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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 Team, 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 selectivity. Such membranes are known as Ion Transport Membranes (ITMs).

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.

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.

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.

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 United States Department of Energy (US 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 membranes that are fabricated from multi-component metallic oxides that conduct both electrons and oxygen ions at high temperatures (greater than approximately 700 °C). These types of membranes are known as ITMs, 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 H2 and CO.

A schematic of the membrane is illustrated in Figure 1. The membrane structure is complex incorporating both the non-porous ITM and oxygen reduction and syngas reforming catalyst layers.

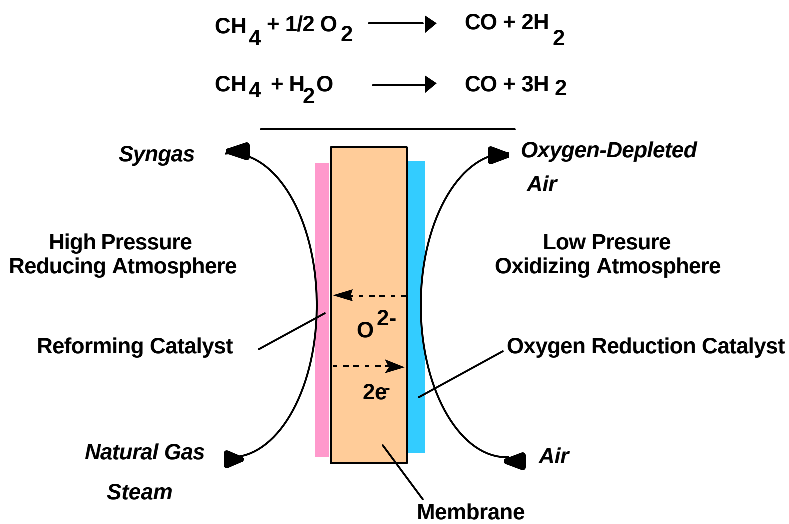

Figure 1 - Functions of the ITM Syngas/ITM H2 membrane

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 pre-reformed mixture 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 oxygen reduction and reforming catalysts.

ITM Syngas and ITM H2 Development Program

The ITM H2 and ITM Syngas technology is being developed in an eight year, $86 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 [2 - 6].

ITM Syngas / ITM H2 is a complex new technology whose successful progress toward a commercial process requires a mix of closely integrated, unique technical and commercial capabilities. Air Products has assembled a highly qualified team from industry, national laboratories, and universities. The ITM Syngas team comprises leading ionic ceramic material scientists, experienced ceramic fabrication technologists, process, design, structural and reaction modeling engineers, and commercial experts. Our team includes;

Air Products and Chemicals, Inc., Ceramatec Inc., Chevron, Eltron Research Inc., McDermott Technology Incorporated, Norsk Hydro, Pacific Northwest National Laboratory, Pennsylvania State University, the University of Alaska, and the University of Pennsylvania.

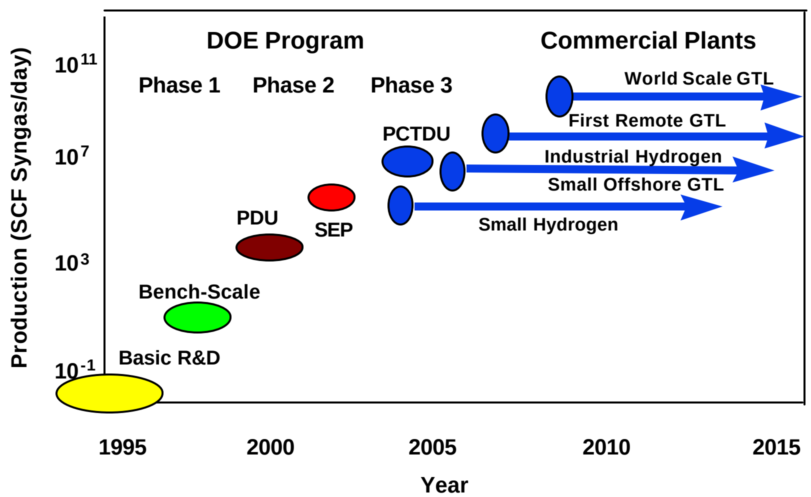

Figure 2 - The Development Schedule for ITM Syngas / ITM H2

The overall development schedule, from laboratory feasibility studies to commercialization, is aggressive and is illustrated in Figure 2. The program has completed Phase 1 and is now beginning Phase 2 with the design and construction of a nominal 24 MSCFD Process Development Unit (PDU).

Phase 1 - ITM Materials and Process R&D

Phase 1 (2.5 years) was divided into three tasks, and studied engineering fundamentals and evaluated materials, ceramic membrane and process concepts at the bench-scale level.

- **Task 1.1 Process Engineering and Economics**

In this task, Air Products, Chevron, Norsk Hydro, and McDermott developed specific process designs and evaluated process economics. The University of Alaska gave input on operations specific to the Alaskan environment The results were used to set objectives for the development of ITM Syngas and ITM H2 materials.

- **Task 1.2 Materials and Seals Development**

Air Products, Ceramatec, Eltron Research and Penn State jointly performed the materials development to achieve the required performance and stability at process conditions. Ceramatec produced ITM powder and laboratory test samples for the materials development tasks. Air Products, Ceramatec and PNNL developed high-temperature seals. Eltron Research and Air Products tested the performance of various ITM materials and seals at pressure in laboratory-scale reactors. Penn State University evaluated mechanical properties, and the University of Pennsylvania provided input on materials.

- **Task 1.3 ITM Syngas Reactor Design and Engineering**

McDermott, Ceramatec and Air Products designed the conceptual ITM membrane and reactor. Ceramatec developed the membrane fabrication process, and produced sub-scale thin film membrane samples. Air Products and McDermott designed and engineered a reactor vessel for a nominal 24 MSCFD PDU which will utilize sub-scale membrane modules.

At the end of Phase 1, a selection was made for further development of the ITM material/catalyst combinations, the membrane seals, and the membrane reactor design. Process economic and performance data were evaluated, and the decision was made to proceed with the scale-up in Phase 2.

Phase 2 - Engineering and Development of an ITM Syngas / ITM H2 PDU and SEP

Phase 2 (3.5 years) will validate process concepts in two stages of scale-up, and create an engineering, operating and economic database.

- **Task 2.1 Commercial Plant Economic Evaluation**

An advanced ITM Syngas and ITM H2 process will be developed, and the economics of operation at the commercial plant scale will be evaluated by Air Products, Chevron, McDermott and Norsk Hydro, based on the results of the Phase 2 program.

- **Task 2.2 Materials and Seals Development and Evaluation**

The combined ITM Syngas testing facilities of Air Products and Eltron Research will be utilized to obtain statistical performance and lifetime data under process conditions for the ITM Syngas materials and seals, fabricated by Ceramatec.

- **Task 2.3 ITM Syngas Membrane and Module Design and Fabrication**

Air Products, McDermott and Ceramatec will carry out the detailed design of the membrane, modules and manifolding for the ITM Syngas reactor. Ceramatec will scale up the fabrication of the ceramic membrane reactor modules in a Processing Development Facility (PDF) to supply the requirements of the SEP.

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

The components of the ITM Syngas and H2 technology will be demonstrated in a laboratory PDU. The PDU will operate at up to an equivalent of 24 MSCFD of syngas capacity, and will be used to performance test sub-scale membranes under process operating conditions for the H2 production and syngas /GTL applications.

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

A Sub-scale Engineering Prototype (SEP) Unit will be built to demonstrate the ITM Syngas and H2 technology using full-size membranes in sub-scale modules. The SEP will demonstrate the operation of the ITM Syngas and ITM H2 processes at up to an equivalent of 500 MSCFD of syngas capacity.

Phase 3

Phase 3 (2 years) will demonstrate the production of syngas from an approximately 15 MMSCFD Pre-Commercial Technology Demonstration Unit (PCTDU) using the ITM Syngas process.

Current Year Tasks

The tasks for the fiscal year 2000 included the completion of Phase 1 and the initiation of Phase 2. Specific objectives for the current year can be summarized as follows:

- Complete the Phase 1 process designs and economic evaluations for ITM Syngas and ITM H2 processes (Air Products, Chevron, McDermott, Norsk Hydro, University of Alaska).
- Develop and demonstrate, under process conditions at the laboratory scale, stable ITM material and seals for syngas and hydrogen production (Air Products, Ceramatec, Eltron Research, Penn State University and University of Pennsylvania)
- Demonstrate sub-scale thin membranes in reducing conditions (Air Products, Ceramatec, Eltron Research)
- Select and develop the ITM membrane and reactor vessel design for scale-up in Phase 2 (McDermott, Ceramatec and Air Products)
- Develop and specify the PDU membrane and module design (Air Products, Ceramatec, McDermott)
- Fabricate the specified PDU membrane design (Ceramatec)
- Design the PDU reactor vessel and initiate construction of the PDU (Air Products, McDermott)
- Deliver the PDU reactor vessel to the Air Products site (McDermott)

Results

All the objectives of Phase 1 have been successfully met by the ITM Syngas Team, and work has been initiated on Phase 2, which is on schedule.

Process Engineering and Economic Evaluation

Air Products, Chevron, and McDermott Technology have developed ITM Syngas processes to produce syngas with H2/CO ratio of 2, suitable for Fischer-Tropsch Gas-to-Liquids (GTL) applications. Preliminary process designs and cost estimates were completed in Phase 1. For an offshore GTL plant processing 50 MMSCFD of associated gas and producing approximately 6000 BPD of syncrude, capital cost savings of greater than 33% were predicted for ITM Syngas when compared to conventional O2-blown Autothermal Reforming (ATR) with a cryogenic Air Separation Unit (ASU) for syngas production.

Air Products and Norsk Hydro have developed ITM H2 processes to produce H2 at various scales. ITM H2 processes are being studied for large-scale H2 applications, where oxidative reforming using the ITM membrane reactor offers opportunities to sequester CO2 while producing fuel-grade H2. This application is attractive in light of the Kyoto Protocol and incentives for reducing CO2 emissions.

Preliminary process designs and cost estimates were completed for “distributed-scale” H2 processes which produce 0.1 to 1.0 MMSCFD of PSA-grade H2. A conceptual design for the ITM H2 process is illustrated in Figure 3 [7]. Applications at this scale include H2 for distributed refueling stations for Fuel Cell Vehicles (FCVs) and H2 for industrial use (e.g. H2 generators). At these scales, oxidative reforming processes offer attractive economics compared to steam reforming.

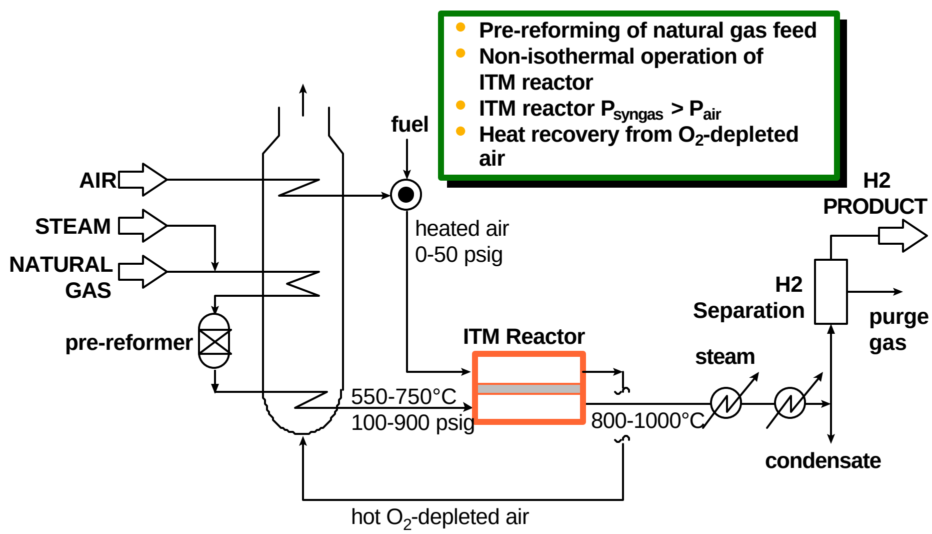

Figure 3 - Conceptual ITM H2 Process Design

The process was evaluated for the production of distributed hydrogen at 5000 psia delivery pressure suitable for fuelling fuel cell powered vehicles, and a design strategy was chosen to minimize process and equipment capital costs. 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 [1]. The costs of hydrogen compression, storage and dispensing were included. Up to 27% savings in high pressure hydrogen production costs were predicted for the ITM H2 process compared with trucked-in liquid hydrogen.

Materials and Seals Development and Evaluation

Air Products, Ceramatec and Eltron developed suitable ITM materials and seals with the characteristics and stability required for the ITM Syngas and ITM H2 processes.

High pressure, laboratory scale, test reactors were designed by Air Products, and constructed and installed at Eltron Research and Air Products. These are illustrated diagrammatically in Figure 4. The test samples are tubular membranes fabricated by Ceramatec and sealed into Haynes 230 alloy tubes using proprietary high temperature ceramic/metal seals. Pre-reformed natural gas mixtures at elevated process pressure are passed over the outer surface of the tubular membrane, while air at atmospheric pressure is fed to the inner surface of the tube. The whole assembly is contained in a heated pressure vessel. The reaction is monitored by GC analysis of the high pressure oxidation products and by measuring the oxygen depletion of the exhaust air stream.

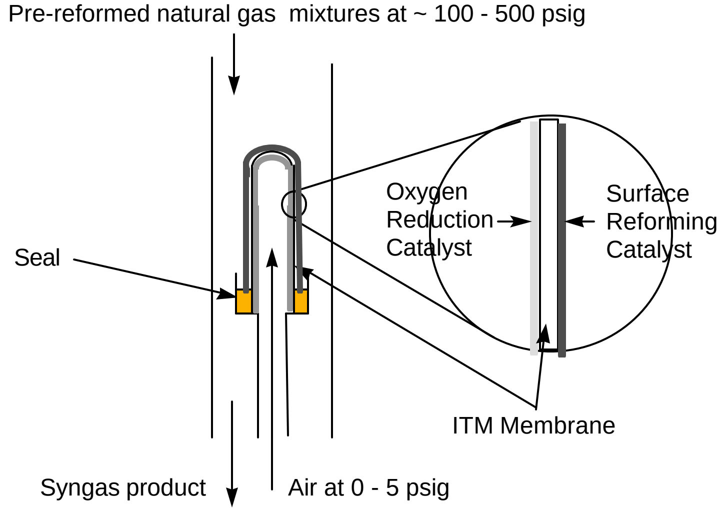

Figure 4 - Laboratory-scale, high pressure test reactor

Using the laboratory scale high pressure reactors, oxidation of gas mixtures simulating the large scale reactor has been carried out at high pressure and temperature at both Eltron Research and Air Products, using ceramic membrane and seal assemblies fabricated from ITM materials by Ceramatec. For example, a membrane and seal assembly was tested, using a feed S/C ratio typical for the ITM H2 process, with oxidation by air at atmospheric pressure under the following conditions and without any leakage:

- > 2400 hours at 825°C and 250 psig.

Other assemblies have been tested with continuous atmospheric air oxidation of a high pressure pre-reformed natural gas mixture under the following conditions:

- > 1000 hours at 250 psia and 900°C, and
- > 160 hours at 400 psia and 825°C.

These tests also evaluated the performance of the seals at high pressure and high temperature. In addition, a seal assembly was thermally cycled eight times from room temperature to 825°C under 250 psig pressure without leakage.

ITM Syngas Reactor Design and Engineering

Initial membrane and membrane reactor designs were developed McDermott, with input from Ceramatec and Air Products. Illustrations of the ITM membrane reactor geometries that were considered are shown in Figure 5.

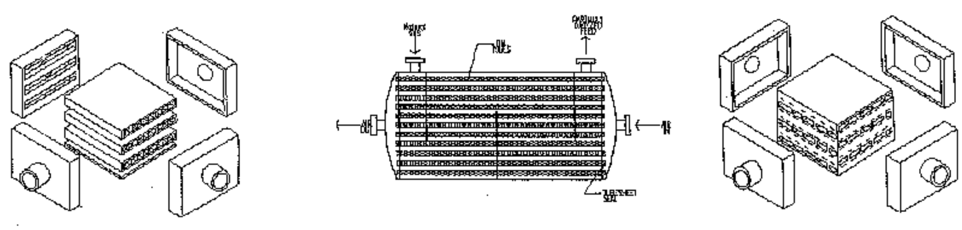

Figure 5 - ITM membrane reactor configurations

After extensive thermo-mechanical analysis, a planar membrane reactor configuration was selected for further development and scale-up. The advantages of this 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.

ITM Syngas Membrane and Module Design and Fabrication

Following selection of the planar membrane reactor configuration, Ceramatec developed the membrane fabrication process, and produced sub-scale test samples of supported thin film planar membranes. Initial tests of the performance of these thin film membranes at Eltron Research under low pressure syngas process conditions has demonstrated the achievement of the design oxygen flux.

Nominal 24 MSCFD ITM Syngas PDU

A process development unit (PDU) with a nominal capacity of 24 MSCFD of H2 and CO has been designed by Air Products, Ceramatec and McDermott. The initial hazards review was completed and the design and construction of the pressure vessel was begun by McDermott

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.

Initial Objectives for Phase 2

The Phase 2 objectives for the ITM Syngas / ITM H2 program in the near term are aggressive and include the following:

- Initial scale-up of the ITM membrane fabrication process
- Design and fabrication of membranes, modules and manifolds for the PDU
- Construction and commissioning of the nominal 24 MSCFD PDU
- Demonstration in the PDU of the commercial ITM Syngas and ITM H2 processes.

Conclusions

The objectives of Phase 1 have been achieved, but substantial technical hurdles remain to be overcome in the scale-up and technology demonstrations planned for Phase 2. The ITM Syngas Team, however, has extensive experience 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. 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.

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