

ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS

Draft

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For the Period 1 October - 31 December 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

LPMEOHTM Kinetics

The development of kinetic models for LPMEOHTM has been completed in the lab group. The new reaction network and rate models are being integrated into the process simulation package and examined for commercially relevant cases in the process group. Hopefully, the new kinetic package will meet the requirements for more accurate process simulations over a wide range of conditions. This quarter's efforts leading to the completion of the kinetic work are as follows:

- The data at lower temperatures (230 and 240°C) were incorporated into model development. For the 3 major reactions (i.e., CO hydrogenation to methanol, CO₂ hydrogenation to methanol, and water gas shift) and 2 of the 12 side reactions, the temperature-dependent terms were added to the models originally developed based on the data at 250°C. For the other 10 side reactions, the models developed at 250°C were reconfigured, and temperature-dependent terms were added. This led to 15 new models for the 15 reactions in the

LPMEOHTM system. All of the new models fit the data much more closely than our existing models.

- The 15 models mentioned above were further refined. Refinement addressed the issue that the methanol catalyst deactivated with time during the kinetic experiments, and this deactivation needed to be taken into consideration to develop accurate models. The refinement went through an iterative process that resulted in good agreement between the aging rates used for correcting the raw kinetic data and the aging rates calculated from the final, refined models.
- We attempted to determine if the kinetic models could be further improved by fitting the data in H₂-rich and CO-rich regimes separately. The results showed little effect from this piecewise approach. Therefore, no changes were made to the models, and they will be used for all conditions.

LPMEOHTM Catalyst Life Study

We have embarked on a new set of LPMEOHTM catalyst life studies. The goal in the first stage is to understand and mitigate lab reactor artifacts, and reduce the lab baseline catalyst aging rate from the current 0.05 to 0.02%/hr at the LaPorte plant. This will allow us to resolve the difference (if any) in catalyst aging under LPMEOHTM conditions for different feed gases and to study catalyst aging under various LP conditions free of potentially misleading artifacts.

- Three life experiments under LPMEOHTM baseline conditions using our standard methanol catalyst were conducted with different slurry fluids. The first one used Drakeol 10 oil (our standard), the second one used Drakeol 10 with an additive, and the third one employed Drakeol 34 oil. All experiments showed fast aging in the first 150 hours on stream, followed by baseline aging. An investigation is underway to determine if this initial fast aging agrees with our previous observations and whether it is due to “super activity” burn-off or to lab artifacts.
- These three life experiments exhibited different initial catalyst activities. We are investigating whether this difference is due to a system error, to true effects of slurry fluid, or to lab artifacts.
- For the baseline LPMEOHTM conditions, the catalyst aging rates calculated from our new kinetic model and the original model are essentially identical. From now on, results will be reported based on the new model.

Screening Alternative Methanol Catalysts

The goal of this effort is to qualify more commercial methanol catalysts for liquid phase (LP) commercial use.

- A commercial methanol catalyst was tested under baseline LPMEOHTM conditions. It showed 300-hour initial fast deactivation before leveling off to the baseline-aging rate. We will investigate whether this long initial fast deactivation is real before concluding on the fate of the catalyst.
- The commercial methanol catalyst described above has lower pore volume than our current standard commercial catalyst, which is an advantage as far as the slurriability of the catalyst is concerned. The catalyst has an unusually large weight loss upon heating or reduction, probably due to inadequate calcination during manufacturing of the catalyst.
- The Air Products Pensacola methanol plant was visited on December 17th and 18th of 2001 to better understand the design and operation of the fixed-bed reactor. The equipment used for dimethyl ether production via methanol dehydration was also visited. The methanol reactor consists of four beds with intermediate cold feed injection and operates at 920 psig, producing 525 TPD of methanol. P&ID and heat and material balance information was obtained and will be evaluated.