per pass conversion drops below 30%..

Fixed capital ranged from \$164.1MM to \$208.2MM for the four cases considered. This translates into \$2.2 to \$2.8 per annual kg of capacity, which seems reasonable for a engineered material. Natural gas is the dominate component of the cash operating costs. The hydrogen coproduct is a significant source of revenue. It contributes approximately one-third of the revenue for all cases considered.

The necessary selling price for the carbon nanotubes, varied from \$0.8 to \$1.1 per kg. The necessary selling price is defined as the price required to obtain a zero net present value for a 15% after-tax internal rate of return in the cash flow analysis; this is the price needed to justify investment rather than a market-derived value. The necessary selling price of carbon nanotubes is inversely related to the per pass yield.

The technical storage goals of the present U.S. DOE Hydrogen Program are 5 kg of storage capacity with storage efficiencies greater than 5.5 wt% and 50 kg/m<sup>3</sup>. The carbon nanotubes selling price results from this study translate into a cost of \$75-97 per vehicle assuming the DOE Hydrogen Program goals are met. This does not include the costs for the rest of the components needed for a hydrogen storage system, or the hydrogen itself. These results indicate that carbon nanotubes could potentially be mass produced at prices that would allow penetration of the transportation market.

The concept of using carbon nanotubes for hydrogen storage is still at a relatively early stage of development. Further fundamental studies on the mechanism of hydrogen adsorption are needed in order to assess whether carbon nanotubes are capable of meeting the DOE Hydrogen Program goals. The technical goals are quite aggressive, especially considering the fact that any useful device will require a certain amount of open volume in order to allow the hydrogen to freely adsorb/desorb. To date, no prototype hydrogen storage devices based on carbon nanotubes have been constructed. An underlying assumption in this study was that the finished nanotube material produced by the modeled system would be capable of meeting the DOE Hydrogen Program goals.

Additional suggestions for future work include:

- Improved catalyst/substrate systems for higher per pass yield.
- Demonstration of higher per pass yield.
- Elimination of inert dilution gas.
- Addition of hydrogen in the feed to improve catalyst performance.
- Economic optimization of reactor operating pressure.
- Further definition of the pretreatment requirements is needed.
- Further definition of the mechanical details for the extrusion reactor and tube cutting equipment are needed.
- Further process definition for the tube finishing area is needed.