

ENGINEERING DEVELOPMENT OF CERAMIC
MEMBRANE REACTOR SYSTEMS FOR
CONVERTING NATURAL GAS TO HYDROGEN
AND SYNTHESIS GAS FOR LIQUID
TRANSPORTAION FUELS

Monthly Report December 1999

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Contract Objectives

The objective of this contract 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 process. Through an eight-year, three-phase program, the technology will be developed and scaled up to obtain the technical, engineering, operating and economic data necessary for the final step to full commercialization of the Gas-to-Liquids (GTL) conversion technology.

Summary of Activity

Task 1.1 Process Engineering and Economics

Task 1.1.1 Process Design and Engineering

Air Products, Chevron and Norsk Hydro continued work on summary reports documenting the process design and engineering task. Revisions were made to both the ITM-based and conventional technology processes based on industrial experience.

Task 1.1.2 Commercial-Scale Plant Economic Evaluation

The preliminary-level ITM Syngas process design and economics are being evaluated for two cases: an offshore GTL plant with 55 MMSCFD (60°F, dry basis) total associated gas feed and a land-based GTL plant with 500 MMSCFD (60°F, dry basis) total associated gas feed.

McDermott incorporated preliminary vessel costs for the planar ITM reactor into the interim results for the land-based process economics. The vessel and membrane cost estimates are being finalized for the Phase 1 Preliminary Economic Evaluation report.

Task 1.1.3 PDU Systems Engineering

The initial PDU Design Hazard Review was conducted. A number of recommendations will be implemented during the design of the process control logic. The development of the PDU reactor internals, as well as the catalyst selection process, was started.

Task 1.2 Materials and Seals Development

Task 1.2.1 Materials Development

Subtask 1.2.1.1 Materials Characterization and Assessment

Material Characterization

A region of the I4 material composition map demonstrated stable oxygen flux, and no decomposition in low P_{O2} atmospheres in high-temperature, accelerated aging tests. A study of I5 compositions was begun, and these were initially shown to be stable in accelerated aging tests.

Mechanical Property Measurement

The mechanical properties of samples of various I4 compositions continued to be measured at Penn State University.

Subtask 1.2.1.2 Powder Production and Test Sample Fabrication

Ceramatec fabricated various I4 samples for syngas testing at Air Products and Eltron Research, mechanical property measurement at Penn State University, and seal development at PNNL.

Subtask 1.2.1.3 Atmospheric Pressure Testing

Testing of I4 membranes were carried out under reducing conditions in the atmospheric pressure screening reactors at Air Products. The oxygen flux performance was found to be stable at the maximum process temperature. Also initiated was testing of the new I5 membrane compositions with improved high-temperature stability.

At Eltron Research, a test of an I4 membrane tube was carried out with a narrow annular space for the reducing gas mixture. Little effect was observed on varying the air flow rate, with no measurable change in the product distribution, contrary to the high-pressure test results. Experiments to study the performance of Ni catalysts supported on an I4 substrate were continued.

Subtask 1.2.1.4 Low DP (<300 psig) Testing

High-pressure reactors 1 and 2 at Eltron continued to be used to evaluate I4 membranes and seals supplied by Ceramatec. The long-term test of an I4 membrane exceeded 2400 hours at a pressure differential of 250 psia and 825°C under a reducing gas mixture. The oxygen flux remained relatively constant, but the flux based on GC analysis of the product stream was consistently higher than that measured by depletion of the air feed. The calibration of all flow meters will be checked next month to determine the reasons for the discrepancy. A second test of a tubular I4 membrane lasted for 528 hours at 900°C and 250 psia under process gas conditions before the tube failed.

Subtask 1.2.1.5 High DP (<500 psig) Testing

The first Air Products 500 psig reactor was operated at full process temperature and pressure, and the shakedown of the system controls continued.

Task 1.2.2 Seals Development

At Eltron Research, ceramic-metal membrane seals fabricated by Ceramatec passed 2400 hours of testing at 825°C and 250 psig, and 500 hours of testing at 900°C and 250 psig.

PNNL studied glass compositions modified with selected filler materials to increase the thermal expansion coefficients. While several compositions were found in the desired thermal expansion range, bonding of ceramic and metal test coupons was unsuccessful due to the expansion mismatch of the components. PNNL also initiated vacuum heat treatment of ceramic and metal coupons with selected commercial braze filler metal (BFM) products to assess the ability of the BFMs to wet the substrate materials.

Task 1.3 ITM Syngas Reactor Design and Fabrication

Task 1.3.1 ITM Syngas Reactor Design and Engineering

Subtask 1.3.1.1 Mechanical/Structural Design of Membranes and Seals

McDermott completed a structural analysis of the planar membrane design, and this is being extended to a manifolded membrane design. The planar membrane module design is being refined to reduce the overall stress in the membrane due to thermal expansion.

Subtask 1.3.1.2 Reaction Engineering and Kinetic Modeling

Kinetic modeling work by Chevron and Air Products concentrated on the planar membrane reactor model using different approaches for solution methodology.

Subtask 1.3.1.3 Conceptual Reactor Vessel Engineering

McDermott continued estimation of the planar membrane reactor vessel costs.

Task 1.3.2 ITM Syngas Membrane Fabrication

Subtask 1.3.2.1 Powder Production, Process Development and Scaleup

Ceramatec continued the development of I4 powder production with further investigation of milling and spray drying procedures. Approximately 30 kg of I4 powder were produced for fabricating membrane test samples. An additional 10 kg of powder was sent to an external vendor for extrusion trials.

Subtask 1.3.2.2 Membrane Fabrication Process Development

The first samples of planar-supported, thin-film I4 membrane structures were fabricated by Ceramatec, and were shown to be leak-tight to He. The dense layers of the membranes are in the correct size range to achieve the target oxygen flux.