ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS

FINAL

Technical Progress Report No. 23

For the Period 1 April - 30 June 2000

Contractor

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DISCLAIMER

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Contract Objectives

The overall objectives of this program are to investigate potential technologies for the conversion of synthesis gas to oxygenated and hydrocarbon fuels and industrial chemicals, and to demonstrate the most promising technologies at DOE's LaPorte, Texas, Slurry Phase Alternative Fuels Development Unit (AFDU). The program will involve a continuation of the work performed under the Alternative Fuels from Coal-Derived Synthesis Gas Program and will draw upon information and technologies generated in parallel current and future DOE-funded contracts.

RESULTS AND DISCUSSION

TASK 1: ENGINEERING AND MODIFICATIONS - no activity this quarter

TASK 2: AFDU SHAKEDOWN, OPERATIONS, DEACTIVATION AND DISPOSAL - no activity this quarter

TASK 3: RESEARCH AND DEVELOPMENT

LPDME™

- **Another set of stable and commercially relevant LPDME™ conditions has been identified.** An experiment was designed to simulate a potential DME production case. The reaction system performed under the optimal production conditions and showed good catalyst stability. This experiment further expands our understanding of the stable reaction conditions for the LPDME™ process.

- **Efforts were made to develop an intrinsically stable catalyst system.** The goal is to develop a catalyst system that can be stable under all LPDME™ conditions of interest. The approaches include using alternative commercial methanol catalysts, modified methanol catalysts and bifunctional DME catalysts.

  The work is in the preliminary screen stage. It is currently performed in 50 cc microclave reactors, which have a much greater baseline-aging rate than 300 cc autoclaves. To

establish reference points for our screening experiments, an additional LPDME™ life test using our current catalyst system was carried out.

The screening experiments in this quarter included the dual catalyst systems containing:
– An alternative methanol catalyst. The aging rates appear to be low. Further tests are planned to verify the observation.

– A modified standard methanol catalyst. The modification was aimed at reducing the mobility of Zn-containing species in the methanol catalyst, therefore preventing them from migrating to the dehydration catalyst. However, the testing results did not show improved stability.

- **Efforts were continued to obtain a more detailed and solid understanding of the mechanism of catalyst deactivation under LPDME™ conditions.** Postmortem analysis of spent catalyst samples remains one of our major ways to probe the problem. A recent LPDME™ experiment using the Robinson-Mahoney basket generated well-aged catalyst samples. More importantly, both spent methanol and dehydration catalysts were in pelletized form, and therefore could be readily separated out for analysis. The spent γ-alumina pellets were analyzed with ICP-AES, XRF and ESEM-EDS. Although the alumina had lost 86% of its dehydration activity, the analysis did not show firm evidence of metal migration. More analyses of this sample are underway.

  Elemental analysis was performed on the oil samples from various LPDME™ and LPMEOH™ experiments to look for evidence of the mechanism of catalyst deactivation. None showed unique features. Metals of interest are below the detecting limit (<20 ppmw) in all samples.

Hydrodynamics

- **The question of whether catalyst materials in our LP processes are hydrophobic or hydrophilic has been answered - they are both.** A method and service for contact angle measurements of porous powder materials has finally been identified. Contact angles of standard methanol catalyst and γ-alumina dehydration catalyst powders with respect to Drakeol 10 oil and water were measured. Both materials are wettable by oil and water. This amphoteric behavior is due to the fact that each material contains both hydrophobic (disperse) and hydrophilic (polar) components. The polar portion in the methanol catalyst is greater than that in the dehydration catalyst. The Drakeol 10 oil itself also contains a significant portion of polar component. These results answered a lingering question regarding the fundamentals of our catalyst slurries and are useful guidelines for our slurribility study.

  Agglomeration of standard methanol catalyst powders in water was observed during particle size measurements. There was no such agglomeration when the powders were dispersed in Drakeol 10 oil.

- **The slurry performance of an alternate methanol catalyst was investigated.** The unique physical properties of this methanol catalyst caused some concerns about its slurribility. It has very large pore volume and particle size. Both may result in higher slurry viscosity for a given solid loading compared to the standard methanol catalyst. However, the particles broke down to 3.1 μm size after being used in a lab LPMEOH™ run. The viscosity of the spent slurry is only slightly greater than that of slurries using the standard catalyst. Therefore, other than the impact on catalyst reduction and initial operation, the catalyst powders under working conditions may not pose the problem we had anticipated using the property data of the fresh powders. These results again demonstrate that our slurribility study should be focused on the slurries under working conditions (e.g., spent slurries), not those made from the fresh powders.

Alternative Commercial Methanol Catalysts

The goal is to identify more commercial methanol catalysts for our LPMEOH™ commercial use. We will also test some of them under LPDME™ conditions if they show the properties that we believe are desirable for LPDME™.

- **Three commercial methanol catalysts have been tested under LPMEOH™ conditions.** These tests yielded the following results:
  - Alternative commercial methanol catalyst #1 showed lower-than-normal activity and poor stability.
  - Alternative commercial methanol synthesis catalyst #2 showed the baseline-aging rate and an activity equal to, if not greater than, that of an older version of the catalyst from the same manufacturer.
  - Alternative commercial methanol catalyst #3 showed very rapid deactivation in the first 300 hours, followed by stable, baseline aging in the next 200 hours. A quick experiment will demonstrate whether this initial rapid deactivation was due to the reactor artifact.