ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS

Draft

Technical Progress Report No. 27

For the Period 1 April - 30 June 2001

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

Continued upkeep of the AFDU was performed during this reporting period.

TASK 3: RESEARCH AND DEVELOPMENT

LPMEOH^{TM} Kinetics

Efforts have been made to refine our kinetic models for the LPMEOH^{TM} process. This refinement is needed to meet the requirements for more accurate process simulations over a wide range of conditions. We have divided the problem into three parts: 1) a better rate equation for methanol synthesis, 2) better rate equations for side reactions, and 3) a better reaction scheme and rate model to account for CO_2 conversion. Progress has been made on all three fronts:

- Kinetic data under a wide range of new conditions have been examined. Different literature kinetic models for methanol synthesis have been compared with these recent kinetic data. Several models fit the data well. One of these models has been chosen as a candidate for further examination. A sequential experimental design using the D-optimal method will be employed to identify new testing conditions. The new experiments will verify the models in the regions where the model is sensitive to the change in reaction conditions and in the regions that have not been covered by the existing experiments.

- Accurate modeling of by-product formation under LPDME^{TM} conditions is important for two reasons. First, under CO-rich conditions, by-products contribute significantly to the overall mass balance (i.e., several percent). Second, the water formed from the side reactions has a significant impact on water-gas-shift-related performance, such as CO_2 conversion. Therefore, we need to take all important side reactions into account and model the rates of the side reactions accurately.

- GC-MS analysis has confirmed that our current model misses a group of high-alcohol by-products. Inclusion of these high alcohols brings the experimental mass balance close to 100%. The formation of these high alcohols has been incorporated into our process simulation package and is modeled by a single, lumped-together reaction (hicohols formation).

- New rate equations for side reactions have been developed based on recent kinetic data. They predict by-product formation much more accurately than our current rate equations. They also predict water formation much better and bring CO_2 conversion closer to experimental observations. Refinement of these equations will continue when more data are available.

- Since developing models for CO_2 conversion requires accurate measurements of the water concentration in the reactor effluent, we conducted a methanol dehydration experiment as a way to calibrate our water GC. This method is more accurate, but also much more time-consuming than the calibration method we have normally used. The results show that the water concentration was 20% too high in the old calibration. All water data from our recent kinetic experiments have been corrected based on the new calibration. The new water data point out the possible directions we should go to model CO_2 conversion more accurately.

LPDME™ Stability: Catalysts, Conditions and Mechanistic Study

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

- A good correlation between copper surface area and methanol catalyst activity was observed for the spent catalysts from stable LPMEOH™ and LPDME™ runs, indicating that copper sintering is the cause of catalyst aging in these experiments. The data from unstable LPDME™ runs fall outside this correlation, indicative of a non-copper-sintering related deactivation mechanism. The results suggest that some copper in the catalysts from the unstable runs does not contribute to methanol synthesis. This observation agrees with our current copper migration hypothesis. The results also confirm a similar correlation we established previously based on copper crystallite size measurements.