ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS

FINAL

Technical Progress Report No. 24

For the Period 1 July - 30 September 2000

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

Screening Alternative Methanol Catalysts

Since we have only a single qualified supplier of LP methanol catalyst, finding a second supplier is a prime need.

- An alternate methanol catalyst with "in situ" reduction showed the same activity as that reduced using the standard procedures. However, its stability was poorer than that of the same catalyst reduced using the standard procedures. We suspect that this behavior was due to the "in situ" reduction's higher susceptibility to a lab reactor artifact. No more work on the stability of the alternate catalyst will be performed; the catalyst has been ruled out for the time being as a candidate due to other considerations.

LPMEOH^{TM} Kinetics–Water Injection

- Water injection is one way of compensating for the shortage of H_2 in coal-derived syngas. A LPMEOH experiment using high-CO gas, typical of that from a Shell gasifier, was conducted while water was added. For 3000 and 6000 space velocity, water injection increased yield. Increases in productivity as high as 32 and 24%, respectively, were found. Some discrepancies between the experimental and simulated results were observed, indicative of the inadequacy of our kinetic models under these previously unstudied conditions. Under water injection conditions, the catalyst appeared to be stable.

LPDME™ Stability: Catalysts, Conditions and Mechanistic Study

- We observed last quarter that close-to-baseline catalyst stability could be obtained under the conditions that simulate a possible DME production case. The close-to-baseline catalyst stability was confirmed using an alternative slurry fluid. This experiment ruled out the uncertainty associated with a laboratory problem.
- An alternate methanol catalyst has shown promising stability performance in our screening experiment in a 50 cc microclave. This catalyst was tested in a 300 cc autoclave reactor for its stability under LPDME conditions. The results show that it is not any more robust than our current methanol catalyst. These results once again demonstrate why we do not use the smaller reactors for stability tests.
- There appears to be a good correlation between the activity and the copper crystallite size of methanol catalyst samples from stable LPDME experiments. This indicates that the main cause of catalyst aging in the stable LPDME runs is due to copper sintering, the common cause of methanol catalyst deactivation. This correlation could be used as a reference point for identifying other non-sintering-related aging mechanisms. Further work is in progress to confirm this correlation.
- A unique catalyst deactivation pattern was observed under some LPDME conditions. The spent samples from these experiments were analyzed to understand the cause of this unique deactivation. The causes that were investigated and subsequently ruled out include lab artifacts and copper sintering. Transfer of materials between catalysts, our common explanation for aging under LDME conditions, could not be ruled out by these findings.

Investigation of Lab Reactor Artifacts

Lab reactor artifacts have become a concern recently for both LPDME and LPMEOH experiments. As we tested more and more new LPDME conditions, misleading results due to lab artifacts have been observed. For LPMEOH, our program has advanced to a new level where a lower baseline-aging rate is required. This would allow us to distinguish the small difference in catalyst aging under different LPMEOH conditions and to have a better correlation between lab and plant stability performance. Our current lab baseline-aging rate is two times greater than that observed at the LaPorte AFDU. We believe that this high baseline-aging rate is associated with lab reactor artifacts. Therefore, to understand the nature of lab artifacts and develop solutions has become a necessary step in the advancement of our program.

- A different slurry fluid (Drakeol 34 oil) has been used both to probe the nature of lab artifacts and as a solution to the problem. Its ability to mitigate lab artifacts was clearly shown in a LPDME experiment. However, the use of this new slurry fluid did not result in a better baseline aging rate under the standard LPMEOH experimental conditions. The effort in this area continues.
- Unusually high iron content has been detected in the samples from recent lab experiments. Efforts are being made to understand the origin of this high iron content. We are also evaluating the effect of this high iron level on our experimental results.

- The reactor system used for the artifact study has shown some erratic behavior in recent months, such as sudden stepwise changes in performance and a high noise level. The GC and sampling system will be examined to correct the problem.

Slurribility Study

- Additives have strong effects on the viscosity of methanol catalyst slurries, especially at high solids concentration and low shear rate. For example, for a 50 wt % slurry (reduced basis) at 10 s^{-1} shear rate and room temperature, an additive can reduce the viscosity by an order of magnitude. It may be that the lower viscosity will eventually lead to the possibility of higher catalyst loading and, consequently, higher reactor productivity.
- A fresh methanol catalyst slurry exhibited greater viscosity than a spent one, especially at low shear rates. This observation may have some implications for plant operation. For example, the high viscosity after reduction may pose some slurribility problems during initial operation.

Task 5: Project Management

LPDME™ Demonstration at LaPorte AFDU

A draft of a topical report on the results of the recent DME run was completed and sent to DOE for review.

A paper entitled "Catalyst and Process Development for Liquid Phase DME Synthesis" was presented at the 17th Annual International Pittsburgh Coal Conference (11-15 September 2000). The paper was included in a session on C_1 Chemistry and was well received.