ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS

FINAL

Technical Progress Report No. 26

For the Period 1 January - 31 March 2001

Contractor

AIR PRODUCTS AND CHEMICALS, INC.
7201 Hamilton Boulevard
Allentown, PA 18195-1501

Prepared for the United States Department of Energy
Under Contract No. DE-FC22-95PC93052
Contract Period 29 December 1994 – 31 July 2002

NOTE: AIR PRODUCTS DOES NOT CONSIDER ANYTHING IN THIS REPORT TO BE CONFIDENTIAL OR PATENTABLE.

DISCLAIMER

Alternative Fuels and Chemicals from Synthesis Gas

Technical Progress Report

1 January - 31 March 2001

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

LPMEOH™ Kinetics

The goal of this effort is to develop more robust rate models for methanol synthesis and water gas shift reactions and better models for important side products.

- There has been a concern about our rate model for the water gas shift reaction in predicting CO_2 conversion. Revisiting the lab results shows that the under-estimated CO_2 conversion may well be due to the model's inability to account for side reactions. The decision was made to determine if we missed any significant side products and to refine the models for the known side products.

- The GC in one of our autoclave units has been calibrated for the known side products from the LPMEOH™ reactor. The kinetic data under four different conditions were collected, and the minor products were measured with good confidence. The results show that the side products are a significant part of the total mass balance under CO-rich conditions, and therefore, should be accounted for properly in our rate model.

- A GC-MS analysis of a liquid sample from the condenser in the reactor effluent line revealed eight high alcohols that currently are not included in our GC-analysis, mass balance and rate model. Further analysis will be performed to determine how significant these alcohols are to the total mass balance and whether they need to be included in our rate model.

- Some discrepancies have been found in our current rate model in predicting the formation of side products, mainly occurring outside the regime where the original rate expressions were developed. These include underestimating the formation of ethanol, 1-propanol and 1-butanol by a factor of 10 under CO-rich conditions and over-predicting methane formation by a factor of 5 under H_2-rich conditions. These problems will be addressed in our model refinement.

- A large number of LPMEOH kinetic data under different reaction conditions have been collected. Some trends in the model's deficiency have been observed and will be used to refine our rate model.

LPDME Stability: Catalysts, Conditions and Mechanistic Study

Efforts were continued to analytically confirm our current hypothesis on catalyst deactivation under LPDME^{TM} conditions. The better understanding derived from the effort will help future development of intrinsically stable catalyst systems.

- Some initial copper surface area measurements have been made for six samples from various LPMEOH and LPDME experiments. This effort is aimed at verifying the sintering curve we have observed previously, i.e., the correlation between the catalyst activity and Cu crystallite size. It may also shed some light on the catalyst deactivation mechanism that is not related to Cu sintering.

Investigation of Lab Reactor Artifacts

Since our LPMEOH program now demands a lower lab baseline aging rate, understanding lab reactor artifacts has become a necessary step in the advancement of our program. Efforts were continued to see if better lab baseline aging could be obtained. A final control experiment using Drakeol 10 oil was finished, and all results show that Drakeol 34 oil has consistently performed better than Drakeol 10. Further work will depend on our understanding of why Drakeol 34 is a superior slurry fluid.

DOE Topical Report

A draft of a DOE topical report entitled "Kinetic Understanding of the Syngas-to-DME Reaction System and Its Implication to Process and Economics" has been finished. The report covers our kinetic analysis of LPDME over the last four years. Most of the report is based on two papers we published previously and on a paper we prepared for a conference. Another part, mathematical analysis of the optimal feed for the LPDME process, is documented for the first time.

Task 5: PROJECT MANAGEMENT

LPDME™ Demonstration at La Porte AFDU

Comments received from DOE on a draft topical report for the fall 1999 LPDME™ design verification test at the AFDU were incorporated into the report. A final version of the report was completed and sent to DOE.