Distributed Hydrogen by Rapid Solar-thermal Dissociation of Methane

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ABSTRACT

A solar-thermal process is being developed for the benign dissociation of natural gas. The process takes advantage of rapid reaction rates at high reaction temperatures near 2000 K. The reactor is a vertical transport reactor and is comprised of multiple concentric tubes. An outer quartz protection tube allows concentrated sunlight to pass through while an inner porous graphite tube provides for a gaseous hydrogen "fluid-wall" that prevents the build-up of carbon black along the inside wall. Single pass methane conversions of 75% have been achieved for residence times less than 100 milliseconds. Various process options being considered for development include distributed hydrogen for a "fleet" service station or to supply hydrogen to a semi-conductor facility in the desert SW. Another variation of the process is for a small utility where produced carbon black supplies a carbon conversion fuel cell while hydrogen supplements natural gas flowing to a conventional turbine. The produced carbon black is amorphous and nanosized with a surface area approaching 100 m2/gram.

INTRODUCTION

The environmental consequences of providing energy will continue to increase as the demand for energy increases throughout the world. The environmental impacts, such as increased carbon dioxide emissions, will be significant and cleaner methods of producing energy will have to be developed. Consequently, new economical and environmentally benign methods for synthesizing hydrogen on-site (distributed) are desperately needed. The ideal process would generate hydrogen in an easily purified form without generating carbon dioxide. One such process is the ultra-high temperature (near 2000 K) thermal dissociation of natural gas to hydrogen and carbon black. While the hydrogen is used to fill fuel cell vehicles or supply hydrogen users, the carbon black produced can displace current carbon black production, thus saving the energy and pollution associated with conventional carbon black production. The carbon black can also be used to supply carbon fuel cells, which are an efficient source of energy. A schematic of a distributed on-site hydrogen facility is shown in Figure 1.

Natural gas from an existing natural gas line can be used for the feed. The natural gas passes through a hydrogenator and then a ZnO bed to remove mercaptans and hydrogen sulfide from the stream. Purified natural gas is then fed vertically down through the inner porous graphite tube where it is rapidly dissociated to hydrogen and carbon black. The exiting stream of hydrogen, carbon black, and un-reacted natural gas passes through a jacketed cooling zone where it is cooled prior to being fed to a baghouse filter. Carbon black is separated in the baghouse and the hydrogen/natural gas mixture is then flowed through a pressure swing adsorber (PSA) where the hydrogen is purified. Incompletely converted natural gas is recycled to the solar-thermal reactor.

Some of the produced hydrogen is recycled and used to pad the annular region between the quartz and solid graphite tube, thus, preventing oxidation of the outer graphite tube. Additional recycled hydrogen enters the annular region between the solid and porous graphite tubes and flows radially inward between the two tubes, thus, providing a fluid-wall that prevents deposition of carbon black on the inside wall of the reaction tube. The bulk of the product purified hydrogen is compressed and stored in a high pressure hydrogen storage tank. If additional hydrogen above that required for fueling fuel cell vehicles is produced, it may be fed to a hydrogen pipeline or to a PEM fuel cell for electrical power generation that can be supplied back to the grid.

The produced carbon black contains no ash and will be of high purity. It can be sold into the carbon black market or fed to a carbon conversion fuel cell for additional electrical power generation. The lack of ash makes the carbon black a very desirable feed stock for carbon conversion fuel cells.

EXPERIMENTAL

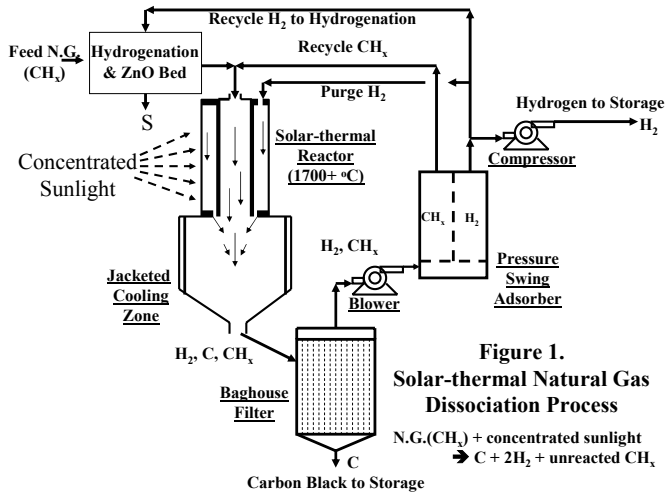

Figure 1. Solar-thermal Natural Gas Dissociation Process

The High Flux Solar Furnace (HFSF) facility at the National Renewable Energy Laboratory in Golden, Colorado is being used for this research. The HFSF uses a series of mirrors that concentrate sunlight to a focused beam at maximum power levels of 10 kW into an approximate diameter of 10 cm. A 74% efficient secondary concentrator distributes 7.4 kW of energy circumferentially around a 2.4 cm diameter x 9.4 cm long graphite reaction tube. The graphite tube is surrounded by a 5.1 cm diameter quartz protection tube. The quartz walled reactor is operated as a cold wall process, because the beam is delivered directly on target to the graphite. The control of solar radiation (on/off) is almost instantaneous. A pyrometer is used to measure the temperature of the graphite tube in the vertical center of the hot zone. In addition, a gas chromatograph/mass spectrometer is located downstream of the reactor to obtain in-line composition. The fine carbon black particles produced during the reaction are collected on a downstream filter. A photograph of the installed and operating reactor is shown in Figure 2.

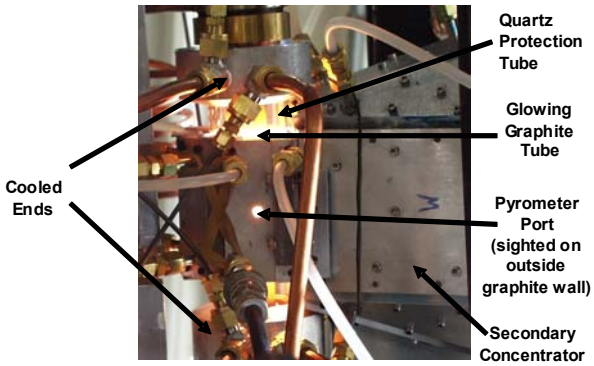

Figure 2. Reactor Tube Close-up On-sun

RESULTS AND DISCUSSION

Initial experimental studies with this reactor configuration are underway and have revealed extremely positive results. The process gas stream easily reaches temperatures greater than 1900 K with residence times less than 0.1 seconds. The effect of reactor temperature and residence time on reactor conversion is shown in Figure 3.

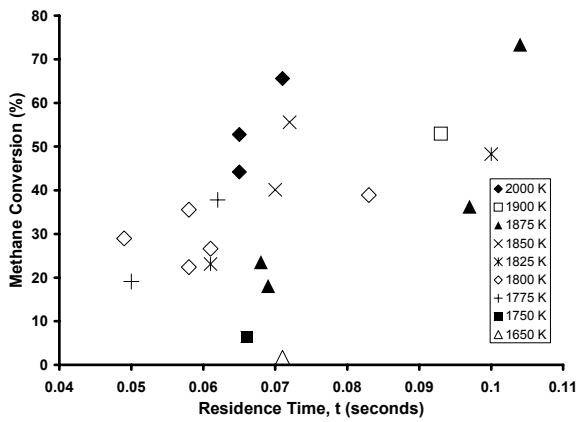

Figure 3. Effect of Temperature and Residence Time on Conversion

CONCLUSIONS

A solar-thermal aerosol flow reactor has been designed to dissociate methane to hydrogen and carbon black. High temperatures (greater than 1900 K) and short residence times (less than 0.1 seconds) are easily achievable using this reactor configuration. High single-pass conversions have been obtained. This process offers a promising method for producing distributed hydrogen to power fuel cell vehicles or supply hydrogen users in an environmentally benign manner.

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