

## **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 (DOE) and other members of the ITM Syngas 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 potential break-through technology that could have a major impact on the cost of distributed hydrogen, especially in the range of 0.1 to 1 MMSCFD. Initial estimates indicate the potential for a significant reduction in the cost of high-pressure hydrogen produced by this new route, compared with the cost of trucked-in liquid hydrogen. A successful development of the ITM technology could be important to emerging hydrogen markets such as hydrogen-based fuel cells for transportation.

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 focus of the program is the construction and commissioning of a nominal 24 MSCFD Process Development Unit (PDU).

## 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.

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. If successful, this technology could be important to emerging hydrogen markets such as hydrogen-based fuel cells for transportation [1].

The new technology utilizes non-porous ceramic ITM membranes, fabricated from multi-component metallic oxides that conduct both electrons and oxygen ions 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 flow through the membrane under a chemical potential gradient. At the opposite surface, the oxygen ions partially oxidize a pre-reformed mixture of hot natural gas and steam to form syngas, a mixture 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 any oxygen reduction and reforming catalysts that are in contact with its surface.

The ITM H<sub>2</sub> and ITM Syngas technology is being developed in an eight-year, \$90MM development program supported by the 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 H<sub>2</sub> processes [2-7].

ITM Syngas/ITM H<sub>2</sub> 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.

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 focus of the program is the construction and commissioning of a nominal 24 MSCFD Process Development Unit (PDU).



Figure 1 – The ITM Syngas Team

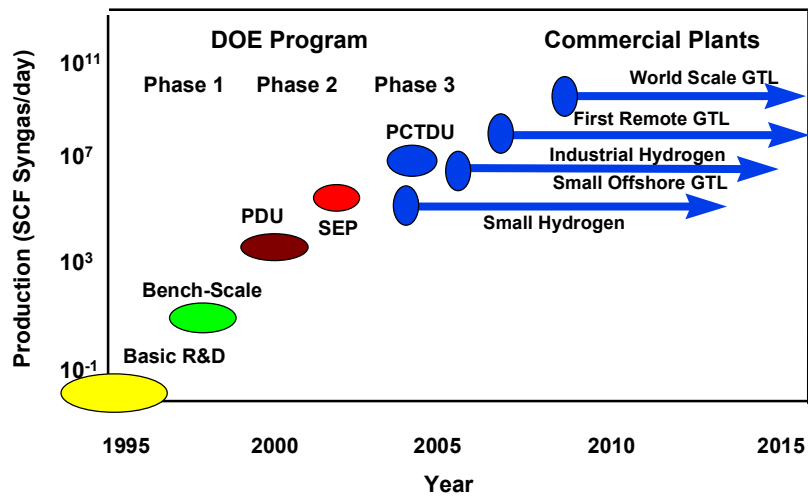


Figure 2 - The Development Schedule for ITM Syngas / ITM H2

### Phase 2 - ITM Syngas / ITM H2 PDU and SEP

In Phase 2, the process concepts and performance are being validated in two stages of scale-up: the Process Development Unit (PDU), which will begin operation in 2001, and the Sub-scale Engineering Prototype (SEP), which will begin operation in 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:

#### Task 2.1 Commercial Plant Economic Evaluation

Air Products, Chevron, McDermott and Norsk Hydro will develop advanced ITM Syngas and 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.

## **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 and ITM H<sub>2</sub> 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.

## **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 H<sub>2</sub> 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.

## **Task 2.4 Nominal 24 MSCFD ITM Syngas PDU**

Air Products will demonstrate the components of the ITM Syngas/ITM H<sub>2</sub> technology in a laboratory PDU. This unit will operate at up to an equivalent of 24 MSCFD of syngas capacity, and will performance test sub-scale planar membranes under commercial process operating conditions.

## **Task 2.5 Nominal 500 MSCFD ITM Syngas SEP**

An SEP unit will be built to demonstrate the ITM Syngas and H<sub>2</sub> technology using full-size membranes in sub-scale modules. The SEP will demonstrate the operation of the ITM Syngas and ITM H<sub>2</sub> processes at up to an equivalent of 500 MSCFD of syngas capacity.

## **Results**

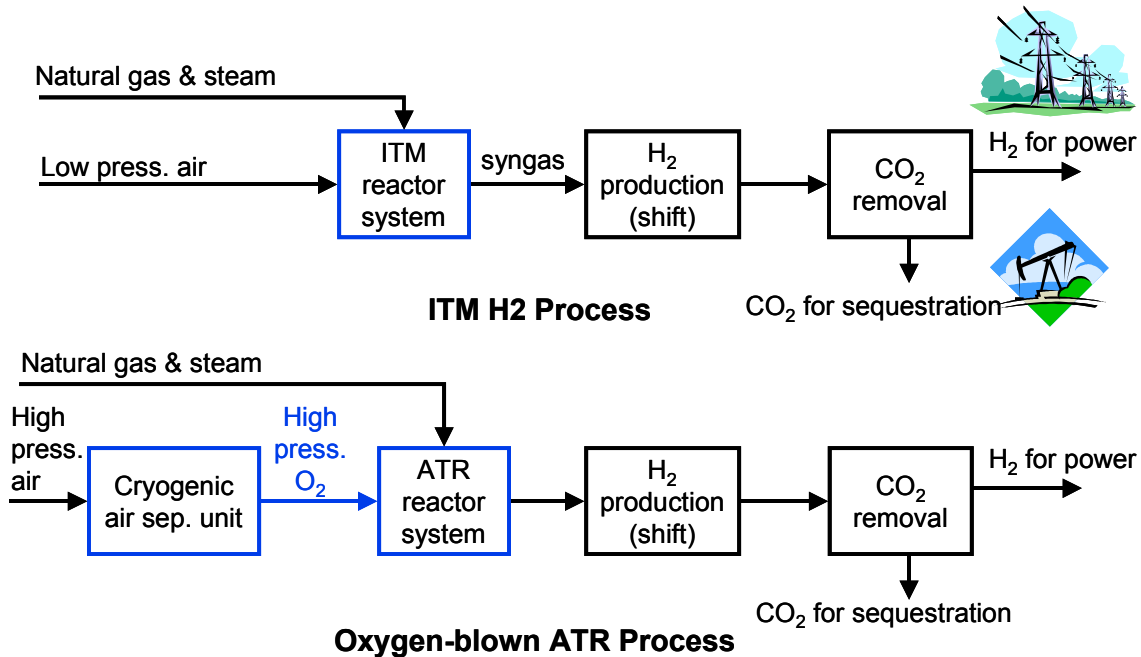
Phase 2 was initiated successfully, and all the milestones through April 2001 were completed on schedule.

## **Task 2.1 Commercial Plant Economic Evaluation**

As reported previously [6], preliminary process design and economic evaluation for ITM H<sub>2</sub> in the “Distributed H<sub>2</sub>” target range of 0.1 to 1.0 MMSCFD H<sub>2</sub> 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 H<sub>2</sub> was selected, and the basis for the evaluation followed the “Hydrogen Infrastructure Report” produced by Directed Technologies and Ford for the DOE [1]. The costs of hydrogen compression, storage and dispensing were included in this analysis. In addition, economic evaluation of the preliminary ITM Syngas process confirmed the potential for >33% capital cost savings compared with conventional technology based on an ATR and ASU [8-11].

In an evaluation of advanced process concepts, the ITM H<sub>2</sub> process was scaled up to a large hydrogen production plant with CO<sub>2</sub> removal. The process produced 760 MMSCFD of fuel-grade hydrogen at 100 bar and 14,000 tonne/day of CO<sub>2</sub> 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/H<sub>2</sub>/CO<sub>2</sub> 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.

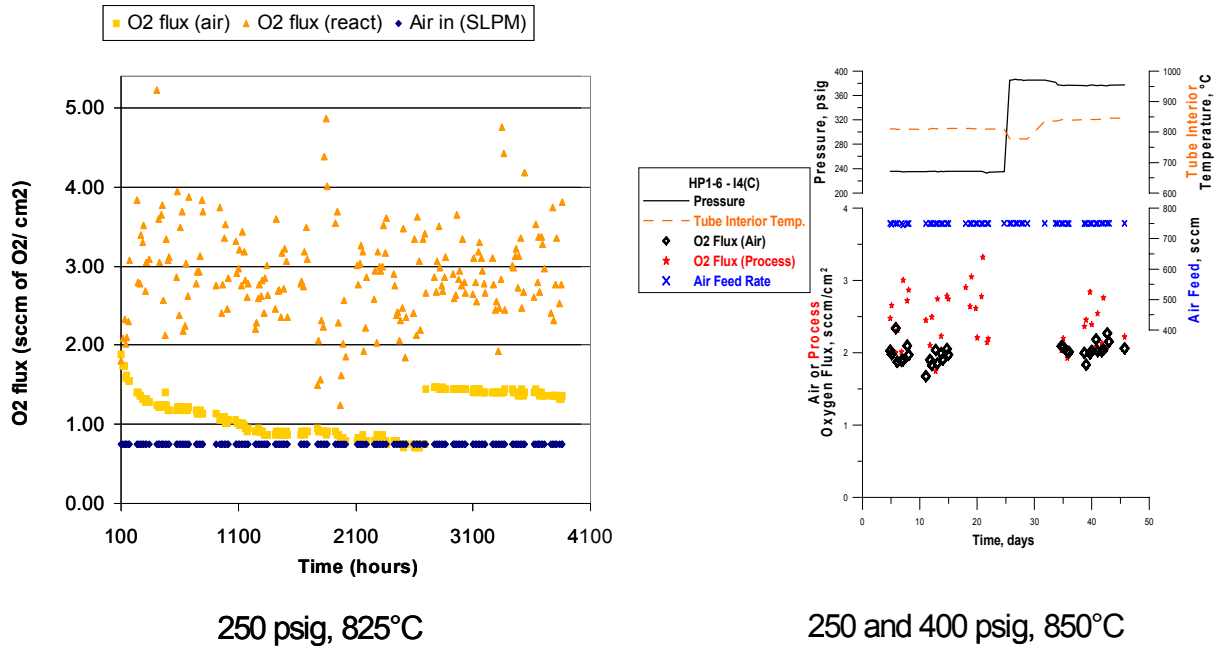


**Figure 3 – The ITM H2 Process Compared to Conventional Oxygen-Blown Autothermal Reforming for H<sub>2</sub> Production with CO<sub>2</sub> Removal**

### Task 2.2 Materials and Seals Development

Air Products and Eltron Research tested tubular membranes and seal assemblies, fabricated by Ceramtec, in high-pressure lab-scale units under ITM Syngas and ITM H2 process conditions. Results of two of these tests are illustrated in Figure 4, which shows oxygen flux measured on the process and air sides of the membrane as a function of time.

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. Two tests under continuous ITM H2 conditions at Eltron Research have demonstrated constant oxygen flux for over 4000 hours at 825°C and 250 psig. The results of one of these six-month continuous tests are shown in Figure 4.



**Figure 4 – High Pressure Tests of Tubular Membranes**

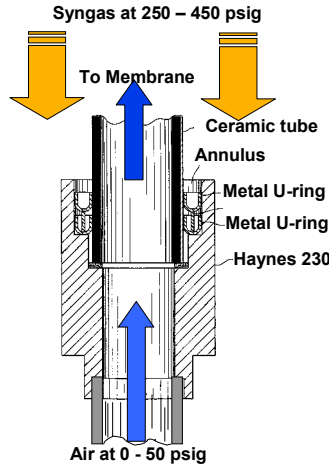
Eltron Research also tested thin membrane discs, fabricated by Ceramtec, at atmospheric pressure with methane mixtures and air contacted on opposite surfaces of the membrane. Tests were carried out at temperatures around 950°C for periods of up to 1200 hours. Oxygen fluxes in the range 5-10 sccm/cm<sup>2</sup> were recorded.

A seal assembly was selected for the PDU membrane module, and PDU membrane seal assemblies were fabricated and demonstrated to be leak tight at 425 psi differential pressure and 850°C.

A typical ceramic/metal seal assembly is illustrated in Figure 5, and was developed by Air Products and Ceramtec [12]. A double U-ring assembly is inserted into the annulus formed between a Haynes 230 sleeve and the outer diameter of the ceramic tube. The double U-ring assembly is oriented such that the open section of each U-ring is toward the higher-pressure syngas side. This activates the seal by pressing the side walls of the seal element apart and against the inner and outer surfaces of the annulus. Because each U-ring is compliant, it can accommodate differences in thermal expansion between the Haynes 230 and the tubular I4 membrane without transmitting undue stress.

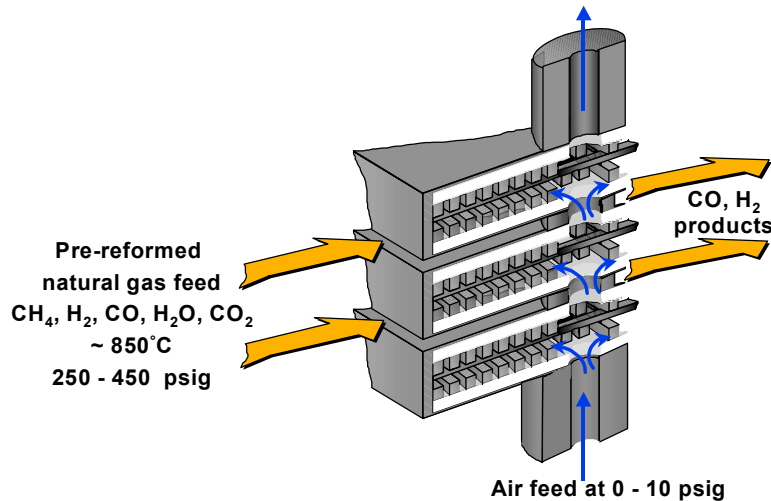
### Task 2.3 ITM Syngas Membrane and Module Design and Fabrication

After extensive thermo-mechanical analysis by McDermott and Ceramatec, a planar sub-scale PDU membrane module design was selected. The advantages of the planar membrane design, compared to the alternative shell-and-tube configuration, include a reduction in the number of ceramic/metal seals per unit active surface area of membrane.



**Figure 5 – Ceramic/ Metal Seal Assembly**

Ceramatec successfully fabricated complete sub-scale PDU membrane modules. An illustration of the planar membrane module concept is shown in Figure 6 [13]. Air at low pressure is passed through the inner support passages constructed within the planar membrane, while the pre-reformed methane mixture is passed at high pressure over the outer surfaces of the membrane module where partial oxidation takes place to produce syngas.



**Figure 6 – Conceptual Design for the Planar PDU Membrane Module**

## Task 2.4 Nominal 24 MSCFD ITM Syngas/ITM H2 PDU

The complete PDU system has been constructed and installed, and is ready for shakedown. The PDU will integrate the various components of the ITM reactor design, and will be used to confirm the performance of the planar membrane modules and seals under commercial process conditions.

The PDU will be able to access the full range of ITM Syngas and ITM H2 process conditions, and will simulate sections of the full-scale non-isothermal ITM Syngas reactor. A process flow diagram of the PDU and an illustration of the reactor vessel are shown in Figure 7. The low-pressure air feed can be blended with additional nitrogen and carbon dioxide to simulate a hot air feed stream produced by partial combustion [8-11].

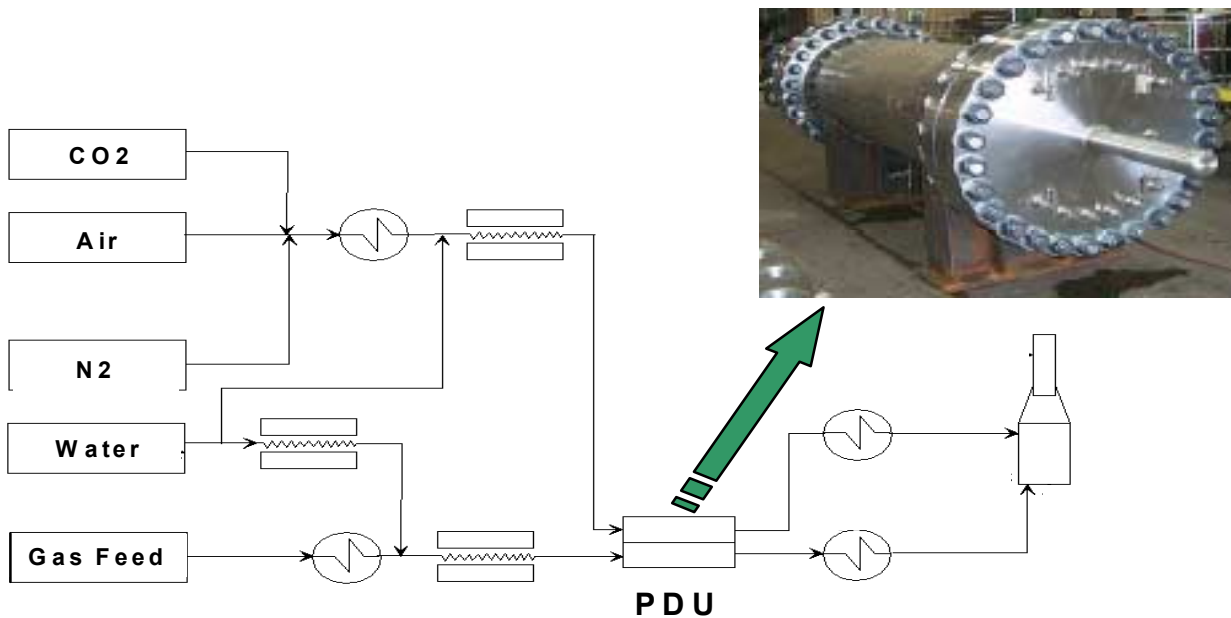


Figure 7 – PDU Process Flow Diagram

### 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 sub-scale membrane modules in the PDU
- Evaluation of the ITM H<sub>2</sub>/ITM Syngas processes using PDU data
- Commissioning the PDF and developing the fabrication of membranes for the SEP
- Design of the SEP reactor and fabrication of the SEP vessel



## Conclusions

All of the initial milestones of Phase 2 have been achieved, and the nominal 24 MSCFD PDU has been constructed. Substantial technical hurdles remain to be overcome in the demonstration of the performance of sub-scale membrane modules in the PDU, and in the further scale-up and demonstration planned for the nominal 500 MSCFD SEP.

Technical success will lead to a potential 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 energy supply with environmental quality. The collaboration between industry, academia, and the government present in the ITM Syngas/ITM H<sub>2</sub> program is critical for the aggressive development of ITM membranes for these important applications.

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