ITM Syngas and ITM H2: 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 United States Department of Energy (U.S. DOE) and other members of the ITM Syngas/ITM H2 Team, is developing Ion Transport Membrane (ITM) technology for the generation of hydrogen and synthesis gas. ITMs are ceramic membranes that are non-porous, multi-component metallic oxides. They operate at high temperatures and have exceptionally high oxygen flux and selectivity.

The ITM H2 process is a break-through technology that could significantly lower the cost of hydrogen. Initial estimates indicate the potential for a considerable reduction in the capital cost of a large-scale plant (150 to 760 MMSCFD) which produces H2 for “clean” power generation with CO_2 capture, compared to conventional technologies. A successful development of the ITM technology could be important to emerging hydrogen markets, such as hydrogen-based fuel cells for transportation, and large-scale centralized hydrogen production facilities with CO_2 capture.

The major goals of the ITM Syngas and ITM H2 development program are summarized in this paper, and the progress of the ITM Syngas Team in successfully meeting those goals and objectives is described. The current focuses of the program are the commissioning of a nominal 24 MSCFD Process Development Unit (PDU) and the scaleup of ceramic membrane fabrication.

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 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 about 1 MMSCFD, on-site steam reforming is typically more cost effective.

Air Products and Chemicals, Inc. in collaboration with the United States Department of Energy and others is developing a potential break-through technology that could significantly reduce the cost of hydrogen. If successful, this technology could be important to emerging hydrogen markets, such as hydrogen-based fuel cells for transportation, and large-scale centralized hydrogen production facilities with CO_2 capture.

The new technology utilizes non-porous ceramic ITM membranes, fabricated from multi-component metallic oxides that have both high electronic and oxygen ion conductivity at high temperatures (greater than approximately 700 °C). In operation, oxygen from a hot air stream is reduced at one surface of the ITM membrane to oxygen ions, which diffuse through the membrane under a chemical potential gradient. At the opposite surface of the membrane, the oxygen partially oxidizes a pre-reformed mixture of hot natural gas and steam to form syngas, a mixture of hydrogen and carbon monoxide. 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 any oxygen reduction and reforming catalysts that are in contact with its surface.

The ITM Syngas and ITM H2 technology is being developed in an 8½ year, $90 MM development program supported by the US DOE. The objective of the program is to research, develop and demonstrate a novel ceramic membrane reactor system for the low-cost conversion of natural gas to synthesis gas and hydrogen for liquid transportation fuels: the ITM Syngas and ITM H2 processes [1-6].

ITM Syngas / ITM H2 is a complex new technology whose successful development to a commercial process requires a closely integrated, cooperative team effort. The members of the ITM Syngas Team are shown in Figure 1. Working with Air Products, the team members contribute in all aspects of the development program.

Figure 1. The ITM Syngas/ITM H2 Team

The overall development schedule, from laboratory feasibility studies to commercialization, is aggressive and is illustrated in Figure 2. Phase 2 of the program was initiated in FY2000 and will extend for 3.5 years. The current focuses of the program are the construction and commissioning of a nominal 24 MSCFD Process Development Unit (PDU) and the scaleup of ceramic membrane fabrication.

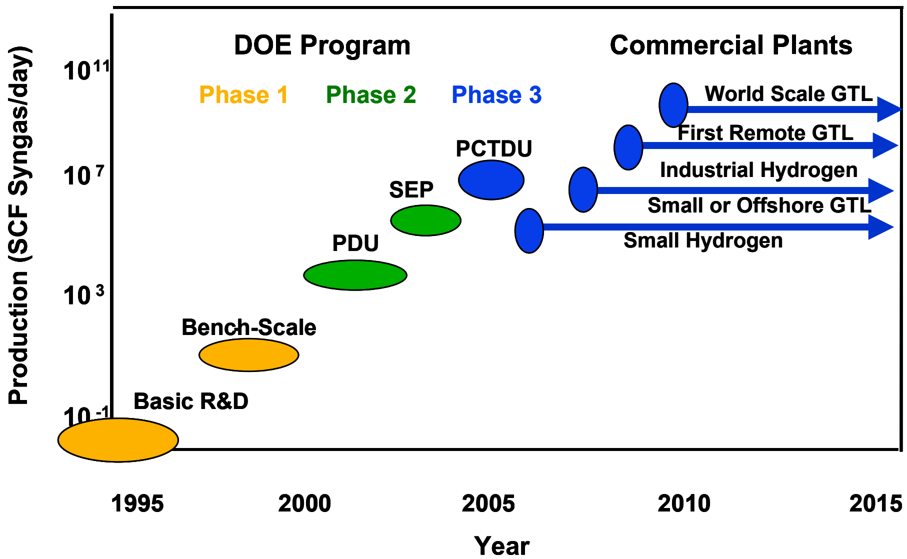

Figure 2. The Development Schedule for ITM Syngas / ITM H2

Program Objectives

In Phase 2, the process concepts and performance are being validated in two stages of scale-up: the Process Development Unit (PDU), which will continue operations through 2003, and the Sub-scale Engineering Prototype (SEP), which will begin operation at the end of 2003. An engineering, operating and economic database will be created based on the performance of these two units. The objectives of Phase 2 by Task are as follows:

In Task 2.1, “Commercial Plant Economic Evaluation,” Air Products, ChevronTexaco, McDermott and Norsk Hydro will develop advanced ITM Syngas/ITM H2 processes, with input from the University of Alaska. The economics of operation at the commercial plant scale will be evaluated based on the results of the Phase 2 program.

In Task 2.2, “Materials and Seals Development and Evaluation,” Air Products, Eltron Research and Penn State University will obtain laboratory-scale, statistical performance and lifetime data for membrane materials and seals under ITM Syngas/ITM H2 process conditions, with input from Norsk Hydro, Pacific Northwest National Laboratory and the University of Pennsylvania. Ceramatec will fabricate the ITM membrane/seal samples for testing.

In Task 2.3, “ITM Syngas Membrane and Module Design and Fabrication,” Air Products, Ceramatec and McDermott will design membrane reactors for the ITM Syngas/ ITM H2 processes at the PDU, SEP and commercial scales. Ceramatec will fabricate sub-scale membrane modules for testing in the PDU. Ceramatec will scale up the fabrication of the membrane reactor modules in a Production Development Facility (PDF) to supply the requirements of the SEP.

In Task 2.4, “Nominal 24 MSCFD ITM Syngas/ITM H2 PDU, “ Air Products will demonstrate the components of the ITM Syngas/ITM H2 technology in a laboratory Process Development Unit (PDU). The PDU will operate at an equivalent of 24 MSCFD of syngas capacity, and will performance test sub-scale planar membranes under commercial process conditions.

In Task 2.5, “Nominal 500 MSCFD ITM Syngas/ITM H2 SEP, “ a Sub-Scale Engineering Prototype (SEP) unit will be built to demonstrate the ITM Syngas/ITM H2 technology using full-size membranes in sub-scale modules. The SEP will demonstrate the operation of the ITM Syngas/ITM H2 processes at up to an equivalent of 500 MSCFD of syngas capacity.

Results

Task 2.1 Commercial Plant Economic Evaluation

As reported previously [2], preliminary process design and economic evaluation for ITM H2 in the “Distributed H2” target range of 0.1 to 1.0 MMSCFD H2 indicated the potential for up to 27% savings in production costs compared with trucked-in liquid hydrogen for 5000 psig fuel cell vehicle refueling applications. A nominal capacity of 0.5 MMSCFD H2 was selected, and the basis for the evaluation followed the “Hydrogen Infrastructure Report” produced by Directed Technologies and Ford for the DOE [7]. The costs of hydrogen compression, storage and dispensing were included in this analysis. In addition, economic evaluation of the ITM Syngas process producing about 150 MMSCFD of a 2:1 mixture of hydrogen and carbon monoxide confirmed the potential for >33% capital cost savings compared with conventional technology based on an autothermal reformer and cryogenic oxygen supply [4-6].

Initial ITM H2 concepts included processes that produced 150 MMSCFD of hydrogen. In an evaluation of advanced process concepts, the ITM H2 process was developed for a large hydrogen production plant with CO_2 removal, producing 760 MMSCFD of fuel-grade hydrogen at 100 bar and 14,000 tonne/day of CO_2 at 80 bar for sequestration. For this application, the ITM H2 process was compared to a conventional oxygen-blown Autothermal Reformer (ATR) with a cryogenic air separation unit (ASU) to supply oxygen, as shown in Figure 3. Economic evaluation of the ITM H2 process showed the potential for over 30% capital cost savings in the syngas generation process area and over 20% capital cost savings for the overall syngas/H2/CO_2 production process. The ITM H2 process also has a higher thermal efficiency of 74% compared to 71% for the oxygen-blown ATR process. The capital cost and efficiency advantages for ITM H2 are due to the combination of oxygen separation and high temperature syngas production into a single unit operation and the ability to use low-pressure air as the oxidant source. The hydrogen product is a “clean” fuel suitable for centralized power generation (approximately 1300 MW) and for distribution to local stationary or mobile applications, including fuel cells.

Task 2.2 Materials and Seals Development

Air Products and Eltron Research tested tubular membranes and seal assemblies, fabricated by Ceramatec, in high-pressure lab-scale units under ITM Syngas and ITM H2 process conditions. In these tests, pre-reformed natural gas mixtures at process pressure were passed over the outer surface of the tubular membrane, while air at atmospheric pressure was fed to the inner surface of the tube. The reaction was monitored by GC analysis of the high-pressure oxidation products and by measuring the oxygen depletion of the exhaust air stream. These tests also evaluated the performance of the seals at high pressure and high temperature. Multiple tests under ITM H2 conditions at Eltron Research ran continuously for over 6 months at 250 psig and 825 °C with good performance stability. The results of one of these six month continuous tests are shown in Figure 4.

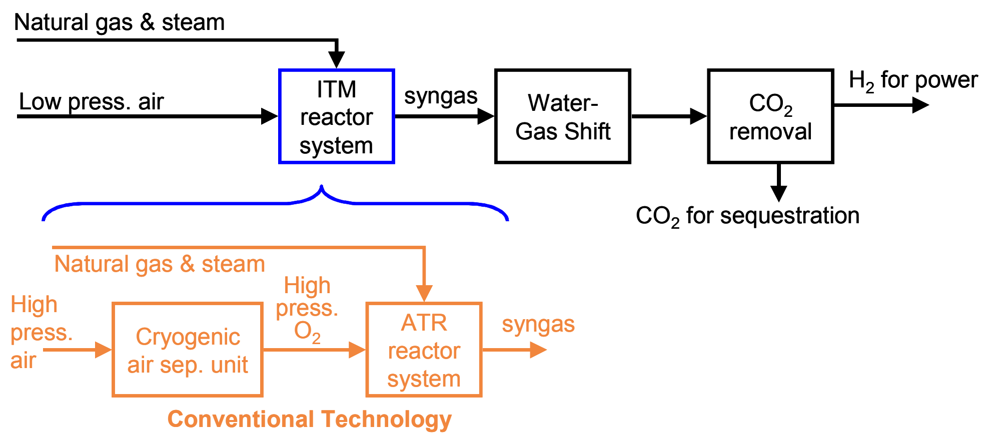

Figure 3. The ITM H2 Process Replaces Conventional Oxygen-Blown Autothermal Reforming for H2 Production with CO_2 Removal

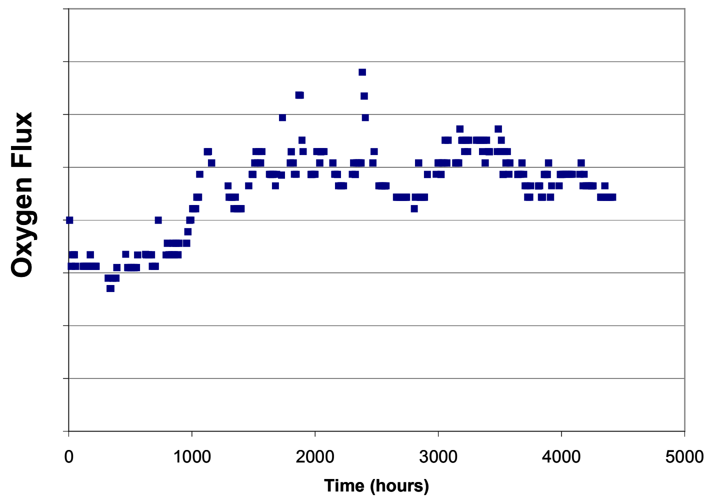

Figure 4. High Pressure Test of Tubular Membranes

Eltron Research also tested thin membrane discs, fabricated by Ceramatec, at atmospheric pressure with methane mixtures and air contacted on opposite surfaces of the membrane. Tests were carried out at temperatures of around 950 °C for periods of over 1200 hours. Tests of advanced catalyzed membranes demonstrated fluxes that approach the commercial flux target range. Improvements in membrane fluxes over time are shown in Figure 5.

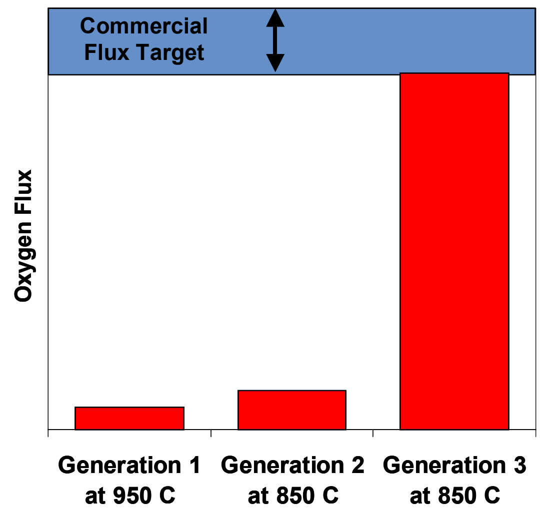

Figure 5. Advanced Catalyzed Membranes Approach Commercial Flux Target for Methane Partial Oxidation

Seal assemblies for PDU membrane modules [3,13] were fabricated and demonstrated to be leak tight at 425 psi differential pressure and 900 °C under both static and pressure and thermal cycling conditions.

Task 2.3 ITM Syngas Membrane and Module Design and Fabrication

Ceramatec successfully fabricated complete sub-scale PDU membrane modules. A PDU planar membrane module is shown in Figure 6. Air at low pressure is passed through the inner support passages (not shown) constructed within the planar membrane, while the pre-reformed methane mixture is passed at high pressure over the surfaces of the membrane module where partial oxidation takes place to produce syngas.

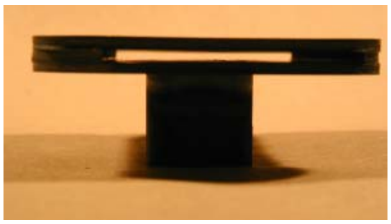

Figure 6. A PDU Membrane Module

Ceramatec and McDermott Technology completed the design of the full-scale membrane for the Sub-scale Engineering Prototype (SEP). Ceramatec has also initiated fabrication development of the SEP membranes and has fabricated sub-scale SEP membrane components. The rapid scaleup in ceramic membranes is shown in Figure 7. Lab-scale membranes (Figure 7a) were developed in 1999-2000 in conjunction with initial materials development and were used to demonstrate oxygen separation performance. Pilot-scale membranes (Figure 7b) were developed in 2000-2001 and have a 40-fold increase in membrane area over the lab-scale membranes. The pilot-scale membranes are being used to demonstrate membrane performance at commercial process conditions in the PDU. Fabrication methods that were developed at the pilot-scale are being scaled-up for full-size membranes. Full-size membranes (Figure 7c) are currently under development and have a 180-fold increase in membrane area over the lab-scale membranes.

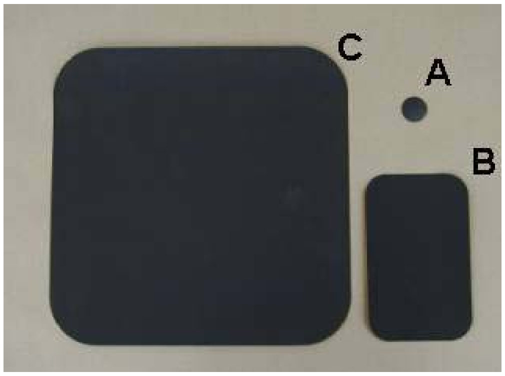

Figure 7. Progression of ITM Syngas/ITM H2 Ceramic Membranes.
(a) Lab-scale (b) Pilot-scale (c) Full-size

Task 2.4 Nominal 24 MSCFD ITM Syngas/ ITM H2 PDU

Installation of the PDU system was completed. The PDU integrates the various components of the ITM Syngas/ITM H2 reactor design, and will be used to confirm the performance of the planar membrane modules and seals under commercial process conditions.

The PDU is designed to evaluate membrane performance throughout the full range of ITM Syngas and ITM H2 process conditions. The PDU reactor system and PDU membrane modules were commissioned at high temperature and pressure with inert gases to fully check out the system prior to the introduction of process gas. The PDU module seals performed successfully at process pressure and temperature in the PDU reactor. The PDU reactor is shown in Figure 8.

Task 2.5 Nominal 500 MSCFD ITM Syngas/ITM H2 SEP

Initial scope definition of the SEP project was completed. Preliminary process flow diagrams were developed and vendor quotes were received for major equipment items. In addition, preliminary design of the ITM Syngas/ITM H2 SEP reactor was completed.

Plans for Future Work

The Phase 2 objectives for the next year include the following:

- Completion of more long-term tests of tubular membranes and seals at high pressure
- Demonstration of the performance of pilot-scale membrane modules in the PDU
- Evaluation of the ITM Syngas/ITM H2 processes using PDU data
- Commissioning the PDF and fabricating membranes for the SEP
- Selection of catalysts for the SEP
- Design of the SEP reactor and fabrication of the SEP vessel

Figure 8. The ITM Syngas/ITM H2 Process Development Unit (PDU)

Conclusions

Technical success will lead to a potential step-change reduction in the costs of hydrogen and syngas required to produce low-cost liquid transportation fuels from natural gas. Both of these goals, lower cost hydrogen and lower cost liquid transportation fuels from natural gas, are important to the United States economy and a secure and environmentally-sound energy supply. The collaboration between industry, academia, and the government present in the ITM Syngas / ITM H2 program is critical for the aggressive development of ITM membranes for these important applications.

Significant progress has been made to develop the ITM Syngas/ITM H2 technology. A database is being built up of performance data from several six-month long membrane tests. Membrane modules and seal assemblies have also been fabricated for testing in the PDU and ceramic fabrication scaleup is continuing the progression from lab-scale to full-size membranes. The PDU has been commissioned at high temperature and pressure. We continue to make excellent progress against the remaining technical challenges in the demonstration and scale-up of the ITM Syngas and ITM H2 technology.

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