ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS

Draft

Technical Progress Report No. --40

For the Period 1 April - 30 June 1999

Contractor

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DISCLAIMER

Alternative Fuels and Chemicals from Synthesis Gas

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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 3: RESEARCH AND DEVELOPMENT

3.1 Improved Processes for DME

3.1.1 Improving DME Catalyst Activity

LPDME™

Higher catalyst loading (e.g., 30 grams) in 300-cc lab autoclave reactors led to greater-than-baseline catalyst deactivation ("30-gram problem"). Progress has been made in understanding the problem:

- The cause has been identified. Addition of slurry oil to the reactor in the middle of a 30-gram LPDME™ experiment reduced the catalyst aging rate to the baseline level. This reduction in catalyst aging was observed in two experiments using the dual catalyst systems containing #2 and #3 dehydration materials, respectively. It indicates that the "30-gram problem" is an artifact related to the loss of slurry oil. This observation rules out catalyst-loading-enhanced detrimental interaction between the catalysts as the cause of the problem.

- Other experiments also produced circumstantial evidence that the "30-gram problem" is possibly an artifact:
  - The spent slurry from a 30-gram LPDME™ experiment using a dual catalyst system containing #2 dehydration material was loaded into the reactor again, and the catalyst activity in this slurry was measured. The measured activity was significantly greater than that at the end of the original experiment. This result suggests that the "30-gram problem" may be due to the loss of catalyst to the walls of the reactor. However, inconsistent results were obtained in this type of experiment for slurries containing #1 dehydration material: some showed recovered activity; but others did not.
  - The greater-than-baseline catalyst deactivation in the 30-gram LPDME™ experiments is not correlated with the copper surface area of the spent catalysts. This indicates that copper sintering, one of the common methanol catalyst deactivation mechanisms, is not the cause of the "30-gram problem."
  - More experiments showed that the deactivation pattern in 30-gram LPDME™ experiments is not reproducible, suggesting the random nature of an artifact.

- An oil loss-related artifact was not observed under LPMEOH™ conditions, indicating that the artifact is unique to the dual catalyst slurries.

- It remains to be understood what the nature of the "30-gram problem" is, and if it would occur in the slurry bubble column reactor.

LPMEOH™

Experiments show that the activity of the 1998-batch methanol catalyst sample is similar to that of the current Kingsport catalyst (batch #2) and a lab sample of catalyst that we received in 1995.

Development of Bifunctional LPDME™ Catalysts

A new set of bifunctional LPDME™ catalysts has been tested. Several parameters in an important preparation step were studied. Some incremental improvement has been made in the past year. The best sample reached 62% of the target productivity and 100% of the target DME selectivity. Air Products met with the manufacturer to review the results and discuss future directions. A new action plan and items were developed.

3.1.2 Understanding Liquid Phase Processes

Arsine, AsH_3, has been shown to act as a catalyst poison for a Shell gas feed. Feed AsH_3 concentrations of 660 and 310 ppbv resulted in increased rates of catalyst deactivation. Elimination of AsH_3 from the reactor feed led to a return to a baseline catalyst deactivation rate. Preliminary XAFS results imply that arsenic is present on the catalyst in a metallic form, possibly as an alloy with Cu.

A review of Eastman analytical data (1995) indicates that substantial quantities of hydrogen cyanide, HCN, were absorbed by the ZnO portion of their guard bed. Although HCN is generally regarded as a methanol catalyst poison, no literature experimental studies on the effects of HCN have been found. Experiments are underway to evaluate HCN as a potential poison.

The UV spectra of mineral oil from Kingsport spent catalyst slurries and from freshly reduced catalyst indicate the presence of unsaturated species. The concentration of unsaturates is low and relatively unchanged with time on stream. The effects, if any, of such unsaturated species on catalyst deactivation are unknown.

Characterization of the 1998 lot of catalyst powder indicates that it should have adequate activity and rheological properties for use in our processes.

Slurry viscosity, as measured by a Brookfield viscometer, is a useful tool for evaluating potential catalysts for liquid phase processes.

Task 5: PROJECT MANAGEMENT

5.1 Liquid Phase Fischer-Tropsch Demonstration

Air Products received comments/questions from DOE on the draft topical report for F-T III/F-T IV. After consultation with SSFI (Shell Synthetic Fuels, Inc.), changes were incorporated in the report, and a final version of the topical report was submitted to DOE in early June. B. L. Bhatt presented the final results for the F-T III/IV demonstrations to DOE at a review meeting on 9 June. The results and the presentation were well received.