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

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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

Process development continued at Air Products, Chevron, and Norsk Hydro to evaluate potentially lower-cost process designs for ITM Syngas/GTL and large-scale ITM H2.

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. The offshore GTL application compares ITM Syngas to conventional Autothermal Reforming (ATR) syngas production and is based on a Floating Production, Storage, and Offloading (FPSO) system located in the Gulf Coast. The land-based GTL scope includes the ITM Syngas process and "conceptual-level" process design and costing of the Fischer-Tropsch and hydrocracking operations, and is being developed for Gulf Coast and Alaskan North Slope locations.

McDermott continued the analysis of the land-based economics with evaluation of the capital costs for the 500 MMSCFD plant. Layouts were completed and installed equipment costs were determined for both the Gulf of Mexico (GOM) and Alaskan North Slope (ANS) cases.

Norsk Hydro completed preliminary capital and operating cost estimates for a 150 MMSCFD large-scale ITM H2 plant.

Task 1.1.3 PDU Systems Engineering

The design and engineering of the PDU were continued. An initial cost estimate targeted a pilot plant size equivalent to approximately 24 MSCFD of syngas.

Task 1.2 Materials and Seals Development

Task 1.2.1 Materials Development

Subtask 1.2.1.1 Materials Characterization and Assessment

Material Characterization

The sintering characteristics of modified I4 materials were studied to maximize density and phase purity. A literature review was carried out that related to the vaporization of chromium-containing species under conditions relevant to the ITM Syngas process. Chromium volatilization may affect membrane performance.

Mechanical Property Measurement

The mechanical properties of samples of various I4 compositions were measured at Penn State University in air and low-oxygen, partial-pressure atmospheres.

Subtask 1.2.1.2 Powder Production and Test Sample Fabrication

Ceramatec fabricated additional leak-tight I4 tubes and seal assemblies for high-pressure syngas testing. At Eltron Research, tubular membranes were coated with porous catalytic layers to study the effects of membrane catalyst layer thickness on syngas conversion.

Subtask 1.2.1.3 Atmospheric Pressure Testing

The atmospheric pressure reactor at Air Products was used to test samples of two modified I4 compositions. Initial conductivity values for the modified materials were quite high; however, their conductivity appeared to decay with time on test in the highest temperature range studied.

At Eltron Research, atmospheric pressure testing of I4 membrane samples continued to evaluate the relative performance of reforming catalyst layers applied to the surface of the membrane. With a mixed composition gas feed at the higher temperature range, approximately 50% of the methane content was converted, and both the hydrogen and carbon monoxide flow rates in the product gas increased by around 30%. Additional experiments were planned to provide information on the performance of a porous layer of surface reforming catalyst for production of synthesis gas at the required rate.

Subtask 1.2.1.4 Low **IP** (<300 psig) Testing

The high-pressure reactors 1 and 2 at Eltron were used to evaluate I4 membranes and seals supplied by Ceramatec. Tests were run at 250 psia pressure differential and 825 and 900°C under a methane gas mixture that simulated the feed to the scaled-up ITM Syngas reactor. Air was fed at atmospheric pressure to the interior of the membrane tubular samples.

Subtask 1.2.1.5 High **IP** (<500 psig) Testing

Pressure testing of components of the Air Products 500 psig reactor continued this month.

Task 1.2.2 Seals Development

Ceramic metal seal samples were exposed at elevated temperature to low $P_{\rm O2}$ atmospheres. Cross-sectional analysis by SEM/EDS indicated differences in interfacial microstructure between sets of samples, which may be related to seal performance.

The thermal expansion coefficients of several potential glass seal compositions were measured at PNNL. The glass compositions were modified to attempt to bring the thermal expansion within the target range.

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 continued analysis of the thermal profile produced by the ITM Syngas reaction within a planar membrane configuration. Several design options were evaluated to minimize the thermal stress gradient.

Subtask 1.3.1.2 Reaction Engineering and Kinetic Modeling

Chevron continued development of the model describing a planar membrane configuration.

Subtask 1.3.1.3 Conceptual Reactor Vessel Engineering

McDermott performed a global thermal analysis to estimate the required membrane surface area and reactor size for the planar membrane configuration. Results from thermal stress analysis of the membrane active region were used to specify membrane design and performance requirements. A cost trade-off analysis will be performed to optimize the vessel arrangement.

Task 1.3.2 ITM Syngas Membrane Fabrication

Subtask 1.3.2.1 Powder Production, Process Development and Scaleup

Ceramatec investigated alternative I4 powder milling procedures as a prelude to scaling up to the production of larger batches of powder. Air Products investigated the correlation of the milling procedure with the purity of the ITM Syngas powder.

Subtask 1.3.2.2 Membrane Fabrication Process Development

Ceramatec continued with the preliminary fabrication of model membrane structures. The development of supported, thin-film membrane sample structures was initiated.