

# **ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS**

**FINAL**

**Technical Progress Report No. 28**

For the Period 1 July - 30 September 2001

Contractor

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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**

#### **LPMEOH<sup>TM</sup> Kinetics**

Efforts were continued to refine our kinetic models for the LPMEOH<sup>TM</sup> process. This refinement is needed to meet the requirements for more accurate process simulations over a wide range of conditions. The activities in this quarter included the following:

- The candidate methanol synthesis kinetic model was further examined under four conditions from a D-Optimal sequential design, four conditions for very CO<sub>2</sub>-rich syngas, and two conditions with water injection. The results showed that the model covers the new conditions well. The new data further establish the candidate model as the best among all models we have considered. The parameters in the model were refined using the new data set.

- A detailed analysis showed that the inability of our current model to predict CO<sub>2</sub> conversion accurately is due to inadequate representation of CO<sub>2</sub>-related reactions in the model. The reaction of CO<sub>2</sub> hydrogenation to methanol was added to the LPMEOH<sup>TM</sup> reaction network to provide the needed degree of freedom for CO<sub>2</sub> conversion modeling. The new rate equations for CO<sub>2</sub> hydrogenation and water gas shift reactions were developed for this new configuration.
- The impact of introducing the CO<sub>2</sub> hydrogenation reaction on our candidate methanol synthesis model (methanol formation from CO hydrogenation) was examined. Not only does the model hold, but the fitting actually is better, as well.
- The rate models for 12 side reactions were further refined using our recent kinetic data. Compared to the last version, the prediction improved significantly, especially in the CO-rich regime.
- The kinetic data at lower temperatures (230 and 240°C) were collected. Incorporation of these data into new models will be conducted in the coming month.

#### **LPDME<sup>TM</sup> Stability: Catalysts, Conditions and Mechanistic Study**

Analytical work was continued to elucidate the deactivation mechanism under LPDME<sup>TM</sup> conditions. The insight from this work will help to develop intrinsically stable catalyst systems.

- Additional analysis of spent samples using EDS/SEM confirms that the rate of catalyst aging under LPDME<sup>TM</sup> conditions correlates with the rate of Cu accumulation on the dehydration catalyst. This provides direct evidence that metal migration is indeed the mechanism by which the methanol synthesis and methanol dehydration catalysts deactivate under LPDME<sup>TM</sup> conditions.