ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS

Draft

Technical Progress Report No. 21

For the Period 1 October - 31 December 1999

Contractor

AIR PRODUCTS AND CHEMICALS, INC.
7201 Hamilton Boulevard
Allentown, PA 18195-1501

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DISCLAIMER

Alternative Fuels and Chemicals from Synthesis Gas

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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

Liquid Phase DME Demonstration

As planned, the DME run was started at the Alternative Fuels Development Unit (AFDU) during October. Calibration of the nuclear density gauge on the reactor was completed. A function test of the CO_2 removal system revealed no major problems; several pressure relief valves were removed and sent for maintenance because the valves lifted at pressures below their respective set pressures. Setup of the AFDU was completed, and carbonyl burnout was started on 8 October. In addition to providing a metal carbonyl survey, this procedure served as a hot function test with oil in the reactor and a syngas flow. Levels of iron and nickel carbonyl were both well below 10 ppb by 10 October. Syngas was then removed from the plant, and the plant was purged and drained in preparation for the start-up.

A 35 wt % oxide catalyst slurry was mixed in the 28.30 Prep Tank as per Test Authorization #56. The Prep Tank was charged with 1747 lb of Drakeol-10 oil, 894 lb of Haldor-Topsoe MK101P methanol catalyst and 47 lb of Englehard AL-3916P gamma alumina on 11 October. The proportion of the two catalysts corresponded to a 95:5 methanol-to-dehydration catalyst ratio. The slurry was heated and agitated in the Prep Tank for about two hours before it was transferred

to the reactor. Catalyst reduction began at 18:00 on 11 October. The reduction gas (3% H_2 in N_2) was set at 12,400 SCFH, with the reactor pressure at 67 psig (Run # A13). The heat up commenced at 18:50 hours and proceeded from 200 to 464°F, as planned (see Figure 1). The reduction appeared normal, as shown in Figure 2, and reached a cumulative uptake very close to the theoretical maximum value of 2.68 SCF/lb oxide. The reduction was essentially complete at 390°F, or 17 hours on-stream. The uptake curve was always above the minimum curve, as the reduction in the bubble column was faster compared to the autoclave. Nuclear density gauge measurements indicated an average gas holdup of 36.8 vol %, with a catalyst concentration of 40.1 wt % at 392°F during the reduction.

Reduction was completed at 18:00 hours on 12 October, and synthesis gas was brought into the reactor at 19:30. The start-up with syngas was smooth, and the operating conditions for Run 17.1 (Shell gas, 6000 sl/hr-kg, 750 psig, 482°F) were reached within 12 hours after the introduction of syngas. Stable reactor temperature and pressure were achieved. The reactor feed composition was then fine tuned, and a mass balance period began at 16:00 hours on 13 October. The catalysts appeared to have good initial activity, with DME and methanol productivity slightly exceeding expectations. This confirmed that the catalyst activation was proper. The DME production rate was estimated to be about 5 TPD compared to an expectation of 4.8 TPD, while the methanol production rate was 3.6 TPD, vs the 3.5 TPD expected. Calculations based on differential pressure measurements indicated that the catalyst concentration in the reactor was about 36 wt %, with a gas holdup of 41-42 vol %.

A 13-hour syngas interruption was experienced on 15 October due to a shutdown in the HYCO plant. The AFDU was put in a standby mode, with nitrogen flowing through the reactor at a lower temperature. The syngas became available at midnight on 15 October, and the plant was brought back to the baseline condition in 8 hours. Operations continued at the baseline conditions, and we reached 320 hours on-stream as of 27 October. Several material balances were generated during this period to track the catalyst performance. Preliminary results on catalyst productivities and activities are shown in Figures 3 and 4. After the expected initial aging, the catalysts appeared to be stabilizing, but there was significant scatter in the data. We found GC as well as sampling problems with methanol analysis that perhaps contributed to the scatter. The problems were fixed within two days. The initial deactivation rate appeared high: 0.08%/hr (2%/day) for methanol catalyst with a very high standard (std) error of 0.05%/hr (1.2%/day), and 0.03%/hr (0.6%/day) for dehydration catalyst with a 0.009%/hr (0.2%/day) std error. We decided to extend the aging run to gain a better estimate of the catalyst deactivation rate, which was our main objective. In order to stay within budget, the process variable study was eliminated. We still planned an extensive tracer study.

Operations continued at the baseline conditions in early November. At that point, we had completed 500 hours on-stream. The AFDU data appeared to follow the autoclave trends, with somewhat higher conversions than the autoclave. The methanol productivity level remained relatively constant, while DME productivity showed a slight decline. The scatter in data (see Figures 3 and 4) decreased significantly after the GC and the sampling problems were resolved (350 hours on-stream). The deactivation rate for both catalysts was estimated at 0.7%/day, which was lower than the 1.2%/day autoclave rate and only slightly higher than the 0.5%/day observed

during the first 3 weeks of the 120-day methanol run. Due to the initial scatter, the standard error was still high for the methanol catalyst: 0.34%/day.

As planned, an extensive tracer study was conducted at the baseline condition to evaluate gas, liquid and solid mixing. We decided to continue the life study after the tracer work instead of proceeding to the high-velocity condition, since we felt it was more important to gather additional life data at the baseline condition instead of more tracer data at a higher velocity. The catalyst life study was continued for two more days after completion of the tracer work. Data for a total of approximately 600 hours on-stream were obtained. The additional data resulted in improved statistics, with no change in the deactivation rates. Following a shutdown test conducted to obtain a better estimate of the gas holdup, the plant was shut down at 10:00 hours on 6 November. The slurry was cooled down under a nitrogen flow and then drained from the reactor.

The following is a summary of the accomplishments of the run:

- Commercial viability of the LPDME^{TM} process was successfully evaluated on a 10 T/D scale, using commercially produced catalysts. The plant was operated for 25 days on-stream to compare catalyst aging in a pilot-scale, slurry bubble column with that in a laboratory autoclave. The catalyst life study was extended to replace a planned process variable study, in order to obtain additional data on catalyst aging. Hydrodynamic information was obtained at the baseline conditions by conducting a detailed survey of the reactor with radioactive tracer injections.

- The deactivation rate for both catalysts was estimated at 0.7%/day. This rate was lower than the 1.2%/day observed for both catalysts in the autoclave, and it was slightly higher than the 0.5%/day rate achieved for the LPMEOH^{TM} process after 3 weeks of operation at LaPorte. Because the stability of the catalyst was better than that produced in the lab, further developmental work is recommended. Economic studies are also suggested to determine the impact of higher catalyst costs compared to those for the LPMEOH^{TM} process. The methanol productivity level remained relatively constant throughout the run, while DME productivity showed a slight decline. These trends are consistent with laboratory observations. The standard error for the methanol catalyst deactivation rate was high (0.25%/day) due to initial scatter in the data. The scatter in data decreased significantly after a GC problem and a sampling problem were discovered and resolved at 350 hours on-stream. The dehydration catalyst activity data were much tighter, with a 0.06%/day standard error.

- The catalysts were activated successfully with an expected hydrogen uptake. The initial productivities of methanol and DME were higher than those from the laboratory, perhaps due to the multiple-CSTR effect in the AFDU. The DME production rate started at 5.1 T/D and declined to 4.1 T/D in 25 days on-stream, while methanol production showed a scatter within the 3.1-3.8 T/D range through the run.

- The reactor operated in a hydrodynamically stable condition, with uniform temperature profile and gas holdups. Differential pressure measurements indicated about a 42 vol % gas holdup and a 36 wt % catalyst concentration.

- Preliminary mass balance calculations indicated good closure.

- The initial start-up was very quick, with the baseline condition reached in 12 hours after the introduction of syngas. A re-start after a syngas outage required only 4 hours, demonstrating the ease and flexibility of the slurry technology.

- Gas, liquid and solid phase mixing were studied at the baseline conditions using radioactive materials. Synetix collected a large amount of data using 34 detectors around the reactor. Several repeat injections were made during the gas and liquid injections to evaluate variability with time. Manganese oxide-doped gamma alumina was injected at four different locations to examine dehydration catalyst mixing. Both short- and long-term observations of irradiated dehydration catalyst suggested no alumina settling in the reactor. A post-run inspection of the reactor bottom head did not reveal any settled catalyst around the sparger, in contrast to the 1991 DME run when significant settled catalyst was found at the bottom. The tracer data will be analyzed with the help of personnel from Washington University in St. Louis as part of the Hydrodynamic Program with DOE.

- This demonstration represents a significant step forward in the development of the LPDME^{TM} process. The 0.7%/day aging rate achieved in the AFDU is a large improvement over the 4%/day autoclave deactivation of the previous catalyst system. Further R&D and economic studies are suggested to continue the developmental work.

Figure 1

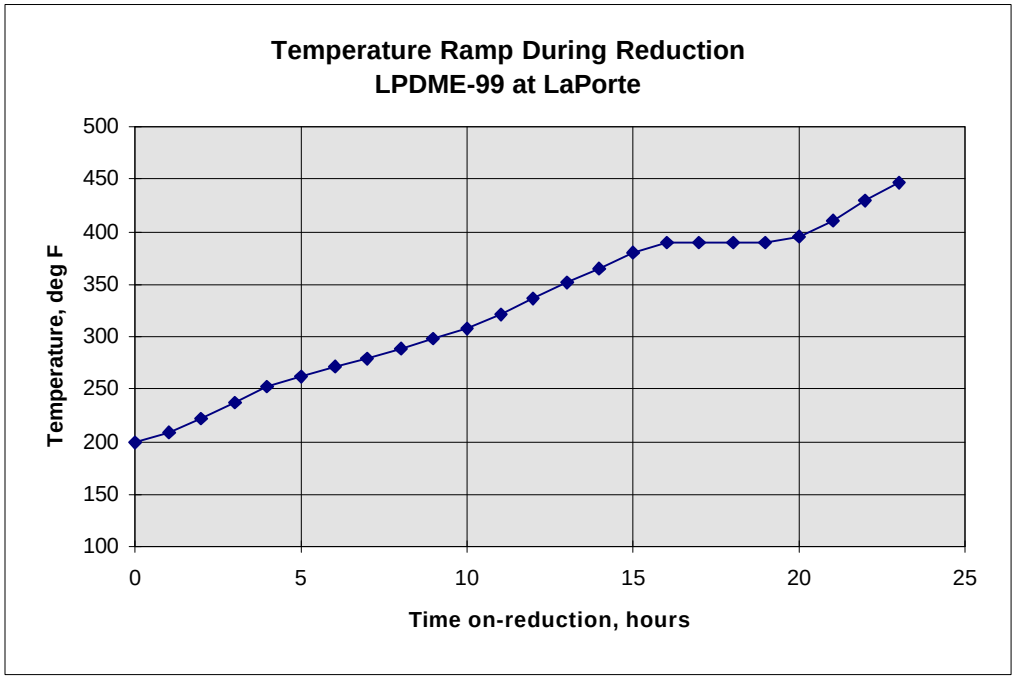


Figure 2

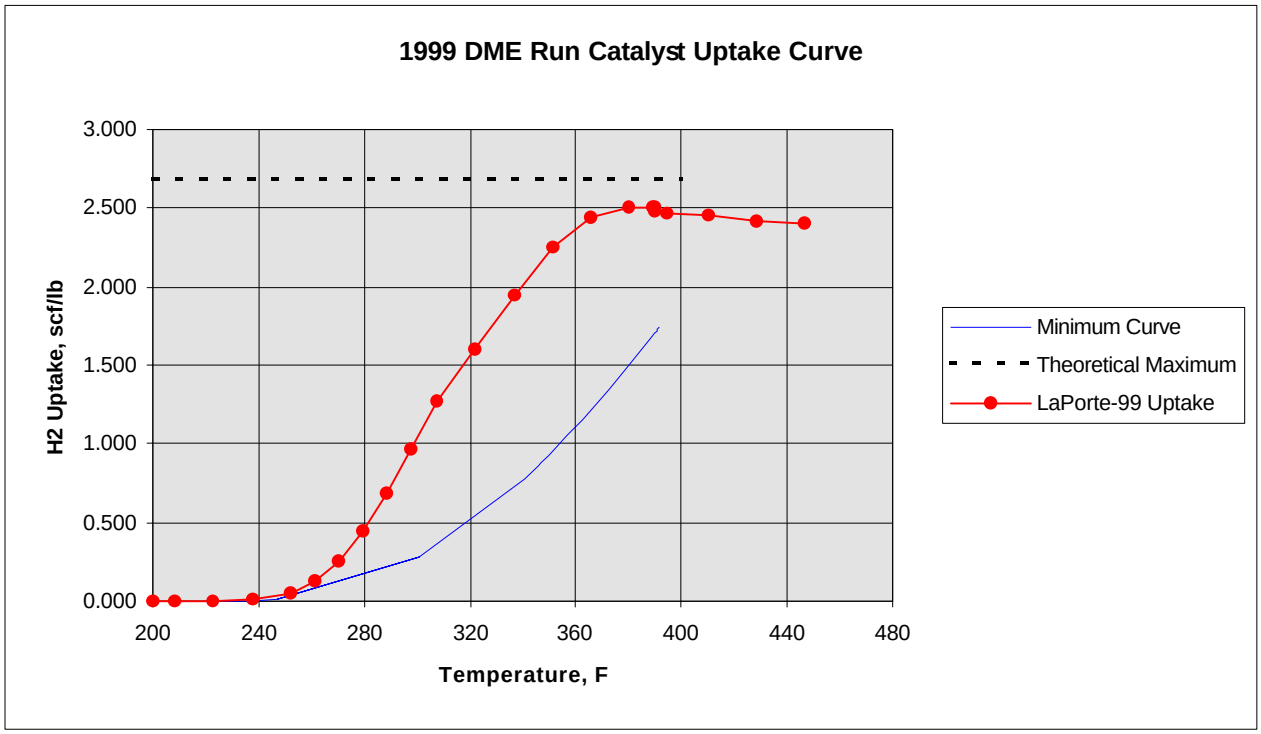


Figure 3

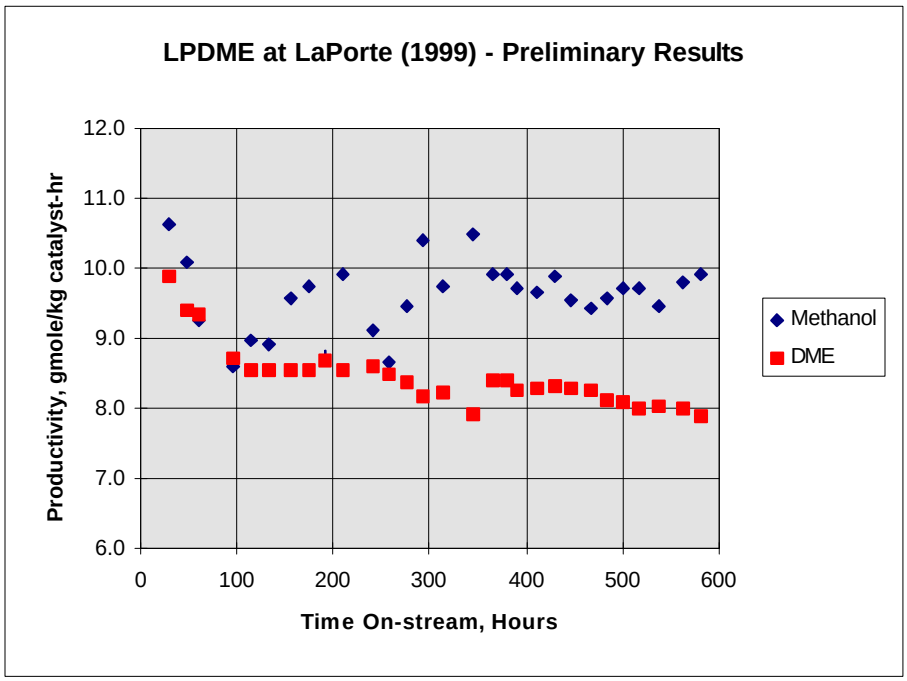
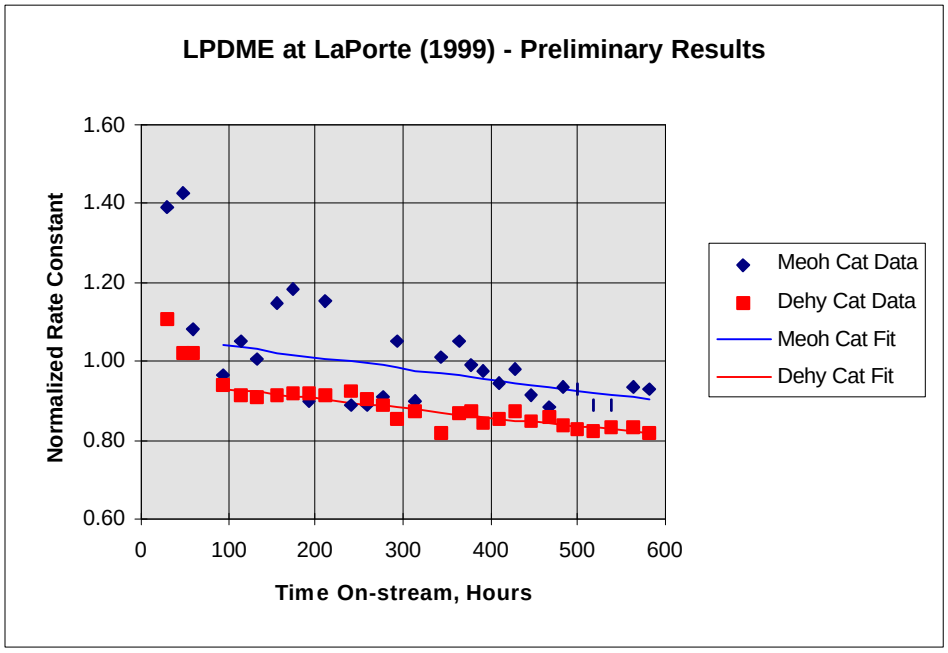


Figure 4



TASK 3: RESEARCH AND DEVELOPMENT

LaPorte LPDME™ Demonstration

- **Spent Catalysts from the LaPorte Trial Showed Expected Properties.** The activity of the spent catalysts from the 1999 LaPorte LPDME^{TM} trial was measured in the lab. The results support the stable performance observed at the LaPorte trial. The lab results also showed that the LaPorte bubble column reactor outperforms lab autoclaves because it is more than one CSTR. XRD analysis showed that the size of the copper and ZnO crystallites in the spent methanol catalyst was in the expected range.

- **Heavy Cu-Doping on Gamma-Alumina Did Not Mitigate Deactivation.** A LPDME™ experiment was performed using a "heavily" copper-doped gamma-alumina catalyst, along with a commercial methanol catalyst. Similar to the results we obtained previously using gamma-alumina doped with a smaller amount of copper, the heavy copper-doping showed little effect on stabilizing the catalyst system.

- **Three More Alternative Dehydration Materials Were Screened.** To conclude an ongoing effort, three alternative dehydration materials were tested for LPDME™ applications. None showed any significant activity.

- **Bifunctional DME Catalysts May Age Differently from Dual Catalysts.** Two preliminary experiments in 300-cc autoclaves showed that the bifunctional DME catalyst may be different from the dual-catalyst systems in terms of deactivation mechanisms. Furthermore, its aging appears to be less dependent on reaction conditions. These observations need to be confirmed using a more appropriate sample.

- **More Evidence for Lab Artifact Related to Catalyst Loss Was Observed.** The catalyst in a spent slurry from a previous LPMEOH^{TM} experiment showed higher activity than that measured at the end of the original experiment. This indicates that loss of catalyst from the slurry to the reactor interiors contributes, at least in part, to the apparently high baseline aging rate in lab autoclaves compared to that in the plant. A more quantitative estimate of the significance of this artifact requires more such experiments.

- **A Method for Lab Study of the Effect of Additives Was Examined.** Efforts were continued to develop an experimental scheme to study the effect of additives on the hydrodynamics of slurry phase reactors. We measured the apparent methanol synthesis activity in a 50-cc microclave as a function of the stirrer speed for slurries with and without an additive and observed different behaviors. Further work is needed to understand what the difference means and if it can be used to study the additive effect.

Kingsport LPMEOH™ Demonstration

The rate of MK101 methanol catalyst deactivation was found to vary in a non-linear fashion with respect to the arsine (AsH_3) feed concentration.

Gas phase analysis at the Air Products guard bed exit during the period 24 September to 17 October 1999 showed that about 40 ppb AsH_3 (or its equivalent) was entering the liquid phase reactor at Kingsport.

Analysis has shown no detectable amounts of fluorine in spent Kingsport catalyst slurries. Fluorine was found on spent MnO_2/Al_2O_3 absorbent from the Eastman guard bed, but only at the bed inlet, implying that fluorine-containing species were removed to below the limit of detection before the gas exited the bed. Exposure of the catalyst to fluorine is unlikely.

A second experiment involving HCN-containing syngas provided no evidence that HCN is a methanol catalyst poison. Using a Kingsport gas feed containing 6.57 ppm HCN, a deactivation rate of 0.0590%/hr was obtained compared with 0.0438%/hr for Kingsport gas alone. Because of considerable scatter in the data, these values are not statistically different. That HCN does not act as a catalyst poison is consistent with Cu(0)-HCN thermodynamics and with the observation that spent catalyst contains little or no bound cyanide.

Methanol catalyst deactivation rates in the presence and absence of acetonitrile, CH_3CN, were found to be the same. Using a Kingsport gas feed containing 11.5 ppm CH_3CN, we obtained a deactivation rate of 0.0895%/hr compared with 0.0870%/hr for Kingsport gas alone. These results imply that CH_3CN is not a methanol catalyst poison, consistent with known chemistry.

To evaluate the potential migration of contaminants in the liquid phase process, the deactivation rate of fresh MK101 catalyst in the presence of spent Kingsport catalyst was determined. Using a Kingsport gas feed, we obtained a deactivation rate of 0.0335%/hr for the fresh catalyst. Addition of an equal amount of spent Kingsport catalyst gave a deactivation rate of 0.0406%/hr. This result argues for minimal migration of poisons, especially for arsenic, the most abundant contaminant on the catalyst.

TASK 5: PROJECT MANAGEMENT - no activity this quarter.