ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS

FINAL

Technical Progress Report No. 30

For the Period 1 January - 31 March 2002

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^{TM} Kinetic Modeling

An initial evaluation of the new kinetic model with Kingsport data was completed for the current campaign 3 operating period (August 2001 to present). This evaluation involved the calculation of catalyst activity and deactivation rates using the new kinetic model and a further comparison of these values to values calculated with the old kinetic expression. This preliminary comparison shows that the new kinetic model generally yields higher deactivation rates and greater data scatter compared to results from the previous model.

Efforts were made to understand why different kinetic models give different aging rates and show different data scatter when they were used to analyze the Kingsport life data. Both types of results were found to be related to the sensitivity of a model to variations, either real or system noise, in the reaction conditions. The effort touches upon several basic issues associated with use of kinetic models for catalyst life study. The main observations include the following:

- The aging rate depends on the sensitivity of a model with respect to the change in reaction conditions. Part of this sensitivity is the result that aging may not be completely captured in the pre-exponential factor.
- Since the sensitivity changes from model to model and from condition to condition, different models may give different aging rates from the same life data. On the other hand, the same model can give different aging rates in different reaction regimes, although the aging in reality could be the same. In the latter case, the sensitivity issue should be accounted for in calculating the final aging rate.

LPMEOH^{TM} Life Study

Efforts were continued to understand and mitigate lab reactor artifacts and reduce the current baseline catalyst aging rate in the lab (0.05%/hr) to that at the LaPorte plant (0.02%/hr). This will allow us to resolve the difference (if any) in catalyst aging under LPMEOH^{TM} conditions for different feed gases and to study catalyst aging under various LP conditions, free of potentially misleading artifacts.

- Attention has been paid to the precision of our autoclave units to make sure the behaviors we have referred to as "reactor artifacts" are not due to system errors. Analysis performed on one of our 300 cc autoclaves showed that the unit can provide reproducible results with good precision. For example, the initial activity of the methanol catalyst can be measured within ±2% at the 95% confidence level. We have also checked the previous results and found that one of the possibly artifact-related behaviors, rapid deactivation in the first 150 hours on stream, has been consistently observed in the past several years.
- Our leading hypothesis on the nature of the reactor artifacts is adhesion of catalyst powders to the surface of reactor internals. The artifacts can occur at different stages of a run, leading to different artifact-related behaviors:
    - It has been shown that the artifact can occur during the reduction and/or very early hours of a run, leading to low initial catalyst activity. This occurrence was evidenced by the low initial activity that cannot be explained by the precision and reproducibility of the measurements, the change in catalyst activity when a run was resumed following an interruption, and the results from the runs using spent catalyst slurries.
    - The artifact also occurs in the first several hundred hours of a run, contributing to the rapid catalyst deactivation in this period (referred to as "rapid initial deactivation"). This occurrence has been shown by several experiments using spent catalyst slurries. Since the methanol catalyst in the spent slurries was stabilized in the original run, the rapid initial deactivation from these runs can only be attributed to lab reactor artifacts.
    - If the artifact persists, to a lesser extent, beyond the initial rapid deactivation period, it may contribute to the 2-times greater baseline aging rate observed from the lab reactors compared to that from the LaPorte plant reactor. Currently there is no definitive evidence for this theory. However, if this would be the case, reducing the lab reactor artifact could improve the lab baseline aging rate, making the catalyst life results from the lab more relevant to commercial applications.

- Coating reactor internals with Teflon was tried as a means to mitigate adhesion of catalyst powders to the surface of reactor internals. However, it did not work out as expected. The catalyst buildup on the Teflon-coated surfaces was very similar to that on the uncoated surfaces. Other methods will be tried.

Screening Alternative Methanol Catalysts

Qualification of a commercial methanol synthesis catalyst was continued. The results are as follows:

- An LPMEOH™ experiment was conducted using the spent slurry from the original qualification run. Similar to the original run, greater-than-baseline deactivation was observed in the first 200 hours on stream, followed by baseline aging. Since there is no reason to believe that the spent catalyst possessed any super-activity, the long, initial rapid deactivation in this run was most likely due to a reactor artifact. This probability makes it uncertain whether the long, initial rapid deactivation observed in the original run is due to the instability of the catalyst or just to reactor artifacts. Additional experiments will be conducted for qualification of this catalyst when an artifact-free LPMEOH™ experimental method is developed.
- TGA/IR analysis shows that the commercial methanol catalyst contains two times more copper/zinc carbonates than our standard methanol catalyst. This again indicates inadequate calcination during catalyst preparation.

DOE Topical Report

A draft of a DOE topical report was completed. The report covers our progress in understanding LPDME™ catalyst deactivation as a function of reaction conditions, developing stable LPDME™ operation with a γ-alumina-containing, dual-catalyst system, and elucidating the mechanism of catalyst deactivation under LPDME™ conditions.