Rapid Solar-thermal Dissociation of Natural Gas in an Aerosol Flow Reactor

Jaimee Dahl [a], Karen Buechler [a], Ryan Finley [a], Timothy Stanislaus [a], Alan Weimer [a], Allan Lewandowski [b], Carl Bingham [b], Alexander Smeets [b], Adrian Schneider [b]

[a] Department of Chemical Engineering, University of Colorado, Boulder, CO 80309-0424, USA
[b] National Renewable Energy Laboratory, Golden, CO 80401-3393, USA

Abstract

A solar-thermal aerosol flow reactor process is being developed to dissociate natural gas (NG) to hydrogen (H_2) and carbon black at high rates. Concentrated sunlight approaching 10 kW heats a 9.4 cm long x 2.4 cm diameter graphite reaction tube to temperatures ~ 2000K using a 74% theoretically efficient secondary concentrator. A pure methane feed has been dissociated to greater than 75% for residence times less than 0.1 s. The resulting carbon black is 20 – 40 nm in size, amorphous, and pure. A 5 million (M) kg/yr carbon black / 1.67 M kg/yr H_2 plant is considered for process scale-up. The total permanent investment (TPI) of this plant is $12.7 M. A 15% IRR after tax is achieved when the carbon black is sold for $0.66/kg and the H_2 for $13.80/GJ. This plant could supply 0.06% of the world carbon black market. For this scenario, the solar-thermal process avoids 277 MJ fossil fuel and 13.9 kg-equivalent CO_2/kg H_2 produced as compared to conventional steam-methane reforming and furnace black processing.

Introduction

The environmental consequences of providing energy will continue to increase as the demand for energy increases throughout the world. Some studies predict that global energy consumption will at least triple in the next 30 years [1]. Consumption is increasing as a result of increases in population and economic development [2]. The environmental impacts, such as increased carbon dioxide emissions, will be significant [3, 4] and cleaner methods of producing energy will have to be developed. Hydrogen enriched natural gas combustion (HCNG) and/or hydrogen powered fuel cell vehicles could help to mitigate the energy supply and environmental problems.

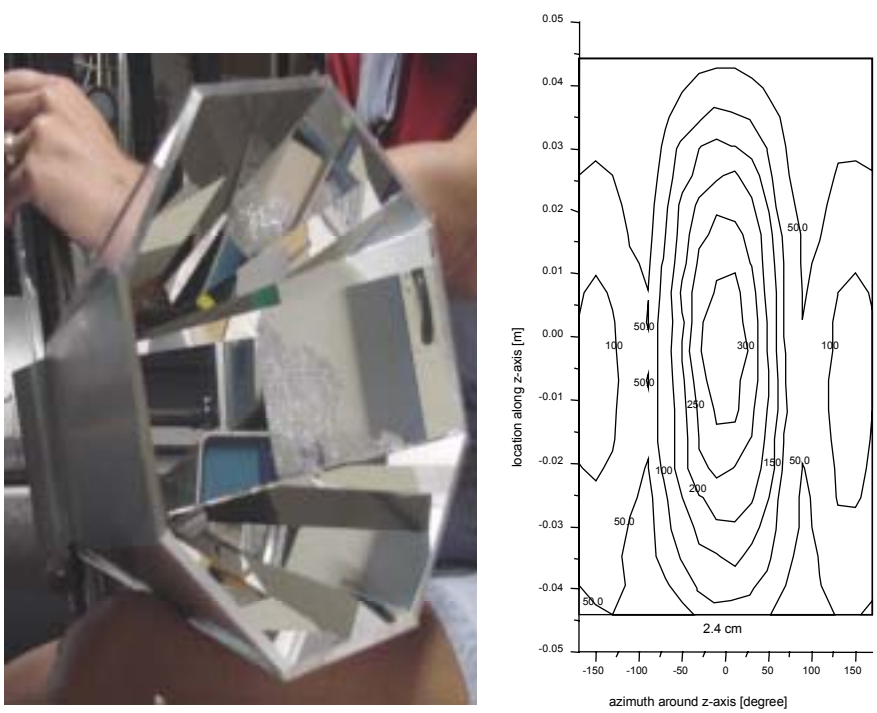
Currently, hydrogen is produced through the steam reforming of natural gas and carbon black is produced by the furnace black process. For steam reforming, steam is reacted with methane over a reforming catalyst to ultimately produce hydrogen and carbon dioxide (a greenhouse gas) [5-8]. For the furnace black process [9], a mixture of liquid fuel and NG is fed to the combustion zone of a reactor. The feed is partially combusted with air to provide the energy needed for the process. Energy released from the partial combustion dissociates the remaining feed mixture to carbon black and hydrogen. The products of these reactions are carbon black, hydrogen, carbon monoxide, carbon dioxide, and water. Large quantities of NOx and SOx are produced. According to Spath and Amos [10], fossil energy use and emissions from a large scale steam reforming plant are 183 MJ fossil fuel and 11.85 kg-equivalent CO_2/kg H_2 produced.

Consequently, new economical and environmentally benign methods for synthesizing hydrogen are desperately needed. One such process is the ultra-high temperature (~ 2000 K) solar-

thermal dissociation of natural gas to hydrogen and carbon black. While the hydrogen is used to fill vehicles or supply industrial users, the carbon black can displace existing carbon black markets, thus saving the energy and pollution associated with conventional carbon black production. For solar-thermal processing, where carbon black is sold, fossil energy usage and emissions are actually avoided (-94 MJ/kg H_2; -2.07 kg-equivalent CO_2/kg H_2) [10]. This is because the solar-thermal process is avoiding the energy and pollution normally associated with carbon black production. Then, in comparing the co-product solar-thermal processing to conventional steam reforming, the overall avoided fossil fuel usage and CO_2-equivalent emissions are -277 MJ and -13.9 kg-equivalent CO_2/kg H_2 produced.

Aerosol Flow Reactor Setup

A vertical aerosol flow reactor was constructed and interfaced to the high-flux solar furnace (HFSF) at the National Renewable Energy Laboratory [11]. The reactor consisted of a 5 cm diameter outer quartz protection tube and a 2.4 cm diameter inner graphite reaction tube. The two tubes and their contents are isolated from each other using water-cooled end caps. Argon flows in the annular region between the two tubes and provides an inert atmosphere that prevents oxidation of the graphite tube while preventing any decomposition products from depositing on the inner quartz wall. Feed methane gas flows downward through the graphite tube. The reactor was placed at the focal point of the primary concentrator that can deliver up to 10 kW of power on-sun. A secondary concentrator (Figure 1) enveloping the reactor allows temperatures greater than 2000 K to be achieved. The secondary is a v-cone type concentrator with an octagonal opening narrowing to a rectangular opening. The back trough piece wraps around the quartz and graphite tubes. The secondary concentrator distributes the irradiation over the circumferential graphite reaction tube surface. The heated length is 9.4 cm long.



(a) (b)

Figure 1. Secondary concentrator for solar-thermal aerosol reactor photograph of constructed secondary enveloping reactor system contour of energy flux enveloping graphite reaction tube (W/cm^2)

The reactor is operated as a cold wall process, because the beam is delivered directly on target. The graphite and quartz design allows for on/off processing without thermal expansion or stress difficulties. The graphite reaction tube can be heated to reaction temperatures in a matter of seconds. A schematic of the reactor system and a photograph of the reactor that was taken after the system had been heated are shown in Figure 2. The flow rates and temperatures of all gas and cooling streams are measured in order to close material and energy balances. A pyrometer is used to measure the outer wall temperature of the graphite tube in the vertical center of the hot zone. A Type C thermocouple is inserted into the center of the graphite tube from above in order to measure the temperature of the process gas stream in the hot zone. The fine carbon black particles produced by the dissociation reaction are collected in a downstream filter. In addition, a gas chromatograph/mass spectrometer is located downstream of the reactor in order to obtain quantitative composition data for the reaction products. A schematic of the overall process is shown in Figure 3.

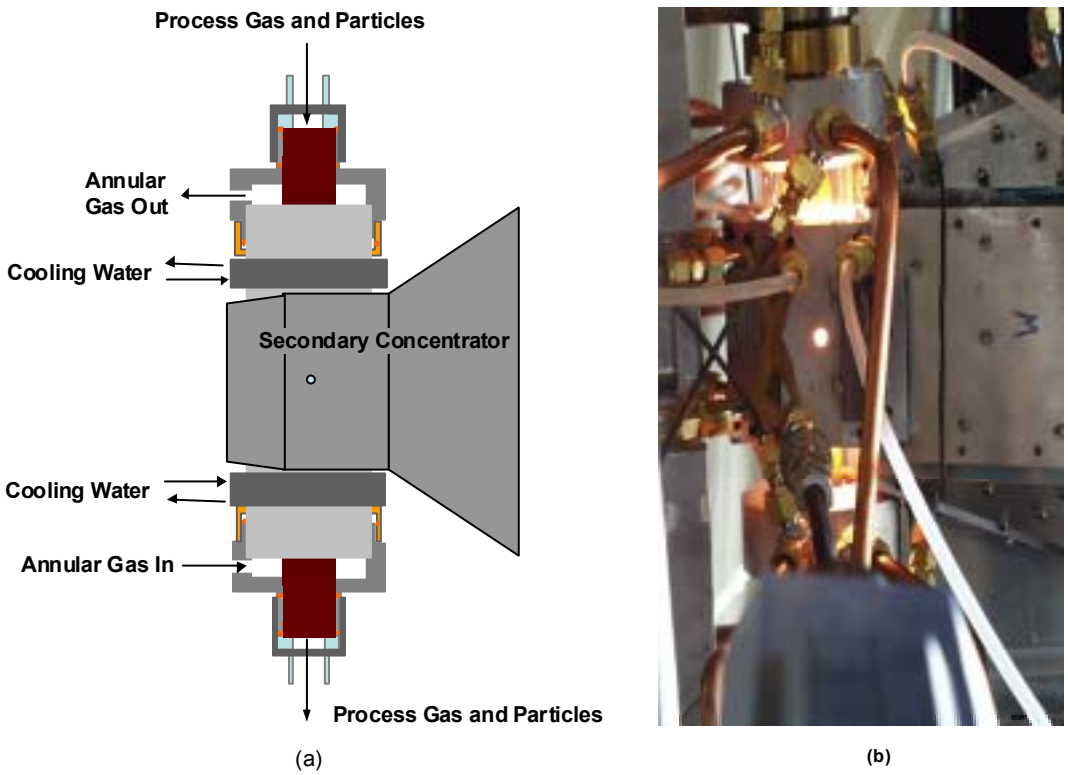


Figure 2. Solar-thermal aerosol reactor (a) schematic, (b) installed

Experimental Results

The temperatures that have been obtained with this reactor set-up are shown in Figure 4. These temperatures were measured using a thermocouple installed in the graphite tube to measure the gas temperature at the center of the hot zone. For these experiments, 5 slpm of N_2 was fed into the graphite tube (no CH_4 flow). At high power levels (8.5 kW), temperatures of about 2100 K have been obtained. The effect of varying the annular flow rate was examined during these experiments. It was found that an increase in the annular argon flow rate from 7 to 10 slpm at high power levels had little effect on the gas phase temperature. A greater effect is seen at lower power levels, such as 2.5 kW.

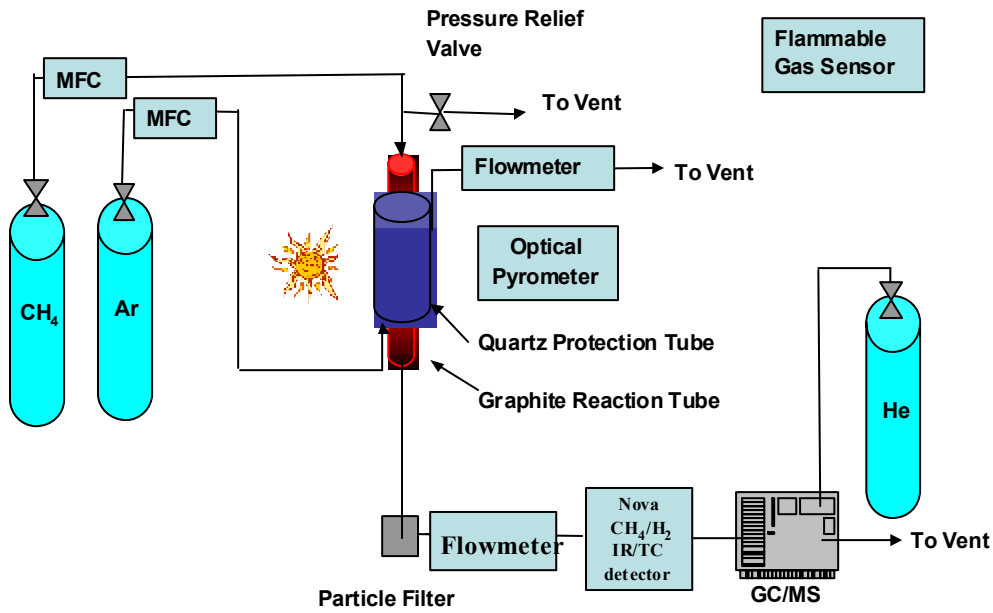


Figure 3. Schematic of pilot facility interfaced to HFSF at NREL (Golden, CO)

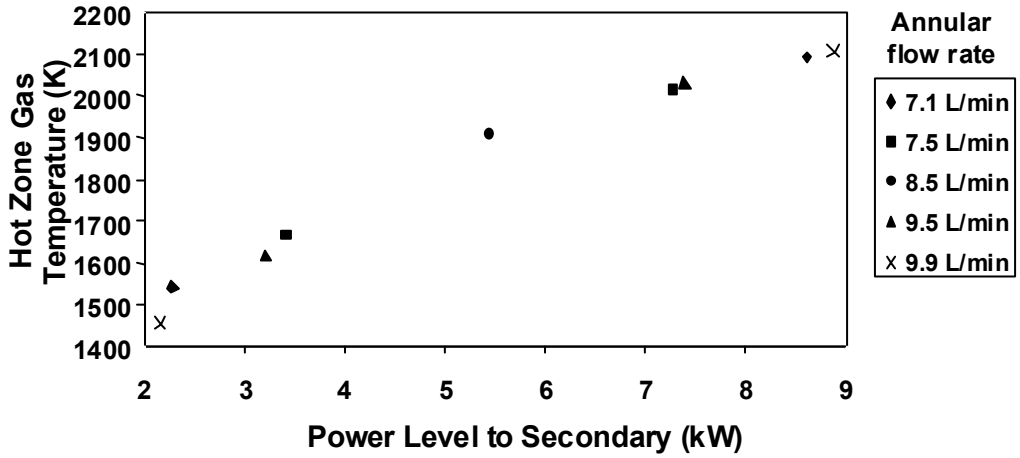


Figure 4. Power level vs. gas temperature for various annular gas flow rates (5 slpm N_2 flow through graphite reaction tube).

Various experiments were run to determine the effect of temperature and residence time on conversion. In all cases, pure methane was fed to the reactor. Conversion was calculated from an atomic H balance. As can be seen in Figure 5, conversions exceeding 75% have been obtained at 1875 K for residence times on the order of 0.1 s. These results indicate that conversion is more sensitive to changes in hot zone gas temperature than to changes in residence time for the range of times considered (0.06-0.12 sec). It should be noted that complete dissociation is expected at these temperatures. It is believed that the conversion was limited by heat transfer. Future experiments will include the co-feeding of fine carbon black particles to act as radiation absorbers for heating the gas.

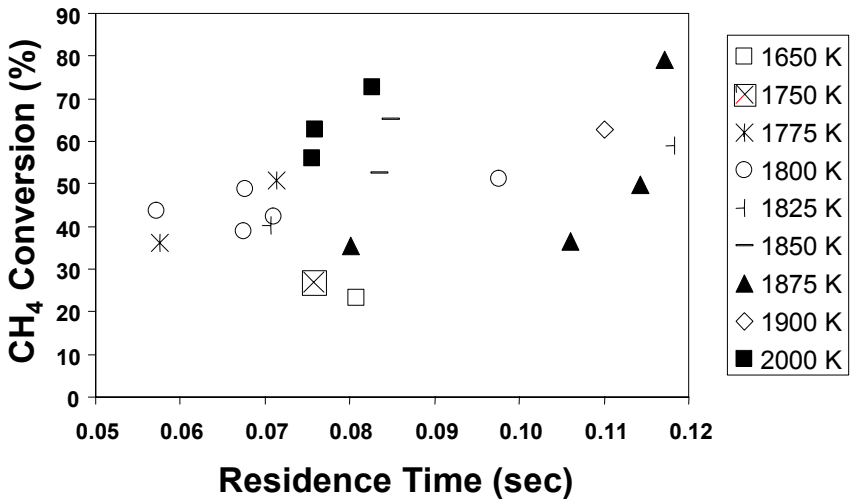
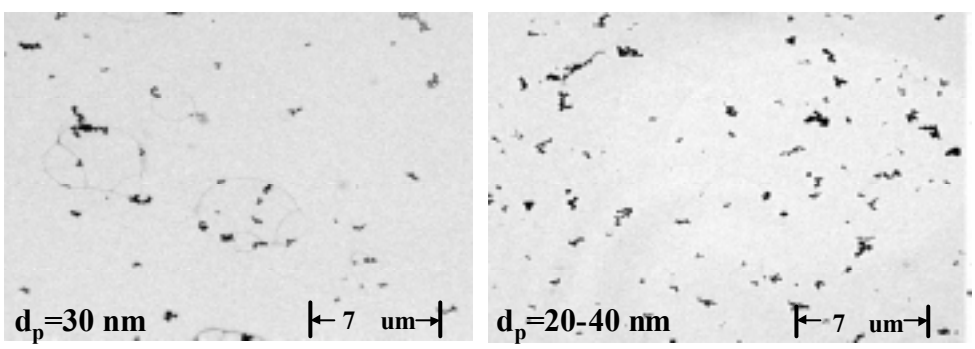


Figure 5. Effect of residence time and temperature on conversion

There is interest in evaluating the quality of the carbon black powder product as it impacts the overall economics of the process. A transmission electron photomicrograh (TEM) of a carbon black powder produced at a power level of 8.5 kW (~ 2000 K) is shown in Figure 6. It is compared to Shawinigan™ carbon black (tradename of Chevron-Phillips Corp.), the high quality world standard specialty carbon black. A higher magnification (Figure 7) image indicates that the carbon particles being formed have primary particle diameters in the range of 20-40 nm. An X-ray diffraction pattern of the carbon black and the TEM show that it is amorphous.



(a) Acetylene Black Shawinigan™

(b) Solar-thermal Black

Figure 6. Transmission electron photomicrographs (TEM) of carbon black powders (a) Chevron-Phillips Shawinigan™(b) solar-thermal produced at 8.5 kW (~2000 K)

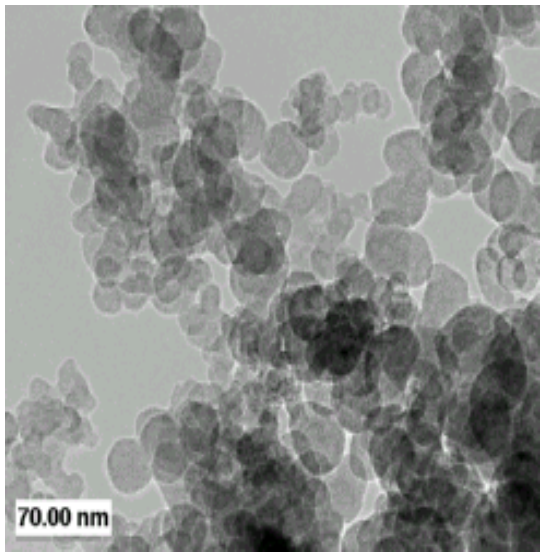


Figure 7. Transmission electron photomicrograph (TEM) of solar-thermal carbon black powder (produced @ 8.5 kW; T ~ 2000K)

Solar-thermal Based Process and Process Economics

A solar-thermal process (Figure 8) for co-producing hydrogen (1670 t/yr) and carbon black (5000 t/yr) has been conceptualized and costed (± 30%; percentage of delivered equipment cost). The 16.6 MW_{th} plant has been designed for the Phoenix, AZ (USA) area (0.38 solar capacity factor). Produced carbon black will be sold into the carbon black market (world market is 7.9 M metric tonnes (t)/yr) and produced hydrogen will be supplied to a hydrogen pipeline at a pressure of 2.2 MPa. The plant will dissociate 7300 t/yr of natural gas (NG). Any mercaptans and H_2S in the NG feed will be removed using an upstream hydrogenation reactor and ZnO bed. The NG will be dissociated at 70% conversion per pass in a fluid-wall aerosol flow reactor operating at 2000 K. The reactor consists of 3 tubes - an outer quartz protection tube and two inner graphite tubes. The most inner graphite tube is porous and allows recycled H_2 to flow radially inward through the pores (fluid-wall), thus, preventing the deposition of carbon black along the inside wall of the reactor assembly. The H_2 and carbon co-products and unreacted NG are then cooled in an expanded cooling zone and passed through a baghouse filter to separate the carbon black. The H_2 and CHx are then fed to a pressure swing adsorber where approximately 80% of the H_2 fed is purified and either sent to the H_2 pipeline as product or recycled as purge and fluid-wall gas to the reactor. The reactor is sized from the kinetics rate expression developed by Dahl et al [12]. The inner porous graphite tube is approximately 20 cm in diameter and 2.2 m long. It is compact because the reaction rate at these temperatures is so rapid. The heliostat field is estimated to be 29,000 m^2 area per calculations described by Spath and Amos [10].

The process has been simulated using the HYSYS™ Plant Process Simulator [13]. Major pieces of equipment have been costed using base cases from Spath and Amos [10] and appropriate scale factors. These were generally checked against those calculated using the ICARUS™ Process Evaluator [14]. The base case economic factors are listed in Table 1. The selling price of H_2 is determined to be $13.80/GJ to achieve a 15% IRR when carbon black is sold at $0.66/kg (tire black per Chemical Marketing Reporter; see ROI, Figure 9). For a carbon black selling price of $0.80/kg, the price of H_2 to achieve the 15% IRR drops to $10/GJ. For a

carbon black selling price of $1.10/kg, the price of the H_2 to achieve the 15% IRR drops to $5/GJ. It is important to note that most specialty carbon blacks sell for between $2 and $3.50/kg. The world market for these specialty blacks is 0.6 M t/yr. Hence, the 5000 t carbon black/yr co-product plant described here is 0.8 % of the world market for specialty blacks. The Total Permanent Investment (TPI) of this plant is $12.7 M (Table 1).

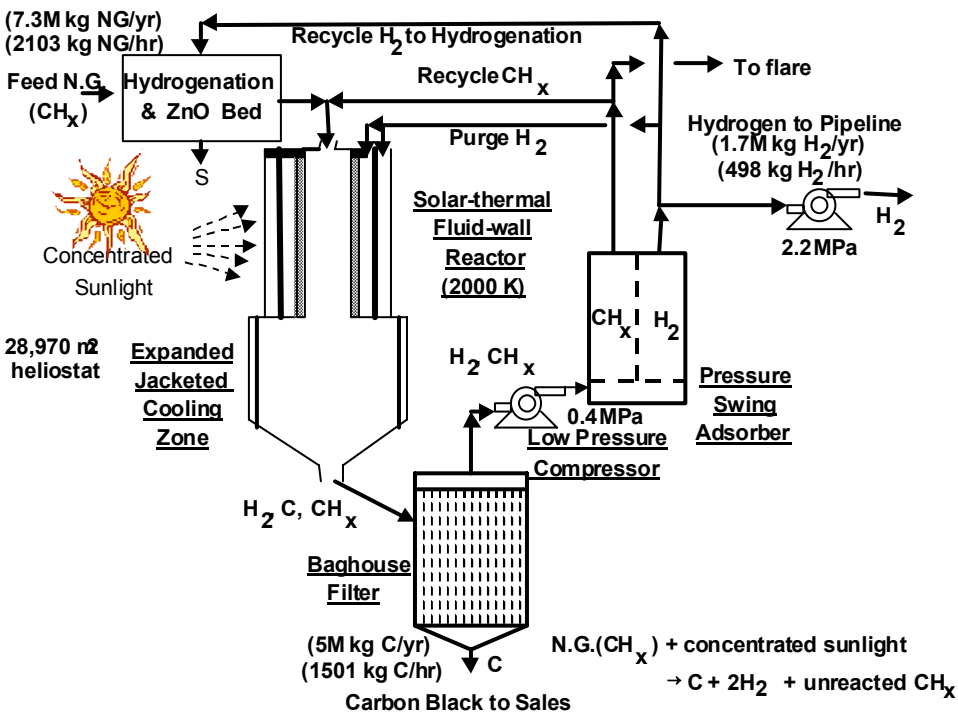


Figure 8. Solar-thermal hydrogen & carbon black co-product plant for

Table 1. Base case process & economics

(5 M kg/yr carbon black; 1.67 M kg/yr H_2)

NG Cost: $3.75/GJ
15% IRR (after tax @ 34%)
20 yr lifetime
5 yr Accelerated Cost Recovery Depreciation
100% Equity Investment
Carbon Sales Price (out the gate): $0.66/kg
Hydrogen Price (varies to get 15% IRR)
14 operators ($91,000 eachincl. overhead)

TPI = $12.7M
- H_2 compressor = 15.2%
- PSA compressor = 18.3%
- Heliostat field = 49.6%
- Reactor/tower = 5.2%
- Baghouse = 9.2%
- PSA = 1.7%
- Other = 0.8%

H_2 selling price = $13.80/GJ

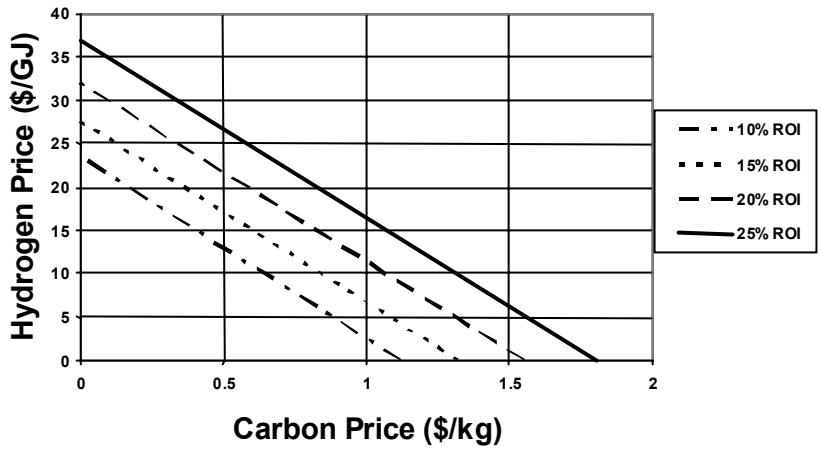


Figure 9. Relationship between H_2 and carbon black selling prices and 3rd year ROI

The base price of the heliostats is $130/m^2 which amounts to approximately 50% of the TPI of the plant. The solar-thermal reactor/tower, consisting of graphite and quartz tubes on a tower, is relatively inexpensive (~ $660,000 installed with overhead) compared to the rest of the plant. For the base case (Table 1), the net cash flow for the plant is shown in Figure 10 where the Net Present Value (NPV) at the end of the period is $36 M. The process has a 3rd year Return On Investment (ROI) of 16% and a payback period of 6 years. The sensitivity of the ROI (3rd year) and IRR to a ± 30% variation in TPI and total variable operating (TVC) costs is shown in Figures 11 and 12, respectively.

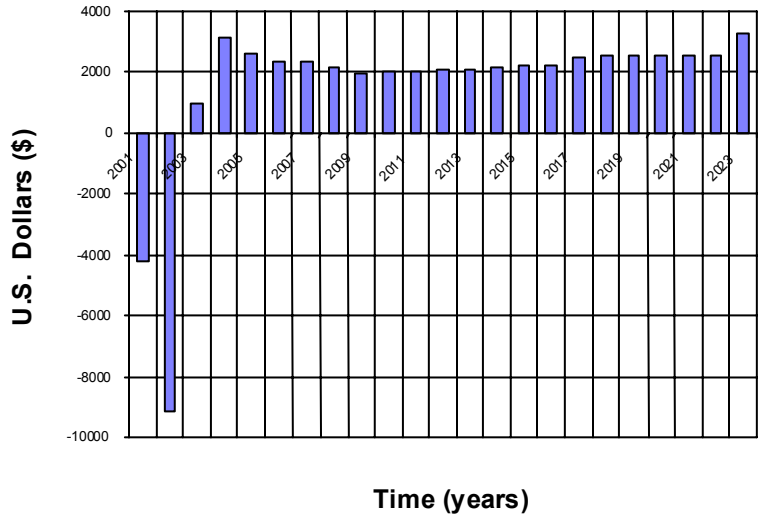


Figure 10. Net cash flow (2 yr construction, 20 year life, 90% capacity)

Conclusions

A solar-thermal process is being developed for rapidly dissociating NG to co-products H_2 and carbon black. The process allows rapid on/off processing that is very compatible with the on/off nature of sunlight. Conversions approaching 80% have been demonstrated at residence times on the order of 0.1 s without the addition of carbon particles to couple radiation heat transfer to

the flowing NG. The product carbon black is a fine amorphous powder having a particle size distribution in the range of 20 to 40 nanometers.

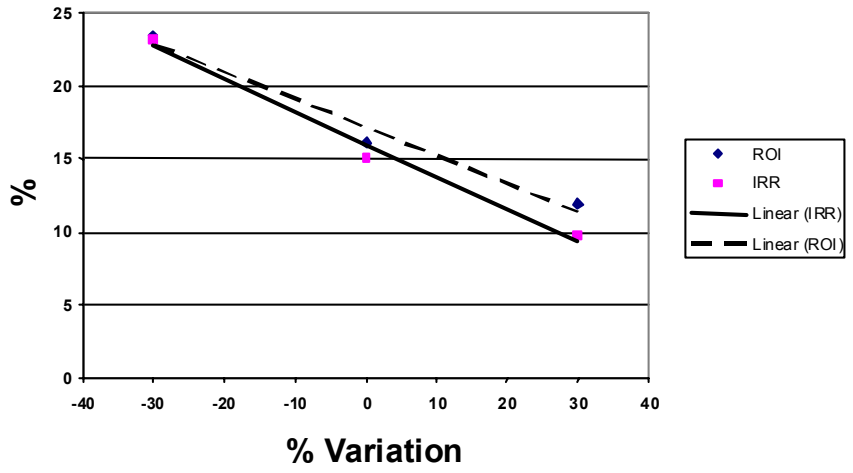


Figure 11. Effect of +/- 30% variation in Total Permanent Investment (TPI) from base case on profitability

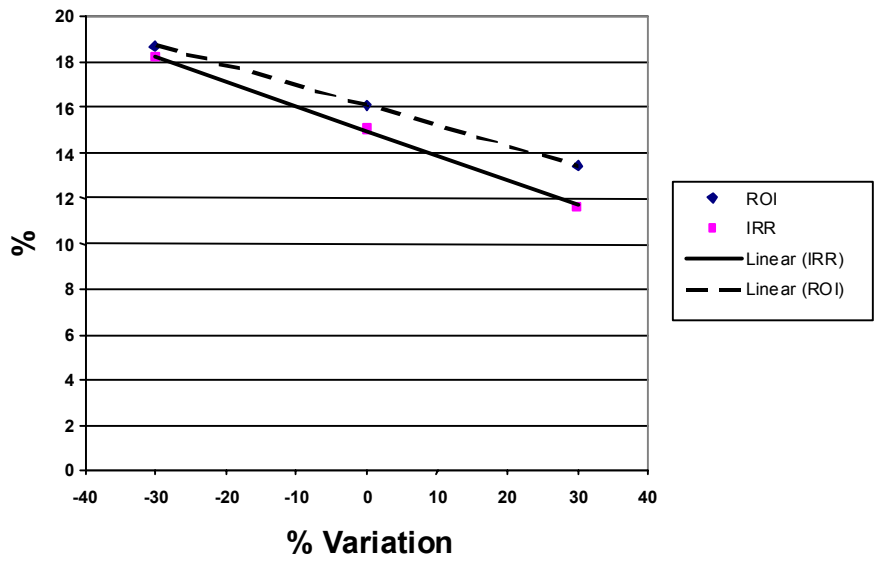


Figure 12. Effect of +/- 30% variation in variable operating cost (TVC) from base case on profitability

A 5 M kg/yr carbon black / 1.67 M kg/yr H_2 co-product plant can be constructed for $12.7 M and achieve a 15% IRR (after tax) when the selling price of carbon black is $0.66/kg and the H_2 sells for $13.80/GJ. The H_2 can be sold for $10/GJ if the carbon sells for $0.80/kg. The world market for carbon black is 7.9 M t/yr. The specialty carbon black market is 8% of this (~ 0.6 M t/yr). The 5 M kg/yr carbon black plant evaluated here represents 0.8% of the world specialty black market and 0.06% of the world carbon black market. The world carbon black market would be saturated with the construction of approximately 1650 co-product plants described here. The operation of these 1650 plants (replacing furnace black processing) would avoid the

consumption of 7.6 x 10^{11} MJ fossil fuel/yr and 3.8 x 10^{10} kg-equivalent CO_2/yr. Nonetheless, this is a bridge process until another use for the carbon black can be found. The demand for H_2 will be so great that the co-produced carbon black via this process will eventually saturate the market. The development of carbon conversion fuel cells [15] to efficiently produce electricity appears to be a key technology for the long-term development of processes that produce H_2 by dissociating NG.

Acknowledgement

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