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ENGINEERING DEVELOPMENT OF CERAMIC MEMBRANE REACTOR SYSTEMS FOR CONVERTING NATURAL GAS TO HYDROGEN AND SYNTHESIS GAS FOR LIQUID TRANSPORTATION FUELS DE-FC26-97FT96052

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Abstract

Air Products, in collaboration with the U.S. DOE and other partners, is developing ceramic membrane technology for the generation of hydrogen and synthesis gas. These membranes are non-porous, multi-component metallic oxides that operate at high temperatures and have exceptionally high oxygen flux and selectivities. Such membranes are known as Ion Transport Membranes, or ITMs.

Synthesis gas is an important intermediate product required for the production of liquid transportation fuels from natural gas. Preliminary cost estimates indicate that ceramic membrane reactors could decrease the capital cost for syngas by more than one third. This reduction would have a very significant impact on the costs of liquid transportation fuels derived from natural gas. Work still in progress also shows significant potential savings for hydrogen production, especially for production capacities appropriate for hydrogen based fuel cell applications.

This paper defines ITMs and explains how they work. The paper also identifies the major program goals and summarizes our progress. The overall program objectives and schedule are also presented.

Introduction

Hydrogen is an important industrial gas with many existing and future applications. Current production technology is typically through the steam reforming of natural gas or, for lower requirements, the purification of off-gas from, for example, refineries. Purified hydrogen can be liquefied and transported to the point of use and vaporized. This is currently the most economic source for hydrogen when the requirement is modest. For larger supply requirements, for example greater than 1 to 10 MMSCFD, on-site steam reforming is typically more cost effective. Figure 1 illustrates typical hydrogen cost data versus flow rate requirements for these two options. Air Products and Chemicals in collaboration with the DOE and others is developing a potential break-through technology that could have a significant impact on the cost of hydrogen, especially in the range of 0.1 to 1 MMSCFD. Target costs for this new technology are also illustrated in Figure 1. If successful, this technology could be important to emerging hydrogen markets such as hydrogen-based fuel cells for transportation and lower cost liquid transportation fuels.

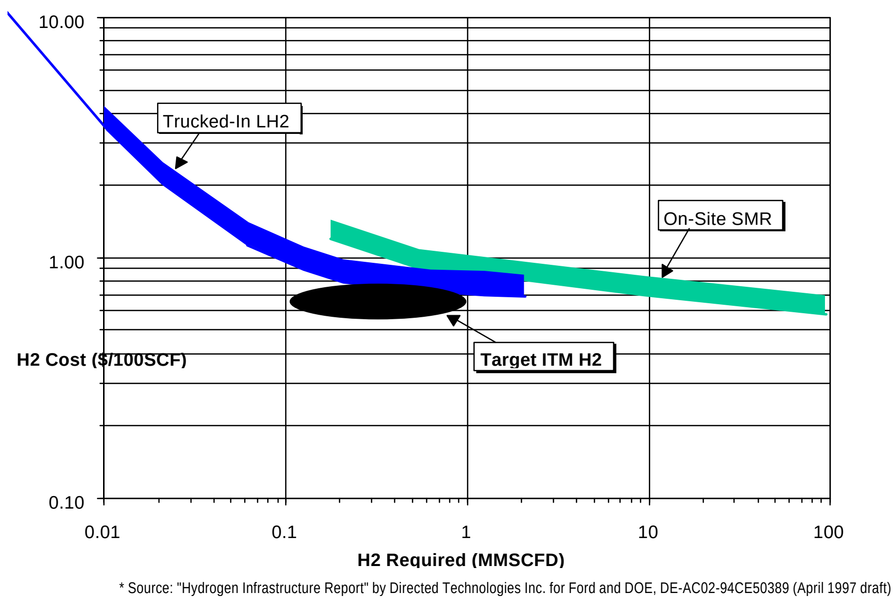

Figure 1 - ITM H_2 is Targeting Distributed Hydrogen

The new technology utilizes non-porous ceramic membranes that can be made from a variety of materials, for example perovskites, brownmillerites, and fluorites. These materials are multi-component metallic oxides that at high temperatures (greater than approximately 700 °C) conduct both electrons and oxygen ions. These types of membranes are known as ITMs (Ion Transport Membranes), and are of special interest because the oxygen ions permeate at a very high flux rate and with infinite selectivity. The oxygen can be separated from air fed to one side of the membrane at ambient or moderate pressure, and reacted on the other surface with natural gas at a higher total pressure to form a mixture of H_2 and CO. Because of the high flux, the reactor is very compact and should be low cost.

A schematic of the membrane is illustrated in Figure 2. The membrane structure is complex incorporating both the non-porous ITM and reduction and reforming catalyst layers.

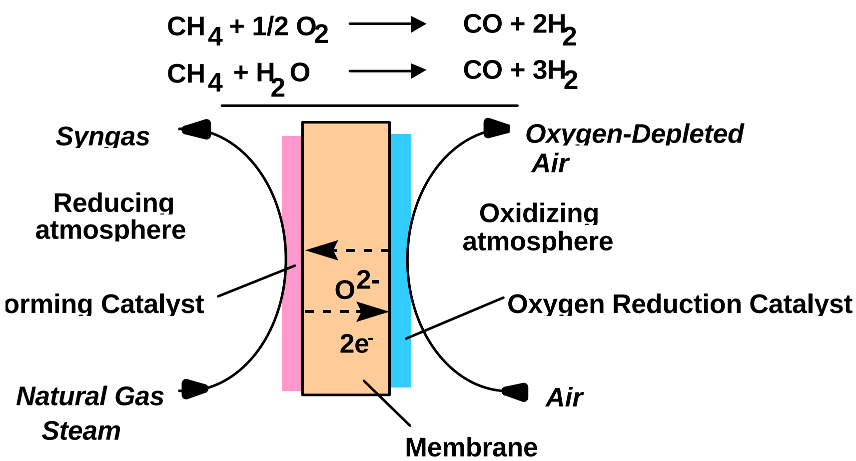

Figure 2 - ITM Syngas and Hydrogen Technology

Oxygen from a hot air stream is reduced to oxygen ions which flow through the membrane where, in combination with a reforming catalyst, they partially oxidize a combination of hot natural gas and steam, thereby forming syngas, a combination of carbon monoxide and hydrogen. The ratio of hydrogen to carbon monoxide is in part dependent upon the amount of steam. The membrane material must show long-term stability in reducing and oxidizing atmospheres, and long-term compatibility with the reduction and reforming catalysts. Intimate contact of the reforming catalyst with the ceramic membrane is critical to accomplish depletion of the oxygen transported through the membrane by reaction at the ceramic membrane/catalyst interface. This is a necessary requirement to control the partial oxidation reaction exotherm and provide a stable thermal operating mode for the membrane reactor.

The overall process is known as ITM Syngas, or ITM H2 depending on the product mix, and it can be used to generate syngas over a wide range of H_2 to CO ratio. The technology has many possible applications, but two important ones are the production of hydrogen and also the production of syngas required for Gas-to-Liquid (GTL) transportation fuels. Figure 3 illustrates the conceptual block diagrams.

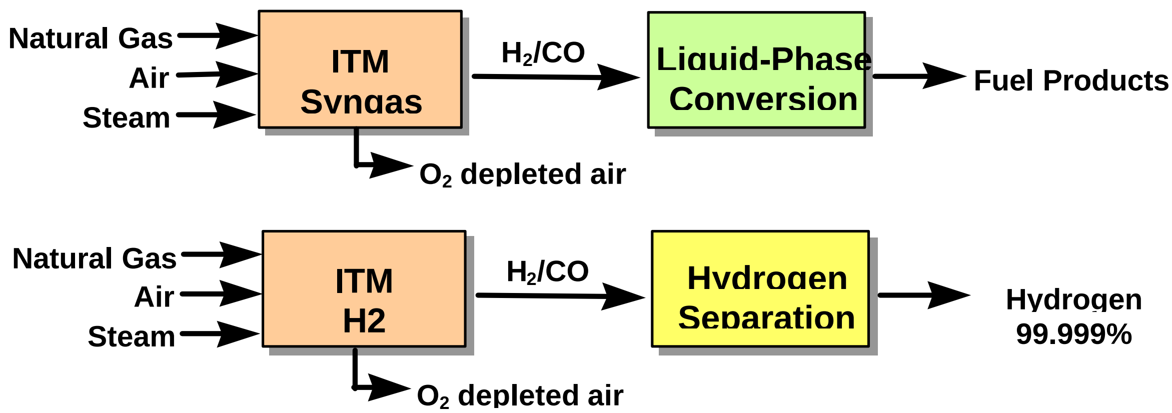

Figure 3 - Conceptual Block Diagram for ITM Syngas & Hydrogen

Air Products Partnership with the U.S. DOE

The U.S. DOE has selected Air Products' team and their technology for an $86 million, three phase, eight year program to develop ITM Syngas for these applications. The development partners are; Air Products, ARCO, Ceramatec, Chevron, Eltron, McDermott, Norsk Hydro, PNNL, Pennsylvania State University, the University of Alaska, the University of Pennsylvania and the U.S. DOE.

Major Technical Goals

The major technical goals for the program include;

- Membrane Material Selection
  Material selection is an iterative process requiring consideration of many factors. The material must have an acceptable oxygen flux, stability, strength and fabricability. It is essential that the development and selection of the ITM material is thoroughly integrated with the process design and engineering, ceramic fabrication, and membrane reactor design tasks to optimize the necessary combination of performance and fabrication properties.

- Reactor Design
  The membrane system must be able to tolerate the pressure differentials, reasonable ramp up and ramp down rates and emergency shutdown transients. The reactor design must address seals, differential expansion, and safety.

- Ceramic Processing Development
  Ceramic membranes require complex multi-step ceramic processing. Feedstock purity, powder preparation, control of potential contamination during processing, part forming, firing

and assembly are among the many considerations in the ceramic fabrication process. Development of technology from a conventional ceramic processing base is necessary to ensure economic membrane fabrication.

- Process Verification and Scale-up
  The fundamental performance of the membrane system must be evaluated under many realistic operating conditions so that a full understanding of performance and stability can be obtained. In addition, tests are needed at a variety of scale sizes so that models developed for flux, conversion and stability can be understood with confidence.

- Manufacturing Scale-up
  The hydrogen-fuel economy and the potential GTL market requires significant ramp-up of ceramic manufacturing operations. The fabrication of commercial quantities of ceramic components at economic yields is a critical issue that will be addressed.

- Risk Management
  Substantial investment is required to properly demonstrate process and manufacturing performance at reasonable scales. We have chosen to understand scale-up in a planned, phased development program.

The first phase of the program is anticipated to take 2.5 years and concentrates on ceramic membrane development, seal development and process development. Phase 2 is anticipated to take 3.5 years and includes a large Process Development Unit (PDU), at 12 MSCFD, and a Subscale Engineering Prototype (SEP) at 500 MSCFD. Phase 3 will take two years and includes a Pre-commercial Demonstration Plant at 15 MMSCFD.

The overall development schedule is given in Figure 4.

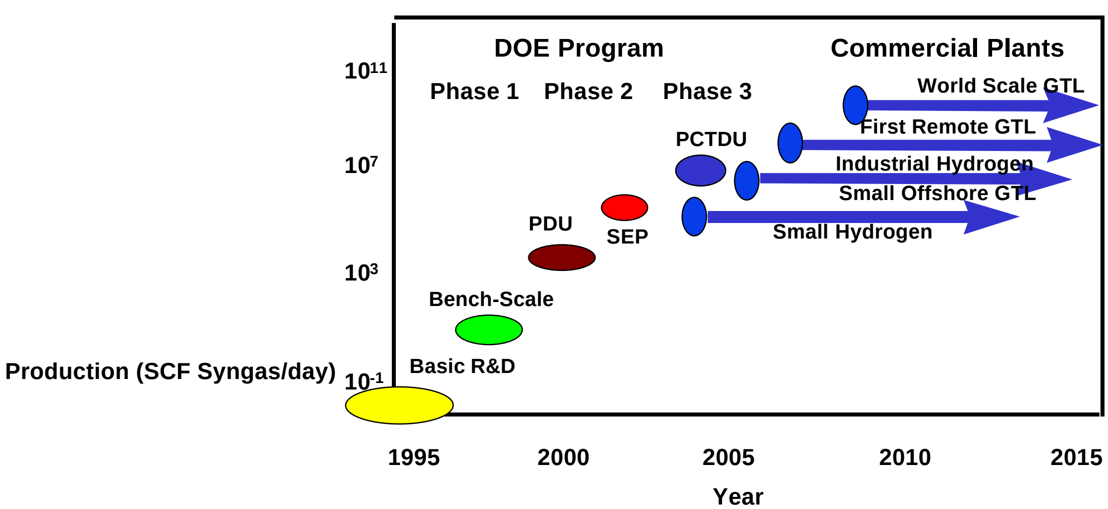

Figure 4 - ITM Syngas Goals and Development Schedule

Results

The program is high risk and contains many technical hurdles. Our progress to date has been very good. Air Products, Ceramatec and Eltron have developed and selected a number of ITM materials that show good flux and stability characteristics for both hydrogen and syngas applications. We have built the necessary experimental reactors for high temperature testing at ambient pressure and also high pressure. Test samples and seals fabricated by Ceramatec have shown to be leak tight for more than 300 hours of operation at 250 psig and 900 °C.

Air Products, Chevron, McDermott and Norsk Hydro have also completed preliminary process designs and economics including comparisons against ATR/ASU conventional technologies that show a greater than one third reduction in capital costs for syngas generation at compositions consistent with GTL production from natural gas. The hydrogen process design and economic assessment is in progress, and the preliminary results are very encouraging. Membrane reactor design studies by McDermott with input from Air Products and Ceramatec have yielded "first

Additional work planned for Phase 1 includes the selection of preferred materials and catalysts, further testing of membrane seal assemblies, selection of preliminary reactor configurations and further development of ITM membrane fabrication processes. Phase 1 should also include design work for the 12 MSCFD PDU.

Conclusions

This is an aggressive program with substantial technical hurdles. Our team, however, has extensive experiences in ITM membrane development and fabrication, and has a broad base of additional skills and commercial incentives. Technical success is likely to lead to, among other advantages, a step-change in the costs of distributed hydrogen and syngas required to produce low cost liquid transportation fuels from natural gas. Both of these goals, lower cost distributed hydrogen and lower cost liquid transportation fuels from natural gas are important to the United States economy and environmental quality. This collaboration between industry, academia, and the government is critical for the aggressive development of ITM membranes for these important applications.

List of Figures