DE-FC22-95PC93052--20

Alternative Fuels and Chemicals From Synthesis Gas

Quarterly Report
July 1 - September 30, 1995

Work Performed Under Contract No.: DE-FC22-95PC93052

For
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Office of Fossil Energy
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Disclaimer

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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.

SUMMARY OF ACTIVITY

- A two-day meeting was held with the DOE and subcontractors to kick off the Alternative Fuels II and Slurry Hydrodynamics programs. Preliminary results from the June run at LaPorte were presented. Discussions were lengthy and valuable.

- Further analysis was conducted on the results from the LaPorte Hydrodynamic run in June. In particular, the gas holdup estimates were investigated, as there appeared to be a systematic difference between gas holdup based on differential pressure (DP) measurements and nuclear density gauge (NDG) readings. DP transmitters were calibrated by filling the reactor with water. The calibrations resulted in only minor corrections in the zero and the span. The NDG-based gas holdup remains 15-20% higher than the DP-based holdup. Holdup based on shutdown tests conducted at three different conditions match well with the DP-based holdups. Discussions with Sandia National Lab personnel revealed that the NDG measurements will typically show higher holdup if a radial profile exists with higher holdup in the center. This occurs because NDG measurements weigh all the sections equally along the path of the radiation. For better accuracy, the sections near the center need lower weight since the amount of slurry with that holdup is smaller than at the sections near the wall. Typically, a radial profile for the holdup shows higher holdup in the center. This is expected to be even more prominent at high velocities studied in this run. An additional artifact could be the extra heat exchanger tubes in the annulus of the reactor, imposing further radial variations.

- A list of targets and objectives was received from Shell for a two-month (October-November 1996) run using their cobalt catalyst. Work has begun to determine design modifications needed to achieve the goals. Shell has agreed to reduce per-pass conversion to 40%. This will require connecting the F-T train to the oxygenate recycle compressor. In addition, proper degassing and possibly stripping of the reactor slurry will be required for filtration at lower temperature. Mass balance information at operating conditions (to be defined) is needed to put together an air emission permit exemption application. Mass balance information is also needed to develop the flow scheme. Information on cross-flow filtration flux is needed to design the filter loop.

- A confidentiality agreement was signed between Air Products and Shell for the Fischer-Tropsch III test run at LaPorte. Proprietary information exchange and related process work can now go forward for the October-November 1996 run. A meeting with Shell personnel is planned in late October.

- In LPDME™ studies, the bifunctional single particle DME catalyst patented by Shell deactivated rapidly in both slurry and gas phase reactions. The slurry run was a repeat of one conducted earlier that showed the same effect.

- Tetraglyme, a hydrophobic ether, is an unsuitable slurry fluid for DME service due to its reactivity with alumina at reaction temperatures.

- Encapsulation of alumina with SiO_2 did not increase LPDME™ catalyst life. Fracture of the alumina particles is the most likely cause of this behavior.

- In LPDME™ studies, modified Catapal B δ-alumina, zinc exchanged Y, and silicon ammonia phosphate were tested for use as the dehydration catalyst. Modification of the δ-alumina with did not help with the stability of the catalyst system. The latter two samples exhibited nil activity. Although the silicon ammonia phosphate sample was inert in the LPDME™ run, fast long-term deactivation of the methanol catalyst was observed in this catalyst system.

- As reported by others, DME life data involving a CuO-modified alumina dehydration catalyst were inconclusive because of (unreported) mass transfer limitation in the testing apparatus. The life run was repeated under the conditions free of mass transfer limitations in our 300-cc autoclave using our version of this catalyst. The results show that the catalyst system deactivated at a rate similar to our standard dual catalyst system.

- Baseline LPDME™ tests using a copper-lined reactor for both MEOH and DME synthesis exhibited the same behavior as seen for the normal reactor. Thus, abrasion of the stainless steel walls was ruled out as a possible source of the faster aging seen in the laboratory reactors compared with the plant.

- At Aachen, a second plug flow reactor has been calibrated. Mass transfer limitations in high temperature CSTR are being studied. Isobutanol catalyst preparation using sol gel techniques continues and should be finished by next month. Undecanol is not stable enough for use as

an inert slurry medium at high temperatures. Theoretical studies indicate that mass transfer should not be a problem in the new slurry reactor; however, unusual pressure behavior continues. The fixed bed reactor is being operated and mass balances are being verified.

- At Lehigh University, the undoped CuO/ZrO_2 catalyst that was first reported in the May monthly report was tested further for reproducible catalytic behavior in $H_2/CO = 70.30\%$ with and without CO_2. The co-production of dimethyl ether during methanol synthesis may be controlled by varying the mol % CO_2 in the synthesis gas.

- The previously tested Cu/ZrO_2 catalyst (10/90 mol %) for alcohol/DME synthesis was tested again, except that water was added to the H_2/CO (70/30 vol %) feed. At 250°C and 1100 psi with an initial GHSV of 6120, the methanol productivity decreased by 83%, DME productivity stopped, and CO_2 productivity increased by over 300%.

- In work at Delaware, the final washing procedure, for example, an acetone final wash, affects catalyst performance. Contrary to results in the factorial experiment, varying copper level had little effect on performance. Interaction between MnO/CuO and ZrO_2/CuO ratios or operation at equilibrium are given as two possible explanations for this difference. Interestingly, the ability to reduce copper may be an advantage at high temperatures. (Yields continue to be about 19 g/IBOH/Kg-hr @ GHSV = 2900/hr, 1000 psi, 400°C).

- During September, Air Products compared the catalytic activity of a polymer-supported, covalently bound Rh complex (USP5371274) to an ionically bound Rh on Reillex for the MeOAc to EDA conversion at 150°C. The covalently bound complex showed a higher activity in the presence of 3-picoline as a promoter. Although the ionically bound catalyst showed a higher initial activity in the presence of 3-picoline, the activity fell rapidly with recycle due to leaching of Rh from the polymer. We feel that the ability of our system to operate at a higher temperature (190°C) without the added promoter offers a distinctive advantage over the covalently bound system. Literature suggests that polymer-supported, covalently bound Rh complexes leach from the polymer with time.

- The cracking of ethylidene diacetate to vinyl acetate (VAM) has proven to be problematic in the gas phase. Liquid phase experiments suggest that equilibrium is a problem. Distillation experiments show that the equilibrium can be shifted by removing the VAM as it is produced.

- At Eastman Chemical, research has been initiated on the synthesis of acetaldehyde from syngas. The current focus is on the sequential conversion of syngas to methanol to acetic acid, followed by hydrogenation of acetic acid to acetaldehyde. A proprietary catalyst has been discovered that can convert acetic acid to acetaldehyde with selectivities of 50-80%.

- At Bechtel, in Task 4.2, Commercial Applications (Mixed Alcohol Synthesis), the model for the third scenario, a stand-alone mixed alcohol synthesis (MAS) plant, was completed and is being tested. Development of a model for an alternative version of the first scenario, IGCC/MAS in a utility setting, was started. This version is based on a cycling power plant,

optimum selectivity from the MAS plant and no production or storage of methanol for peaking fuel. The effect of MAS productivity on MTBE cost will be examined.

- At Bechtel, in Task 4.5, Syngas Generation and Cleanup, calculations were made for several IGCC/MAS scenarios for the two coal feedstocks and the three gasification technologies to bracket a range of syngas flow rates to the sulfur removal processes. Nonproprietary information was obtained on three types (chemical, physical, hybrid) of conventional regenerable solvent-based sulfur removal processes. The heat and material balance and the process flow diagram for the syngas generation and cleanup for the petroleum coke case were completed. Work continued on the trace contaminants investigation.

- Electrical utility work and ventilation work on the Field Test Laboratory are essentially complete. This project is still on time and within budget.

- A meeting was held with Reema International (now REMTECH) and DOE on August 29 to discuss Reema's interest in demonstrating its F-T process at LaPorte. Reema is a small, privately owned oil and gas company based in Denver, Colorado. Significant business and technical discussions are required before the project can be kicked off. Reema will visit Air Products in mid September. An operating window of April-June 1996 was given, assuming that we do not need significant modifications and the project can be kicked off in the October-November time frame.

RESULTS AND DISCUSSION

TASK 1: ENGINEERING AND MODIFICATIONS

1.1 Liquid Phase Fischer-Tropsch Demonstration on Behalf of Shell Oil

A list of targets and objectives was received from Shell for a two month (October-November 1996) run with their cobalt catalyst. Work began to determine design modifications needed to achieve the goals. Some immediate issues needed resolution before further evaluations could be made: (1) It appeared that at high conversion (~80%) and high pressure (750 psig), the dew point for water (~235°C) is very close to the operating temperature (240-250°C). The heat exchanger tubes would be significantly colder (170°C) and the target temperature for filtration was 150°C. (2) Mass balance information at operating conditions (to be defined) is needed to put together an air emission permit exemption application. It is a long lead item that needs immediate attention. Mass balance information is also needed to develop the flow scheme. (3) Information on cross-flow filtration flux is needed to design the filter loop.

Response from Shell on issues was limited, pending signing of confidentiality agreements. Shell agreed to reduce per-pass conversion to 40% with a recycle in order to avoid water condensation in the reactor. This will require connecting the Fischer-Tropsch (F-T) train to the oxygenate recycle compressor. In addition, proper degassing and possible stripping of the reactor slurry will be required for filtration at lower temperature.

At the end of September, a confidentiality agreement was signed between Air Products and Shell for the F-T III test run at LaPorte. Proprietary information exchange and related process work can now go forward for the October-November 1996 run. A meeting with Shell personnel is planned in late October, followed by an update with DOE.

Tasks 1.2, 1.3, and 1.4 No progress to report this quarter.

TASK 2: AFDU SHAKEDOWN, OPERATIONS, DEACTIVATION AND DISPOSAL

2.1 Liquid Phase Hydrodynamic Run

Further analysis was conducted on the results from the "Hydrodynamic" run in June. In particular, the gas holdup estimates were investigated, as there appeared to be a systematic difference between gas holdup based on differential pressure (DP) measurements and nuclear density gauge (NDG) readings. DP transmitters were calibrated by filling the reactor with water. The calibrations resulted in only minor corrections in the zero and the span. The NDG-based gas holdup remains 15-20% higher than the DP based holdup (see Figures 2.1 and 2.2). Holdups based on shutdown tests conducted at three different conditions match well with the DP-based holdups. In addition, estimated holdups from correlations based on NDG data at low velocities have a better match with holdups from DP data. Discussions with Sandia National Lab personnel revealed that the NDG measurements will typically show higher holdups if a radial profile exists with higher holdups in the center. This occurs because NDG measurements weigh all the sections equally along the path of the radiation. For better accuracy, the sections near the center

FIGURE 2.1

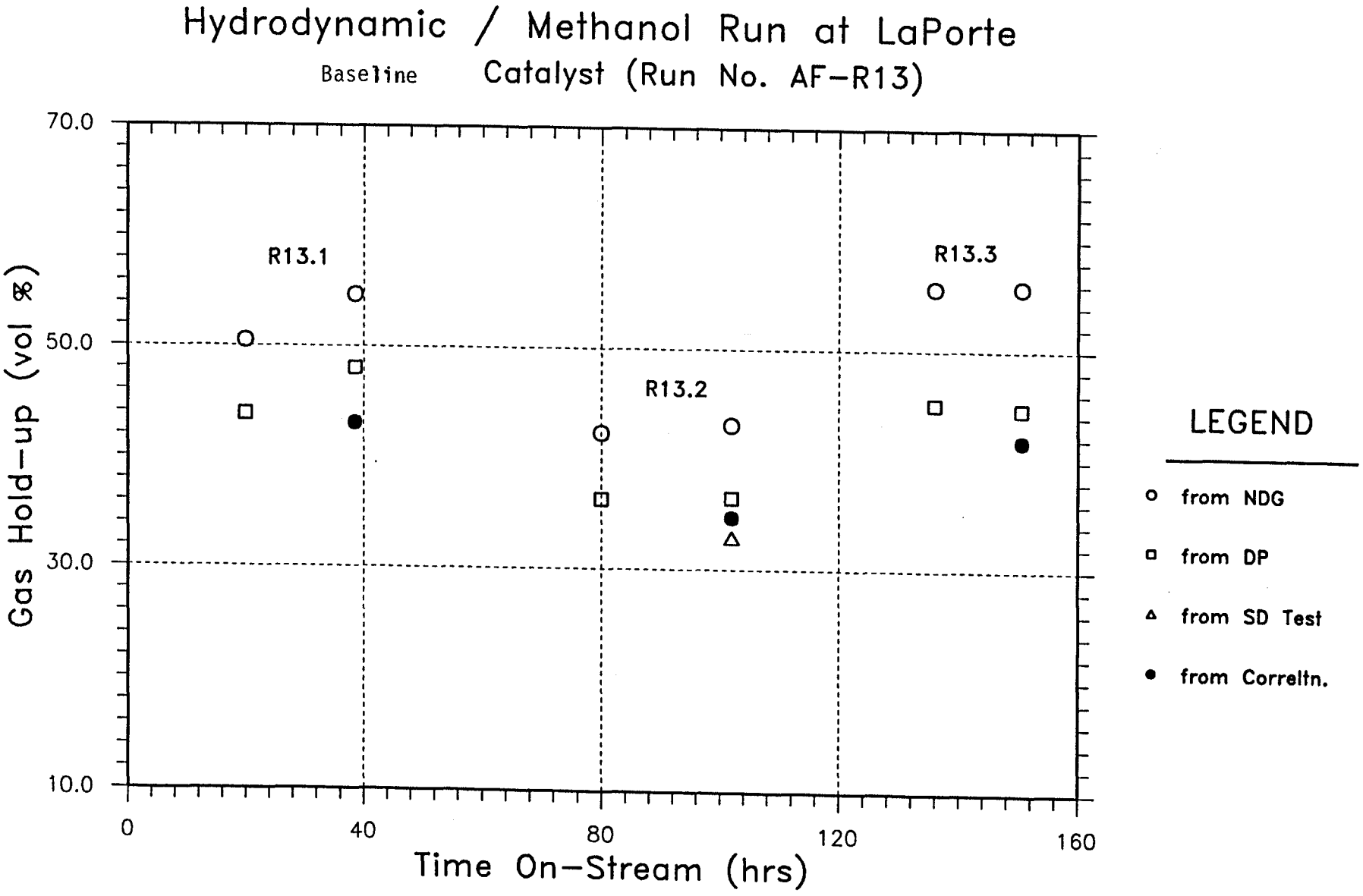
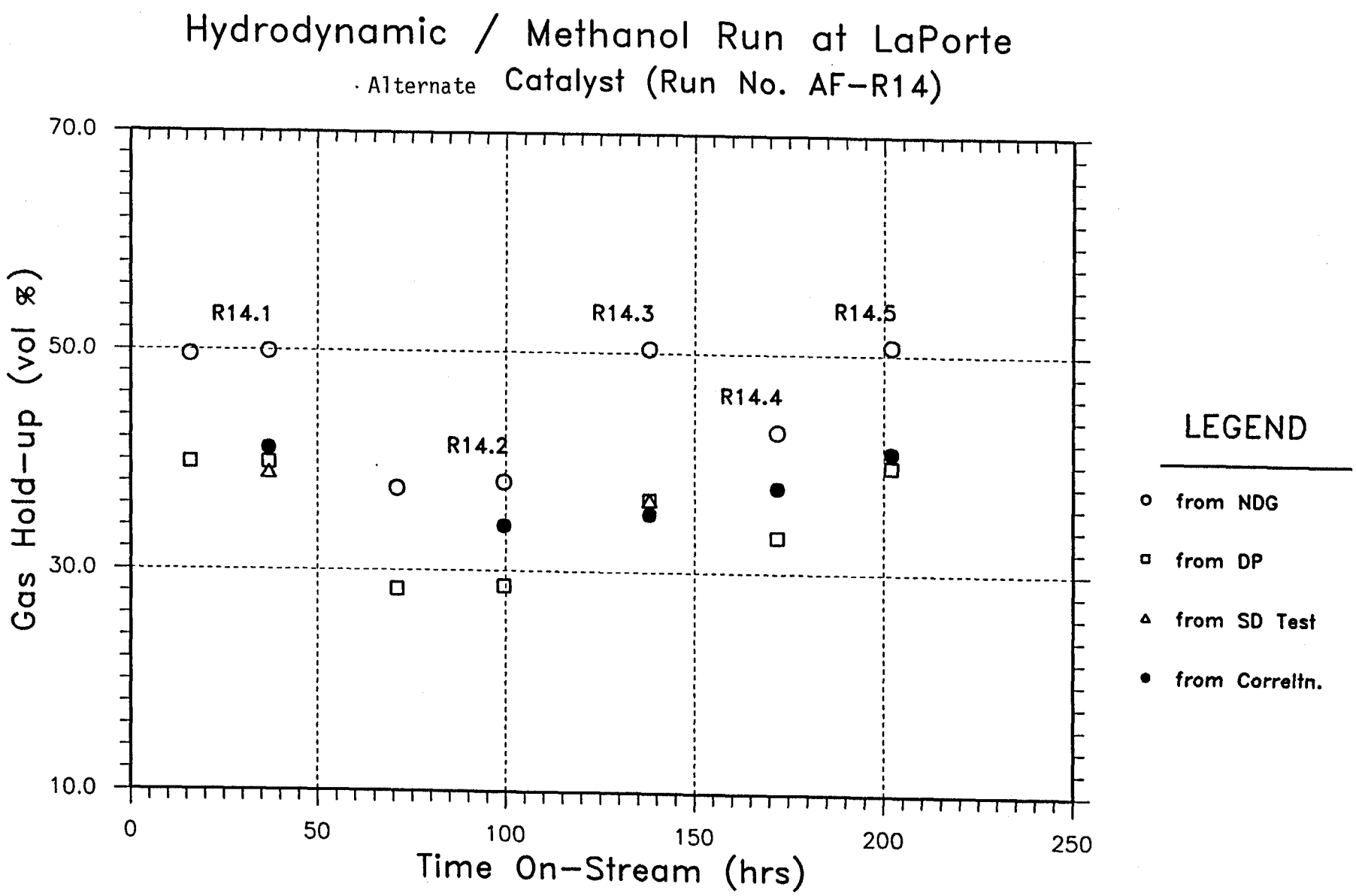

Hydrodynamic / Methanol Run at LaPorte
Baseline Catalyst (Run No. AF-R13)
70.0
50.0
30.0
10.0
Gas Hold-up (vol %)
R13.1
R13.2
R13.3
0
40
80
120
160
Time On-Stream (hrs)
LEGEND
from NDG
from DP
from SD Test
from Correltn.

FIGURE 2.2


Hydrodynamic / Methanol Run at LaPorte
Alternate Catalyst (Run No. AF-R14)
Gas Hold-up (vol %)
70.0
50.0
30.0
10.0
0
50
100
150
200
250
Time On-Stream (hrs)
R14.1
R14.2
R14.3
R14.4
R14.5
LEGEND
from NDG
from DP
from SD Test
from Correltn.

need a lower weight since the amount of slurry with that holdup is smaller than that of the sections near the wall. Typically, a radial profile for holdup shows higher holdup in the center. This is expected to be even more prominent at the high velocities studied in this run. An additional artifact could be the extra heat exchanger tubes in the annulus of the reactor, imposing further radial variations.

TASK 3: RESEARCH AND DEVELOPMENT

Task 3.1 Improved Processes for DME

This quarter's work concentrated on the screening of alternative LPDME™ catalysts. The candidates were chosen from the following categories based on our current understanding of catalyst deactivation:

- Chemically modified alumina to reduce the driving force of the interaction between methanol and dehydration catalysts.
- Physically modified alumina to eliminate the contact between the two catalysts.
- Other solid materials of moderate acidity.
- Alternative methanol catalysts such as single catalyst systems.

Most catalysts tested exhibited poorer stability than the standard dual catalyst system (S3-86 plus Catapal B δ-alumina). One catalyst system exhibited improved long-term stability of the methanol catalyst.

A Japanese laboratory has recently reported a catalyst system that is stable under LPDME™ conditions. However, the life data are not reliable, or are at least inconclusive, since our analysis of the article showed that the life-test experimental conditions were subject to severe mass transfer limitations. We repeated the life run under the conditions free of mass transfer limitations. The results show that the catalyst system deactivates at a rate similar to our standard dual catalyst system.

Efforts were also made to understand the nature of the detrimental interaction between the methanol synthesis and dehydration catalysts under LPDME™ conditions. SEM (scanning electron microscopy) and EDS (energy dispersive X-ray spectrometry) analysis of different catalyst systems were used to determine if deactivation is due to the migration of zinc and copper from the methanol catalyst to the dehydration catalyst (e.g., δ-alumina). Some of the results indicate that migration of zinc and copper from the methanol catalyst to alumina occurred under the reaction conditions. However, other inconsistent observations call for more complementary analyses before a definite conclusion can be made.

3.1.1 Screening of Alternative Catalyst Systems

3.1.1(i) δ-alumina

In the last quarterly we reported a dual catalyst system in which improved long-term stability of the methanol catalyst under LPDME™ conditions was observed for the first time. The dehydration catalyst in that system is a γ-alumina heavily doped with potassium. Improved long-term stability of the methanol catalyst was observed again this quarter when a δ-alumina (Condea Puralox scca-5/90) was used along with the S3-86 methanol catalyst. The run was carried out under the standard reaction conditions (250°C, 750 psig, 6,000 GHSV, 80:20 catalyst ratio) using Texaco gas. The results from this run are depicted in Figures 3.1.1a & b, along with those from the catalyst systems containing the K-doped γ-alumina and virgin γ-alumina (e.g., standard system). As can be seen in Figure 3.1.1a, the long-term stability of the methanol catalyst in this catalyst system is improved.

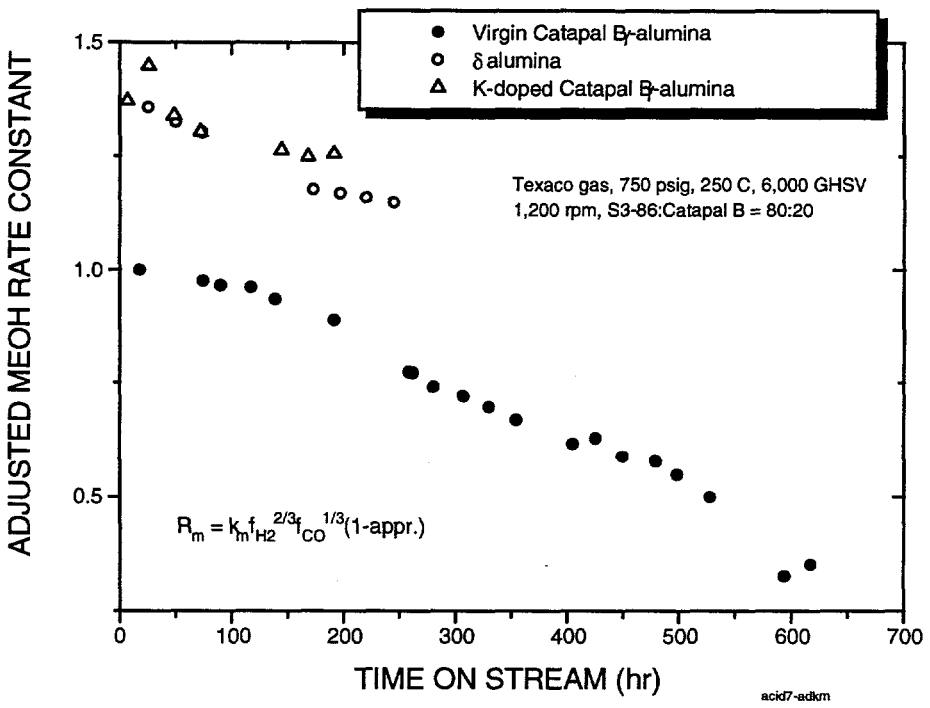
Currently, we are trying to understand why the long-term stability of the methanol catalyst is improved in this system and in the system that contains the K-doped γ-alumina. As shown in Figure 3.1.1b, the dehydration activity of both δ-alumina and K-doped γ-alumina are very much lower ($k_d \leq 3.0$ and 1.3, respectively) than that of γ-alumina. We have tested systems with similar and poorer dehydration activity, such as those using Chabazite ($k_d \leq 1.3$), Mg-Y ($k_d \leq 0.9$), and a silica alumina sample ($k_d \leq 0.6$) as dehydration catalysts (see April-June quarterly). However, the long-term deactivation of the methanol catalyst in these systems is similar to the relatively rapid deactivation of the standard system. This indicates that lower dehydration activity does not guarantee better long-term stability of the methanol catalyst. What we would like to understand is whether the low dehydration activity is a necessary condition for the long-term stability of the methanol catalyst. If it is, we should look for weakly acidic materials with high site density as dehydration catalysts, since it is assumed that the low activity seen in these two systems is related to the weak acid sites. If low activity is not a necessary condition, we need to understand what is special about these two systems so that screening guidelines can be developed for alternative dehydration catalysts.

3.1.1(ii) Modified γ-alumina

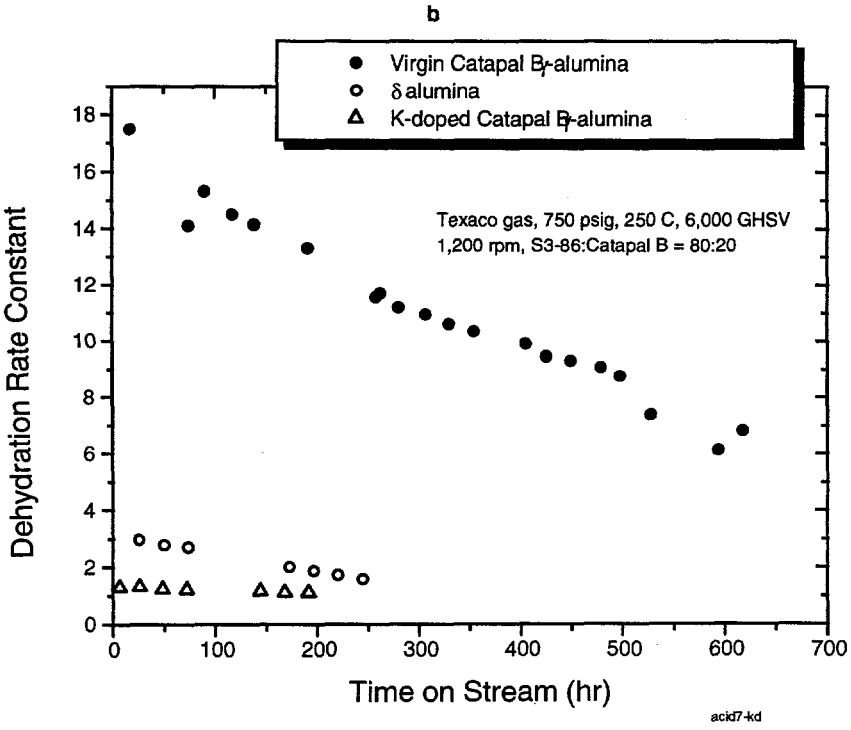
Three modified Catapal B γ-alumina catalysts have been tested. The modification methods include impregnation using potassium, silylation using $(Me_3Si\text{-})_2NH$, and encapsulation with SiO_2. The potassium-impregnated sample was prepared by the incipient wetness method using a KOH aqueous solution. This sample had higher dehydration activity due to a lower K loading than the K-doped sample discussed in section 3.1.1(i) (0.15 vs. 0.8 wt% of K). The goal of this new preparation was to determine if the improved long-term stability of the methanol catalyst seen in the sample with 0.8 wt% K loading could still be retained with a more active K-doped alumina. Silylation using $(Me_3Si\text{-})NH$ was aimed at removing the strong acid sites on Catapal B γ-alumina. The sample was prepared by refluxing Catapal B γ-alumina in $(Me_3Si\text{-})_2NH$. If an inert, porous layer of SiO_2 can be formed on the outside of alumina particles, intimate contact between the alumina and the methanol catalyst should be prevented. This, in turn, should lead to good stability of the catalyst system. The encapsulation of the alumina with SiO_2 was carried out according to a DuPont patent (US Patent 4,677,084). The LPDME™ runs using these three

Figure 3.1.1 LPDME™ Life Runs of Different Catalyst Systems

a



b



dehydration catalysts were all conducted under the standard reaction conditions using BASF S3-86 as the methanol synthesis catalysts. The results are plotted in Figures 3.1.2a and b against those from the standard catalyst system.

In contrast to the previous result obtained using 0.8 wt% K loading, doping the alumina with 0.15 wt% of K did not result in better long-term stability of the methanol catalyst. Figures 3.1.2a and b show that the long-term stability of both methanol synthesis and dehydration catalysts in this system is poorer than that of the standard dual catalyst system. We do not understand why the potassium doping at different levels leads to different effects on the long-term stability of the catalyst system. The effect cannot be attributed to the acidity of the dehydration catalyst because the dehydration activity of the 0.5 wt% sample (k_d = 8.5) lies between the virgin alumina (k_d = 17.5) and the 0.8 wt% sample (k_d = 1.3).

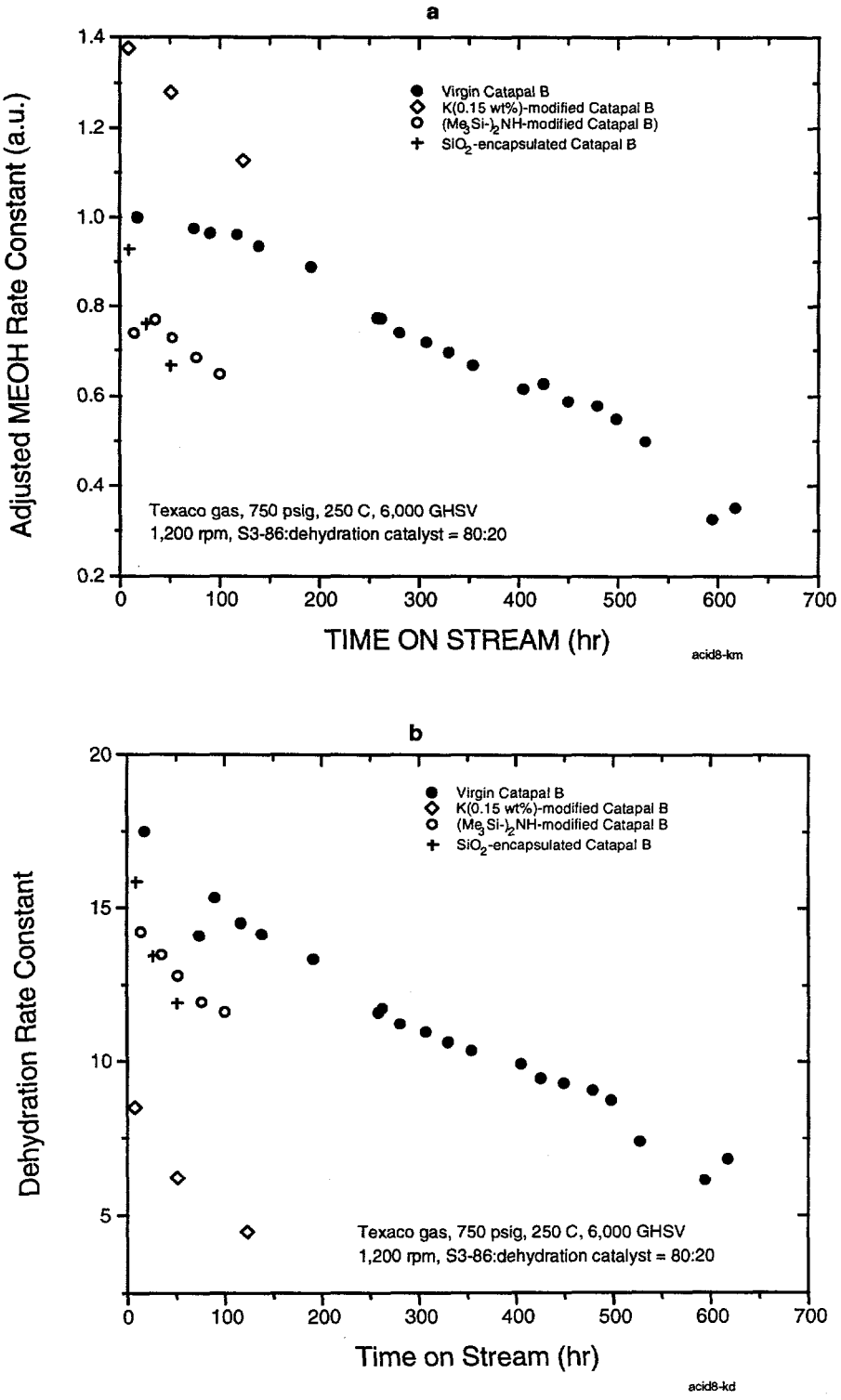
Figures 3.1.2a and b shows that silylation of Catapal B γ-alumina with $(Me_3Si\text{-})_2NH$ does not result in better long-term stability. The initial deactivation of the methanol catalyst in this system is also greater than that in the standard system. Since silylation in general is believed to passivate the strong acid sites on acidic solid materials, this greater initial deactivation is probably due to the poisonous species in the $(Me_3Si\text{-})_2NH$-modified alumina.

The SiO_2-encapsulated alumina sample was analyzed prior to the run by scanning electron microscope (SEM) and energy dispersive X-ray spectrometry (EDS). The results show that most of the silica, as desired, was on the exterior of the alumina particles. However, this sample did not bring about the better stability we expected. As shown in Figures 3.1.2a & b, the stability of this system is poorer than the standard catalyst system; both methanol and dehydration catalysts deactivated very rapidly. Another run (not shown) using the same sample calcined at a higher temperature yielded a similar result. The poor stability may have been due to the poor mechanical strength of the encapsulated alumina particles. Evidence of this hypothesis is the observation that during the SEM/EDS experiments the preparation of the cross section of alumina particles was much more difficult compared to virgin Catapal B γ-alumina because the particles broke apart readily. The SEM cross section of an alumina particle also appeared flaky. The exposure of the alumina to a fairly strong acidic environment (pH = 2) during the encapsulation may be the reason for the lower strength. If the particles cannot retain their integrity, a protective layer of SiO_2 will be useless. The cleavage of the particles under the reaction conditions (strong agitation) will create an active alumina surface, which then interacts with the methanol catalyst to cause the deactivation of both catalysts. This issue will be examined in greater depth, and further efforts will be made to prepare encapsulated alumina samples.

3.1.19(iii) Other Acidic Materials

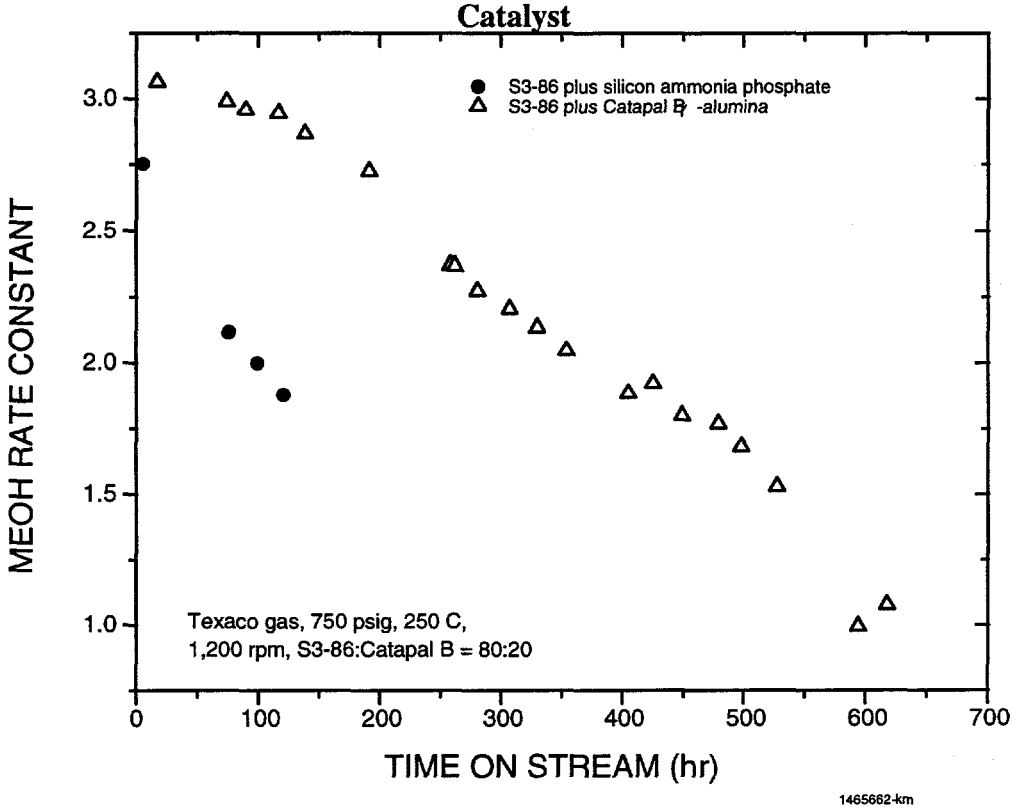
Two samples we tested in this category are silica ammonia phosphate and zinc ion-exchanged zeolite Y (Zn-Y). The LPDME™ run using the silicon ammonium phosphate sample as the dehydration catalyst was conducted under the standard conditions (250°C, 750 psig, 6,000 GHSV) using Texaco gas. It has been shown in Air Products' laboratory that the activity of this sample toward isobutanol dehydration at 300°C is similar to γ-alumina. Surprisingly, little

Figure 3.1.2 The Stability of Different Catalyst Systems under LPDME™ Conditions



dehydration activity was detected in the LPDME™ run. Increasing the temperature to 280°C had little effect. An interesting observation from this run is that the long-term deactivation of the methanol catalyst in this system is faster than in the standard catalyst system (Fig. 3.1.3), even though the phosphate sample did not show any dehydration activity. This again indicates that the dehydration activity, or acidity, is not necessarily the cause for the long-term deactivation of the methanol catalyst. When the reactor was taken apart after the run, it was observed that the spent catalyst stuck to the surface of the reactor hardware more strongly than it did in the standard catalyst system.

Figure 3.1.3 A LPDME™ Life Run Using Silicon Ammonia Phosphate as the Dehydration Catalyst



Zn-Y was chosen on the basis of the migration hypothesis. If Zn migration from the methanol catalyst to the dehydration catalyst is the cause of catalyst deactivation, it is unlikely that migration will take place in a dehydration catalyst that has already been saturated with Zn, such as Zn-Y. However, this sample did not exhibit any dehydration activity.

3.1.1(iv) Single Catalyst System — Cu and Zn Supported on γ-Alumina

It was reported in the April-June quarterly that a single particle catalyst system consisting of Cu, ZnO supported on γ-alumina has a poorer stability under LPDME™ conditions than the standard dual catalyst system. That catalyst was prepared by impregnating Catapal B γ-alumina powders with zinc and copper nitrate followed by calcination in air, in accordance with a Shell patent (US 4,375,424, 1983). To find out if the poor stability is intrinsic to the catalyst or related to the slurry phase operation, a similar catalyst was prepared from Catapal B γ-alumina pellets and

tested in a packed bed reactor. The final Cu and Zn content based on an elemental analysis was 4.0 and 4.6 wt%, respectively. The catalyst bed was diluted with quartz chips. The reduction was carried out using 2% H_2 in N_2 at 700 psig and a ramp from room temperature to 250°C in 3 hr, mimicking the Shell procedures. Two packed bed runs were conducted because some equipment problems were encountered in the first run. The results from these two runs are displayed in Figure3.1.4, along with the runs conducted in the autoclave using the single catalyst and the standard dual catalyst system.

Figure 3.1.4 The Stability of a Single Catalyst System

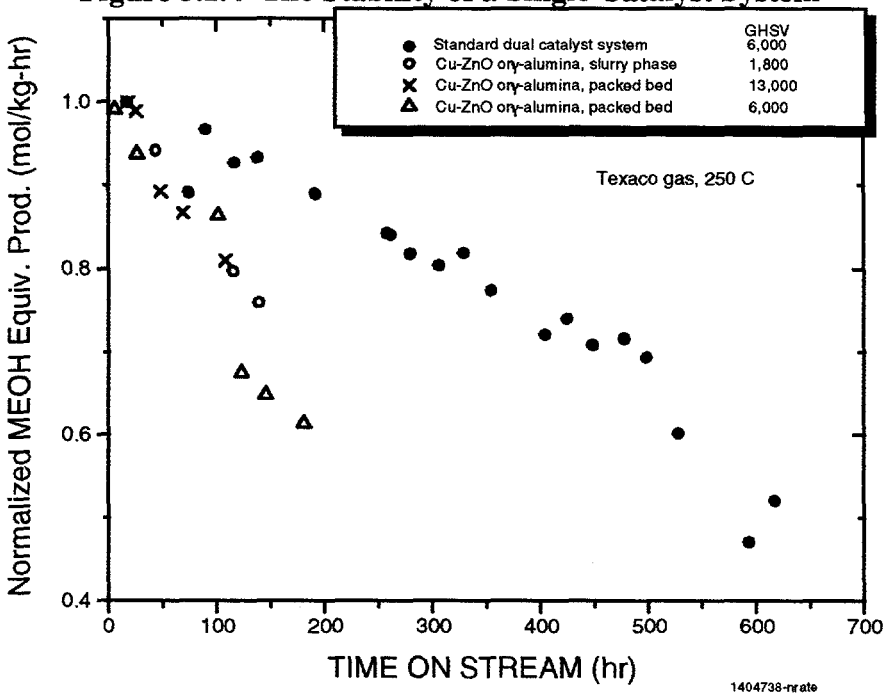


Figure 3.1.4 shows that the aging pattern of the single catalyst system in the packed bed runs is similar to that in the slurry phase run. This indicates that the poor stability is intrinsic to the catalyst sample, rather than to the slurry phase operation. In order to test the single catalyst concept, a DME catalyst that is at least stable in the gas phase operation is needed.

Several data points were collected at 270°C in order to compare the activity of the single catalyst system to that of the catalysts reported in the Shell patent. The results show that the catalyst made in the laboratory had about one-half of the activity of a corresponding sample in the patent. This may be partly due to 20% lower Cu loading and 10% Zn loading in our catalyst.

3.1.2 A Repeat Life Run of a Reported Dual Catalyst System for LPDME™

According to the work in a Japanese laboratory, a dual catalyst system consisting of ICI 51-2 methanol catalyst and Cu-doped γ-alumina (5 wt%) powders, with hexadecane as the slurry fluid, exhibited no loss in activity under LPDME™ conditions for 700 hours (private communication). A close examination of the data reveals that the life run is suspect since the catalyst was subject to

severe mass transfer limitations. (After our experiments were completed, the authors of the report acknowledged this problem and stated that the catalyst system may actually deactivate faster. No elaboration was offered.) We decided to examine the stability of the catalyst system in our 300 cc autoclave under the conditions free of mass transfer limitations. A Cu-doped γ-alumina sample was prepared according to the method reported in a patent by the Japanese authors. The same gas composition (50:50 H_2 to CO), catalyst ratio, solid concentration in the slurry, and slurry fluid were used. The run was conducted first at 250°C, 750 psig, and a space velocity of 1980 sl/kg-hr for 142 hr. Afterward the run was continued at 280°C, 426 psig, and 1980 sl/kg-hr for 43 hr, which are the exact conditions used in the reported life study. The activity of our version of the catalyst system was similar to that in the report, but stable activity was not observed. As shown in Fig. 3.1.5, the catalyst system deactivated under both sets of conditions. The rate of deactivation is similar to our standard catalyst system (S3-86 plus Catapal B γ-alumina). These results suggest that the LPDME™ run in the Japanese laboratory may also have had a stability problem, unless certain factors were not disclosed in their report and patent.

3.1.3 SEM/EDS Analysis of LPDME™ Catalysts — Examination of the Migration Hypothesis

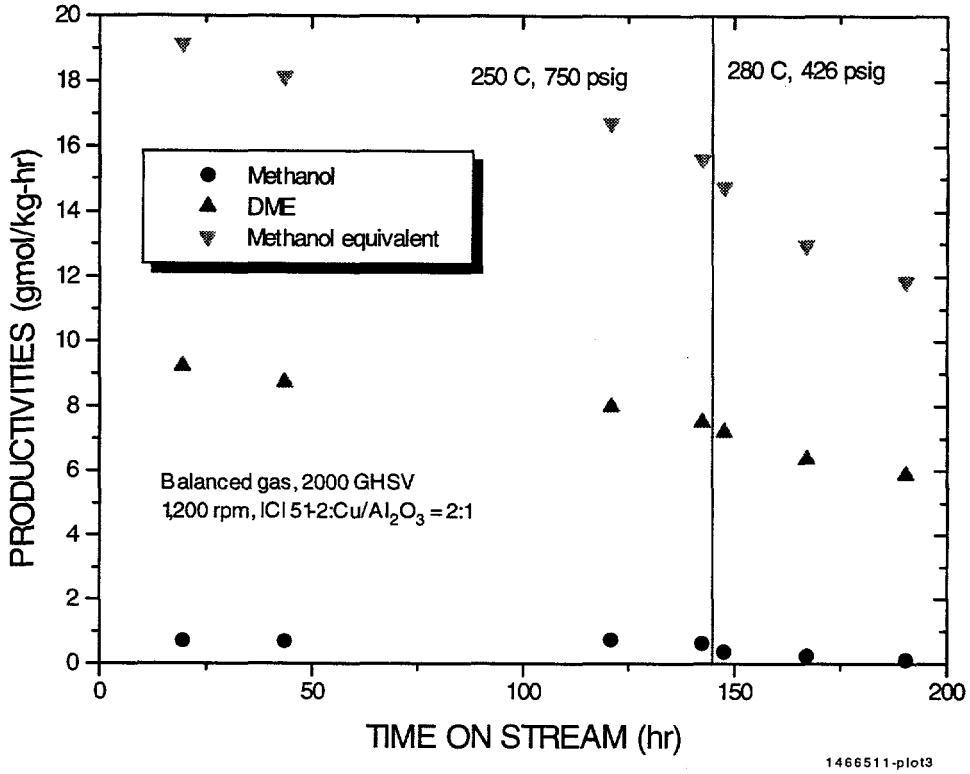
Summary

This section summarizes the analytical results of methanol catalyst and alumina mixtures using SEM and EDS. The analysis was performed to confirm the hypothesis that the deactivation of the LPDME™ catalyst system is caused by inter-catalyst migration of one or more types of atoms. The questions to be answered by this analysis are: Does the migration take place? And if it does, is the migration correlated to the catalyst deactivation?

Zinc and copper were detected on alumina particles in the spent catalyst mixtures, but not on virgin alumina, and the ratio of copper to zinc was significantly different from that found for the methanol catalyst itself. This indicates that migration occurs, at least in some cases. Furthermore, no migration of zinc or copper was found in the Robinson-Mahoney experiment in which the catalyst did not deactivate rapidly. Unfortunately, the zinc and copper content of alumina particles in catalyst mixtures of different histories does not correlate with the activity of the catalyst systems. Several explanations for this behavior have been proposed:

1) methanol catalyst fines may exist in the alumina particles and thus, confound the analysis;
2) migration is only responsible for the initial deactivation of the catalyst system; or
3) the sampling may not be statistically sound.

Figure 3.1.5 The Stability of a Reported LPDME™ Catalyst System Tested in Air Products' Laboratory



This lack of correlation is not sufficient to reject the migration of zinc and/or copper as the primary cause of catalyst deactivation. Work on understanding the mechanism of migration continues.

Introduction

We reported previously that an interaction between a methanol synthesis catalyst (e.g., BASF S3-86 Cu-ZnO-based low pressure methanol catalyst) and a dehydration catalyst (e.g., γ-alumina) in the standard dual catalyst system is responsible for the deactivation of both catalysts under LPDME™ conditions. Several observations have suggested that this interaction could be due to *inter-catalyst migration of zinc and copper*, that is, the zinc- or/and copper-containing species from the methanol catalyst migrate onto the surface of the dehydration catalyst during reduction and/or under the reaction conditions. By this mechanism, the methanol catalyst deactivates because it loses its active components. The dehydration catalyst is poisoned by these migrating species by reacting with the acid sites. Possible driving forces for the inter-catalyst migration are:

1) *acid-base reactions* - solid state reactions such as acid-base reactions between ZnO in the methanol catalyst and the acid sites on the dehydration catalyst,
2) *ion exchange* - solid-state exchange of copper/zinc ions from the methanol catalyst with the protons (i.e., Bronsted acid sites) on the dehydration catalyst,

3) *spontaneous dispersion* - migration simply driven by the concentration gradient of copper and zinc between the two catalysts, considering that γ-alumina, and most other types of dehydration catalysts, for that matter, have good dispersing capability toward metal, metal oxide, and salts.

These processes must take place where two catalysts contact each other, that is, at the outer surface of alumina particles. The migration may or may not continue into the inner surface of the alumina particles. However, the extent of the deactivation we have seen suggests that the inner surface of the alumina should be affected, unless the alumina particles break apart considerably under the reaction conditions. Efforts have been made to confirm the hypothesis by analyzing the copper and zinc content in the alumina in spent catalyst mixtures. This report summarizes the results based on the analysis using SEM and EDS.

Method of Analysis

SEM and EDS were used because the different types of catalyst particles are inseparable. The catalyst system under study consists of a powder mixture of the two catalysts. The mean diameter of fresh methanol catalyst and alumina powders is around 60 microns. The particle size in the spent catalyst mixture is smaller because of the attrition in the reactor. This makes it virtually impossible to separate the alumina from the methanol catalyst and use it for conventional elemental analysis. SEM enables us to pick out individual alumina or methanol catalyst particles, while EDS provides elemental information on these particles. The smallest features that can be "seen" by SEM are 0.1 to 1 micron. The spatial resolution of EDS of 1 micron, and the lower detecting limit of EDS is believed to be 0.5 wt.%.

We looked at both the outer surface and the cross section of alumina particles. Inter-catalyst migration will initiate on the outer surface due to the contact of the two catalysts. Figure 3.1.6 is a SEM micrograph of the outer surface of an alumina particle in a spent catalyst mixture. The bright spots are methanol catalyst powders, judging by EDS analysis and the brightness of these powders. (Heavier elements like Cu and Zn have a brighter image in SEM than lighter elements like Al.) These powders are physically attached to the alumina, a phenomenon that can be inferred since treating the sample with an organic removes most of the metal particles through dispersion. As shown in Figure 3.1.7, the outer surface of an alumina particle in a catalyst mixture dispersed using an organic solvent is much cleaner, although some methanol catalyst particles can still be seen. In both non-dispersed (or dry) and dispersed samples, "clean" areas where no methanol catalyst particles are found exist as illustrated in Figures 3.1.6 and 3.1.7. The "clean" area was assumed to be free of physically attached methanol catalyst particles, and used for the analysis.

We also looked at the cross section of the alumina particles as a way to circumvent the physical attachment problem. Moreover, this indicates if the migration into the inner surface of alumina particles has occurred. The cross section was prepared by freezing the sample in epoxy and cutting it to expose the cross section. Precautions were taken to make sure that copper and zinc from the methanol catalyst were not smeared onto the alumina cross section by the cutting. This was checked by EDS examination of the epoxy around the sample particles. Little copper and zinc were detected.