

ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS

Draft

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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

Liquid Phase DME Demonstration

The DME run plan for the LaPorte AFDU was finalized at a meeting with R&D on 26 August (see Table 1). It will include 18 days of life study, as well as a process-variable study to evaluate the process at a lower space velocity, a higher superficial velocity, at stoichiometric feed composition and at a higher catalyst concentration. In addition, tracer studies will be conducted at two different velocities. The run plan is consistent with the objectives agreed upon with DOE (Table 2). Revised material and energy balances were calculated for the baseline condition ($SV = 6000$ and catalyst weight = 35%), as well as other process conditions. The MeOH and DME productivities determined experimentally compared well with the productivities calculated by simulation, as shown in Table 3. The simulations predicted maximum productivities based on fresh catalyst activity and two CSTRs in series. Hence, they were somewhat higher than experimental results.

Table 2
Liquid Phase DME Synthesis Run Objectives

- DETERMINE COMMERCIAL VIABILITY OF THE LPDME™ PROCESS ON A 10 T/D SCALE, USING COMMERCIALY PRODUCED CATALYSTS.
- OBTAIN INFORMATION TO CORRELATE SCALEUP OF CATALYST AGING FROM AUTOCLAVE TO BUBBLE COLUMN.
- CONDUCT PROCESS VARIABLE TESTING
- PERFORM EXPERIMENTS TO BETTER UNDERSTAND REACTOR HYDRODYNAMICS

Table 3
Comparison of Experimental and Simulated Productivities (gmol/hr kg)

	MeOH Productivity		DME Productivity	
	Experimental	Simulation	Experimental	Simulation
Baseline	9.5	9.9	8.9	9.4
Low Velocity	3.1	3	6.3	8.1
Stoichiometric Feed	21.7	23.6	8.2	7.7
High Velocity	13.7	14.1	8.5	9.8
High Concentration	13.7	14.1	8.5	9.8

A meeting was held with Syntex (formerly known as ICI Tracerco) to make plans for the hydrodynamic work. Radial gamma scans, as well as radioactive tracer injections, will be conducted. A fan type of source-detector arrangement will be used to improve reproducibility of the data. Detectors will be permanently installed to avoid alignment problems. The system will be checked out with empty tube and cold oil scans first, to determine if there are significant collimation issues with this type of arrangement. Gas and liquid, as well as solid mixing, will be studied at two different conditions using three different tracer materials. As in the past, argon will be used for the gas phase and

Mn₂O₃ fine particles will be used for the liquid as well as the methanol catalyst. A manganese oxide-doped gamma alumina sample was prepared by R&D and sent to Texas A&M for irradiation to examine the gamma alumina mixing.

Process Engineering, Operations and Safety personnel conducted a hazards review on 23 and 24 August to revalidate the LaPorte AFDU for the DME operations in October. Changes since the initial hazards review in 1994 were discussed, and safety documents were updated. The AFDU was approved for syngas operations starting 1 October.

TASK 3: RESEARCH AND DEVELOPMENT

Preparation for the LaPorte LPDME™ Trial

- A commercially available, in-stock dehydration material (Material #3) was qualified for the LaPorte LPDME™ trial. The dual-catalyst system containing this material appeared to be less susceptible to a lab artifact associated with high catalyst loading.
- One of the proposed cases for the LaPorte trial uses Shell gas and water injection. Several experiments under this condition set were conducted. The enhancement in productivity predicted by simulations was confirmed. Both stable performance and greater-than-baseline aging were observed. Further work is needed to map out the stable operation regime under water injection conditions.
- Another proposed LaPorte trial case involves using a stoichiometric feed gas (H₂:CO = 1:1). Experiments using this feed exhibited strong dependence on the reaction conditions. A specific set of conditions leading to stable performance for this feed has been identified and will be proposed for the upcoming LaPorte LPDME™ trial. The other two sets of conditions tested led to very rapid catalyst deactivation. XRD analysis ruled out hydrothermal sintering as the cause of the rapid deactivation.
- All four proposed cases for the upcoming LaPorte LPDME™ trial have been tested in a single lab simulating run, including using the catalyst materials that have been delivered to LaPorte. The run went smoothly, giving a baseline aging rate for all cases and expected productivity and selectivity.
- The tracer material has been prepared for the upcoming LaPorte trial. The Mn-loading measured by Texas A&M is very close to the loading expected from the preparation
- (4.6 wt %). The particle size distribution of the tracer material is almost identical to that of the dehydration catalyst to be used in the trial.

Other Research and Development

- A TGA method has been developed for determining the solid loading in catalyst slurries. The reliability of this method has been cross-checked using cyclohexane wash and found to be accurate. The details of this method are documented in a memo entitled “Determining Solid Loading in a Slurry by TGA.”

- The spent slurries from a LPMEOH™ and a LPDME™ experiment behaved differently when added to an oil-water mixture. This observation indicates that the two slurries have different surface properties. More work is needed to determine if and how these differences are related to the catalyst-loading-related lab artifact and to the performance of slurry phase reactors in general.

Kingsport LPMEOH™ Demonstration

Exposure of MK101 methanol catalyst to arsine (AsH_3) showed that arsine is a methanol catalyst poison. With unpoisoned Kingsport feed gas, a catalyst deactivation rate of 0.0731%/hr was obtained. Introduction of 578 ppb of AsH_3 into the feed gas increased the deactivation rate to 0.310%/hr. When the AsH_3 flow was stopped, deactivation returned to approximately the baseline rate, 0.0775%/hr. Subsequent exposures to lower AsH_3 concentrations showed that the deactivation rate was concentration dependent: 248 ppb, 0.202%/hr; 150 ppb, 0.177%/hr.

Experimental results involving exposure of MK101 methanol synthesis catalyst to hydrogen cyanide (HCN)-containing feed gases imply that HCN is not a methanol catalyst poison. Exposure to Kingsport or Shell gas feeds containing 2.3 or 4.2 ppm HCN resulted in the same catalyst deactivation rate as in the absence of HCN. These results are surprising in light of known Cu(I)-cyanide chemistry and suggest that HCN may react with the ZnO portion of catalyst to form $\text{Zn}(\text{CN})_2$. However, analysis of spent catalyst from Kingsport (528 days on stream) revealed less than 2.5 ppm of cyanide on the catalyst, which is consistent with a lack of cyanide reactivity.

A mixture of poisoned, spent Kingsport catalyst and an unpoisoned lab catalyst of known deactivation rate showed no evidence of increased deactivation over that of the lab catalyst. This result argues for minimal migration of poisons, especially arsenic, the most abundant contaminant on the catalyst.

Analysis of spent guard bed materials collected on 7 June 1999 revealed absorption of significant quantities of arsenic-, sulfur-, and cyanide-containing species. The $\text{MnO}_2/\text{Al}_2\text{O}_3$ portion of the Eastman guard bed contained absorbed sulfur and arsenic. The bed profile suggests that sulfur and arsenic compete for common absorption sites. Lower concentrations of iron, nickel, and copper were also observed. Analysis of the ZnO portion of the Eastman guard bed indicated substantial quantities of zinc cyanide, $\text{Zn}(\text{CN})_2$, approximately 30 mol % throughout the bed. The most reasonable source of $\text{Zn}(\text{CN})_2$ is the reaction of ZnO with gaseous HCN. Analysis of spent carbon from the Air Products guard bed indicated absorption of arsenic, manganese, and zinc. The arsenic concentrations were approximately constant throughout the bed, indicating saturation.

Monitoring for arsenic at Kingsport was accomplished by passing feed gas through carbon traps. Quantitative analysis led to the concentration of trapped arsenic, which was used to calculate concentrations of the most reasonable gas phase arsenic species, AsH_3 . One week after the Eastman and Air Products guard bed change-outs of 7 June 1999, gas stream analysis showed average AsH_3 concentrations of 39 ppb at the Eastman guard bed inlet and 18 ppb at the Air

Products guard bed inlet. AsH₃ concentrations at the Air Products guard bed exit were below the limit of detection, about 1 ppb. Subsequent analysis on 22-24 September 1999 indicated an AsH₃ concentration of 25 ppb at the Air Products guard bed exit.

TASK 5: PROJECT MANAGEMENT

Liquid Phase Fischer-Tropsch Demonstration

In July a meeting was held with personnel from Washington University in St. Louis to review the progress of their analysis work for the Fischer-Tropsch IV hydrodynamic data, discuss plans for potential hydrodynamic tests during the upcoming DME trial and review their progress under the hydrodynamic program. It appeared that they were just beginning the F-T IV analysis work, and significant effort was still pending. They requested specific information from the run, which both Air Products and SSFI (Shell Synthetic Fuels, Inc.) subsequently provided. In addition, data obtained using energy-sensitive detectors were obtained from Syntex (ICI Tracerco). With respect to the quality of data, it is clear that the improvements instituted for the tracer work have resulted in significant enhancements. As a result, the same protocol will be employed for the DME study.