

**ALTERNATIVE FUELS AND CHEMICALS
FROM SYNTHESIS GAS**

FINAL

Quarterly Status Report No. 6

For the Period 1 January - 31 March 1996

Contractor

AIR PRODUCTS AND CHEMICALS, INC.

7201 Hamilton Boulevard
Allentown, PA 18195-1501

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Alternative Fuels and Chemicals from Synthesis Gas

Quarterly Technical Progress Report

1 January - 31 March 1996

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

- The LaPorte Fischer-Tropsch III modification project was kicked off in January. A preliminary PFD and a list of modifications were issued. The modifications include a new high-pressure (1000 psig) filtration system. The filtration system will consist of a slurry degasser, a slurry cooler, a catalyst-wax circulation pump, and four cross-flow filters in series. In addition, some of the existing equipment will be lined up differently for wax handling. In order to recycle the unconverted syngas, the F-T train will be connected to the existing 01.20 Recycle Compressor. Miscellaneous changes include installation of instrumentation for water analysis during activation, DP taps on the 27.10 Reactor, radial thermocouples in the reactor, optical fiber probe to measure radial bubble size distribution, erosion test pieces, and a new sparger from Shell. The planned modifications were documented and sent to Radian Corporation to evaluate their impact on air emissions. Radian will evaluate the proposed modifications and operations to determine if we need a new exemption for this run or if a letter documenting that these changes is sufficient. Due to an anticipated long delivery time for the slurry pump, a process specification for the pump was quickly issued.
- Work continued through March on the modifications for the F-T III run. The PFD was completed and approved, while P&ID development continued. Process specifications were issued on the 27.15 degasser. Kinetic and mass balance information was obtained from Shell and used to conduct ASPEN simulation work. Close agreement was obtained with Shell's gross predictions, and more detailed mass balance information was generated compared to Shell's simulation.
- Emission calculations were completed for a LaPorte F-T material balance case corresponding to maximum production and emissions. Both exemption and non-attainment estimates were made and transmitted to Radian. Radian will evaluate the estimates to determine if a new exemption is required for this run or a letter documenting these changes is sufficient. Our target date for completing any required action is 1 May.

- A second trial in January of the new LPDME™ dual catalyst system showed the same excellent stability and high activity as reported in December. Increasing the reaction temperature led to an increase in dehydration activity, but gave rather high deactivation rates. Additional work on catalyst development is needed, but with the repetition of last month's results, we are confident in the observation that a catalyst with greatly increased life has been identified.
- February saw continued improvement of the aluminum phosphate dehydration catalyst in LPDME™ studies. Changing the solvent in the final step of the aluminum phosphate catalyst preparation gave a stable catalyst with higher activity than seen previously.
- In the higher alcohol work at Aachen, the effect of intraparticle diffusion on activity and selectivity in the gas phase reactor was measured. As expected, the trend in the PFR is the same as for the CSTR when the smallest size particles, which are not diffusion limited, are used. A new catalyst made with copper instead of manganese in the standard catalyst system shows higher activity at a relatively low temperature (400°C). Testing of systematically varied components in the base catalyst continued through March. Several components (e.g., base) have been shown to have a positive influence on rate. Testing of catalyst at lower pressure shows a large effect. Decreasing pressure to 2500 psi reduces productivity to about 250 g IBOH/kg-hr. Further reduction of pressure results in a marked decrease in productivity.
- Lehigh University studies have shown that a dual bed of the same catalyst, 3 mol% Cs/Cu/ZnO/Cr₂O₃, held at two different temperatures (325 and 370°C) increases the productivity of isobutanol. As an example, synthesis gas consisting of H₂/CO=0.75 at 7.6 MPa with GHSV=18,375 l(STP)/kgcat-hr produces 369 and 180 g/kgcat-hr of methanol and isobutanol, respectively, at 6% CO conversion.
- In acetyl chemistry work at Air Products for the carbonylation of methyl acetate to acetic anhydride, the phosphinated heterogeneous catalyst proved to be slightly better than the Reillex catalyst with similar loadings of rhodium. For the hydrogenation of acetic anhydride, the rhodium on Reillex was found to be the best catalyst. Finally, for the DME to ethylidene diacetate (EDA) conversion, the Reillex catalyst proved to be the most stable under recycling conditions in contrast to the phosphinated heterogeneous catalyst that rapidly lost activity.
- The use organic bases to catalyze the cracking of EDA to VAM showed little potential, but led us to try organic iodides. Lithium iodide (LiI) was shown to be catalytic in the cracking of EDA. Other iodides and other lithium salts did not show this same activity. Lithium iodide also catalyzed the unwanted retro-reaction to acetaldehyde and acetic anhydride. Controlling the reaction profile with LiI has not been reported in the literature.
- Air Products continued to examine catalysts through March for the cracking of EDA to vinyl acetate (VAM) and acetic acid. The suppression of retro-reaction using acetic anhydride led to a decrease in performance for LiI. MgI₂ was shown to perform cracking of EDA. Addition of acetic anhydride resulted in a less significant drop in performance with MgI₂. Several other iodide systems showed cracking, but also exhibited unwanted side reactions.

- Eastman Chemical has continued its investigations of the hydrogenation of acetic acid to acetaldehyde and the subsequent conversion of acetic acid and acetaldehyde to vinyl acetate. Most of the progress has been in the latter reaction, in which yields for the conversion of acetic acid and acetaldehyde are now excellent. The process has been run on a continuous basis, and scale-up and designs amenable to commercial operation are being checked out.

Several catalysts have been identified that are able to facilitate the combination of acetaldehyde with "activated acetic acid," and an optimal class of catalysts has been selected. Yields are now good to excellent. Several reactor designs have been tested for utilizing the unique activation process in this reaction. The details of the activation process and their application to the generation of acetaldehyde and vinyl acetate are possibly patentable.

- Project review meetings were held in Bechtel's San Francisco office on 6 February and 28 March 1996. The major focus of the meetings was to present and discuss the material on Mixed Alcohol Synthesis and sulfur removal to be presented at the April DOE project review meeting in Allentown.

Task 4.2, Commercial Applications (Mixed Alcohol Synthesis). The latest results from the testing of the revised revenue models for the three scenarios for the production of gasoline blendstock ethers via mixed alcohol synthesis were discussed at the project review meeting. Comments were made to clarify some of the results and to add details to improve the presentation. The material is being revised subsequent to the presentation in Allentown.

Task 4.5, Syngas Generation and Cleanup. The revised results of the evaluation of deep sulfur acid gas removal designs versus mild sulfur removal to sulfur levels consistent with the operation of a sulfur-tolerant catalyst were presented. Comments are being incorporated into the presentation.

The six vendors who had supplied information on their contaminant removal systems later supplied information on their commercial experience. This commercial experience is being analyzed in an attempt to validate the process and cost details they originally supplied.

- Hazards review of the AF₂DU (Alternative Fuels Field Development Unit) was completed in March. Everything is ready for an initial run beginning in April. The project is on schedule and on budget. Dialogue with Eastman has been initiated and no difficulties are anticipated in being on-site at Kingsport during April/May.

RESULTS AND DISCUSSION

TASK 1: ENGINEERING AND MODIFICATIONS

1.1 Liquid Phase Fischer-Tropsch Demonstration

A meeting was held with DOE personnel on January 16 to discuss the Fischer-Tropsch III (F-T III) run. The current plan as discussed between Air Products and Shell in mid-December was presented. In general, the plan was well received and DOE is looking forward to the run. Some issues raised by DOE need attention from Shell: DOE is going to need the LaPorte product and its analysis in order for DOE and its contractors to study downstream processing. DOE also suggested including a tracer study if Air Products/Washington University's current analysis of the 1995 hydrodynamic run shows significant understanding and the value of doing more under the F-T III program. ICI-Tracerco expenses can be covered under DOE's separate hydrodynamic program; however, operation time has to come out of the 30-day program. Data/results from the optical fiber probe (if obtained) need to be shared. Sparger information is needed to feed the data into DOE's hydrodynamic program. The information will have to be shared with other subcontractors.

The F-T III modification project was kicked off in January. A preliminary PFD and a list of modifications were issued. The modifications include installing a new high-pressure (1000 psig) filtration system. The filtration system will consist of a slurry degasser, a slurry cooler, a catalyst-wax circulation pump, and four cross-flow filters in series. In addition, some of the existing equipment will be lined up differently for wax handling. In order to recycle the unconverted syngas, the F-T train will be connected to the existing 01.20 recycle compressor. Miscellaneous changes include installation of instrumentation for water analysis during activation, DP taps on the 27.10 reactor, radial thermocouples in the reactor, optical fiber probe to measure radial bubble size distribution, erosion test pieces, and a new sparger from Shell.

Due to an anticipated long delivery time for the slurry pump, a process specification for the pump was quickly issued. Discussions were held on new equipment layout at LaPorte. The PFD was updated, and P&ID development began. A Preliminary Hazards Review was conducted on 15 February. A Design Hazards Review will be conducted following completion of P&ID development. HTRI heat exchanger simulations were performed for the 21.70 slurry cooler. Process specifications were issued for the cooler, as well as for the 22.62 cross-flow filters. The PFD was completed in March, while P&ID development continued. Ideas were exchanged with Shell for the design of the 27.15 degasser, and a final design was agreed upon. A process specification was issued for the 27.15 degasser.

Mass balance simulation work continued on ASPEN in February. Kinetic and mass balance information became available from Shell in March. ASPEN simulation based on data from Shell resulted in close agreement with Shell's gross predictions. More detailed mass balance information was generated on ASPEN compared to Shell's simulation.

The planned modifications were documented and sent to Radian Corporation to evaluate their impact on air emissions. Radian will evaluate the proposed modifications and operation to

determine if we need a new exemption for this run or if a letter documenting these changes is sufficient. Emission calculations were completed for a material balance case corresponding to maximum production and emissions in March. Both exemption and non-attainment estimates were made and transmitted to Radian. Our target date for completing the evaluation is 1 May.

A meeting was held with personnel from Energy International (E. I.) to discuss a Fischer-Tropsch demonstration run at LaPorte for E. I. Their overall process scheme and specific LaPorte objectives were discussed. Funding and timing for the run are key issues. The run must be fully funded by E. I. because all available DOE and Air Products funding is already committed. Furthermore, due to the existing schedule for F-T III and the Kingsport start-up, the next window for a LaPorte run is mid-97, and that window may be used for an oxygenates run such as DME synthesis. E. I. prefers the demonstration in a timeframe sooner than mid-97.

Task 1.2 AFDU Modifications - No progress to report this quarter.

Task 1.3 Fischer-Tropsch Support - No progress to report this quarter.

Task 1.4 AFDU R&D Support - No progress to report this quarter.

TASK 2: AFDU SHAKEDOWN, OPERATIONS, DEACTIVATION AND DISPOSAL - No progress to report this quarter.

TASK 3: RESEARCH AND DEVELOPMENT

Task 3.1 New Process for DME

Aluminum Phosphate

Two repeat runs reproduced the excellent stability and high activity reported in the last quarterly from a dual catalyst system containing an aluminum phosphate dehydration catalyst (referred to as AP01 hereafter). Furthermore, another aluminum phosphate sample (referred to as AP02), when used along with BASF S3-86 methanol synthesis catalyst in a LPDME™ run, resulted in 6% higher productivity than AP01 at similar stability. With the repetition of the good results from different runs and different catalyst samples, we are confident that a new dual-catalyst system with greatly increased life has been identified.

The catalyst system performance, especially the stability of the methanol catalyst, was very sensitive to the preparation procedure for the aluminum phosphate catalyst. Washing with water gave a catalyst that performed better than a catalyst that had been washed with isopropanol. The dehydration activity of aluminum phosphate increased with increasing Al/P ratio initially, reached a maximum at a ratio of about 1.6 and then dropped. The stability of the methanol catalyst decreased monotonically with increasing Al/P ratio. The dehydration catalyst itself was always stable, regardless of the Al/P ratio. In the catalyst preparation itself, reversing the order of solution addition in precipitation led to a very poor catalyst system. A catalyst prepared by using $\text{Al}_2(\text{SO}_4)_3$ as the aluminum precursor, instead of the standard $\text{Al}(\text{NO}_3)_3$, also resulted in a poor catalyst system.

The stability of the dual catalyst system containing AP01 showed a strong dependence on the reaction temperature. While stable at 250°C, both the methanol synthesis catalyst and the AP01 deactivated rapidly at 270 and 290°C. This finding illustrates the need for developing a better understanding of the new catalyst system.

The other work covered in this quarterly includes the test of a single-particle, dual-function catalyst. In addition, the effort in understanding why catalysts deactivate more rapidly in reactors of smaller volume-to-surface ratios continues. The dual-function catalyst, Pd on La₂O₃-modified δ -alumina, showed high selectivity toward DME, but low production rate and rapid aging.

1. Stable Dual-Catalyst Systems Containing Aluminum Phosphate as the Dehydration Catalyst

In the last quarterly, we reported excellent stability and high activity from a dual-catalyst system containing an aluminum phosphate dehydration catalyst (#1407x1-1x1 or AP01). We repeated the experiment in the same reactor (#1 300-cc autoclave) to demonstrate that the results are reproducible. We also repeated the run in the other 300-cc autoclave (Unit #2), because all three runs in that unit using aluminum phosphate samples of small variation (Runs 14665-44, -47, -51) have shown poor methanol catalyst stability. We wanted to ensure that this poor stability was not an experimental artifact (e.g., poisoning) of the unit.

Both runs were conducted under syngas stream for ~200 hours. As shown in Figures 3.1.1 to 3.1.3, the new data track the original data very well. Some discrepancy is observed in Figure 3.1.2. It appears that, in the repeat runs, the methanol catalyst deactivated more slowly than in the original run (14656-90) in Unit #1, but more rapidly than in Unit #2. This discrepancy can be attributed to the experimental noise caused by the large variation in the atmospheric pressure during the runs. (Both GC readings and flow rate measurements are affected by changes in atmospheric pressure, and this effect is more pronounced in the calculation of the methanol rate constant.) However, even in the worst case with Unit #2, the deactivation rate was 0.051%/hr., falling into the range of methanol catalyst deactivation observed from lab LPMEOH™ runs (0.042 to 0.053%/hr.). This rate is definitely smaller than that of the other three aluminum phosphate samples tested in Unit #2 (> 0.084%/hr), reported in the last quarterly. In summary, the repeat runs demonstrated that the good results reported previously are real and reproducible, and that Unit #2 does not have an experimental artifact. Therefore, the previous results from that unit should be valid.

Figure 3.1.1 Methanol Dehydration Rate Constant as a Function of Time on Stream

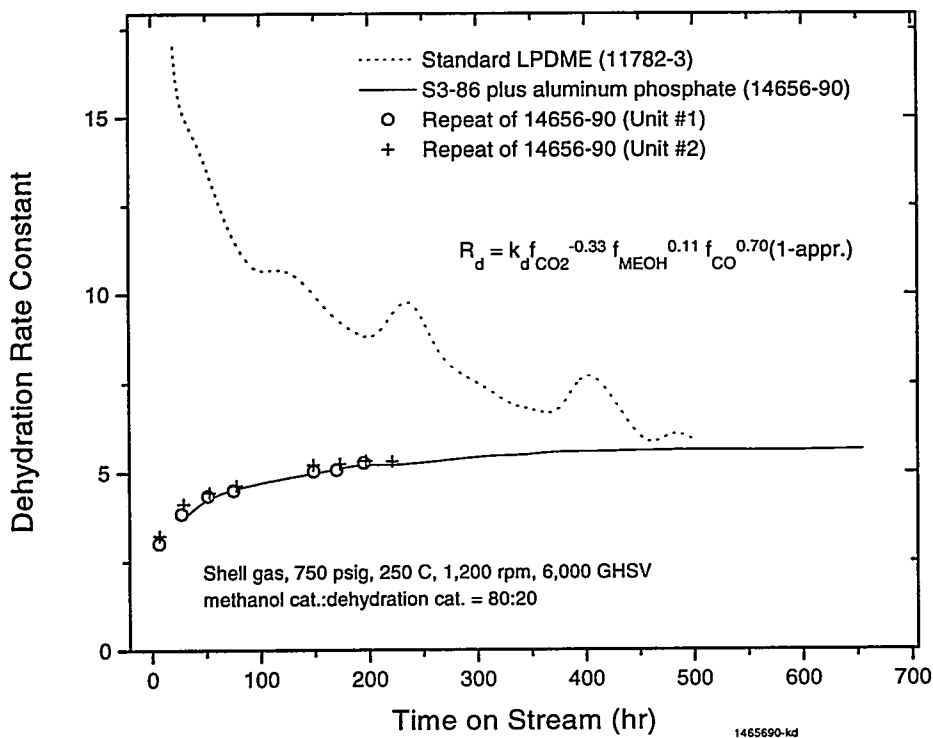


Figure 3.1.2 Normalized Methanol Synthesis Rate Constant as a Function of Time on Stream

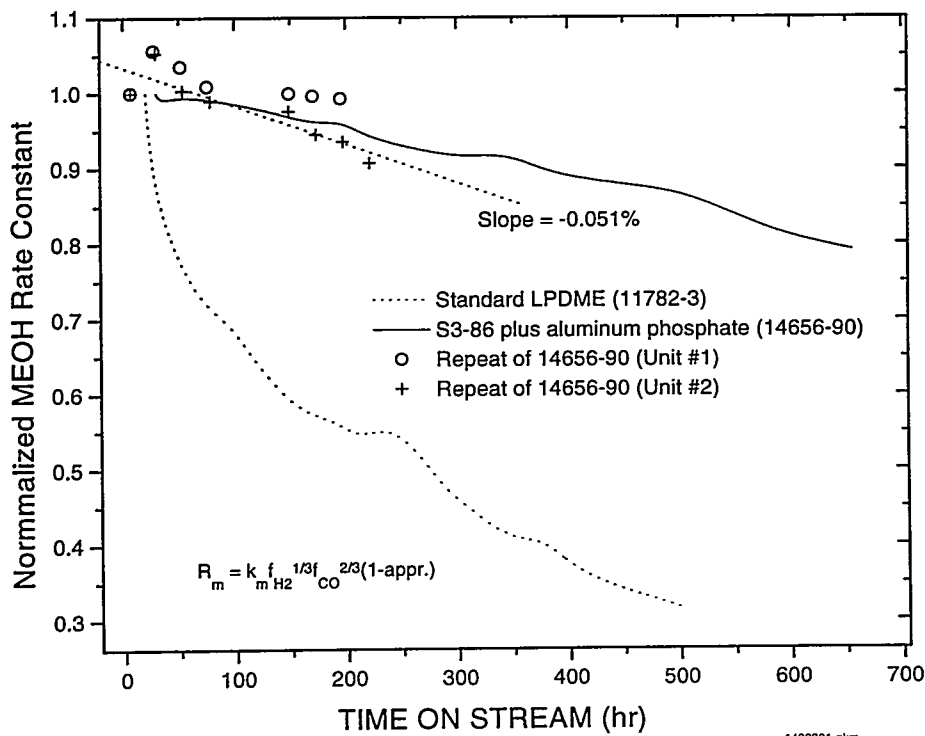
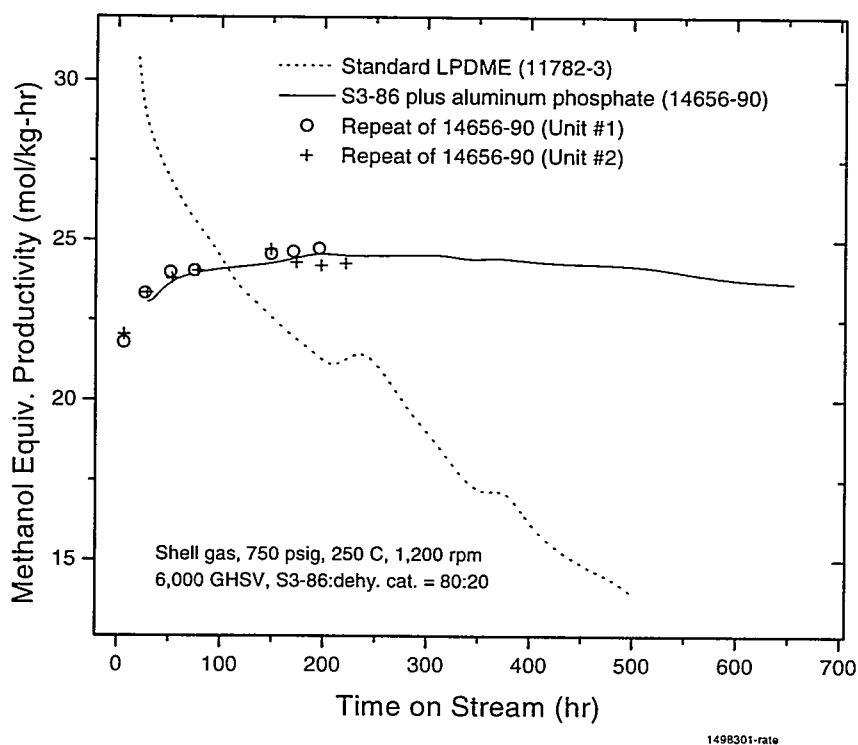


Figure 3.1.3 Methanol Equivalent Productivity as a Function of Time on Stream



Performance similar to that of AP01 was observed from a different aluminum phosphate sample (# 1416x1-1x1 or AP02). This sample was prepared according to similar procedures used for AP01, except that it was washed with water instead of isopropanol after filtration. The performance of AP02 under the standard LPDME™ conditions, along with that of AP01 and the original dual catalyst system containing δ -alumina, is shown in Figures 3.1.4 to 3.1.6. Figure 3.1.4 shows that the dehydration activity of AP02 is higher than that of AP01. The methanol catalyst in this system has a slightly faster deactivation rate than the system containing AP01 (Fig. 3.1.5); however, the deactivation rate, $0.049\% \text{ hr}^{-1}$ shown in Figure 3.1.5, is within the range of methanol catalyst deactivation in lab LPMEOH™ runs ($0.042 - 0.053\% \text{ hr}^{-1}$). The methanol equivalent productivity of this system, after the induction period, is 6% higher than the AP01-containing system (Fig. 3.1.6). The analysis shows that different washing procedures and/or solvent results in significantly different properties between AP01 and AP02, such as surface area and Al:P ratio.

Figure 3.1.4 Methanol Dehydration Rate Constant as a Function of Time on Stream

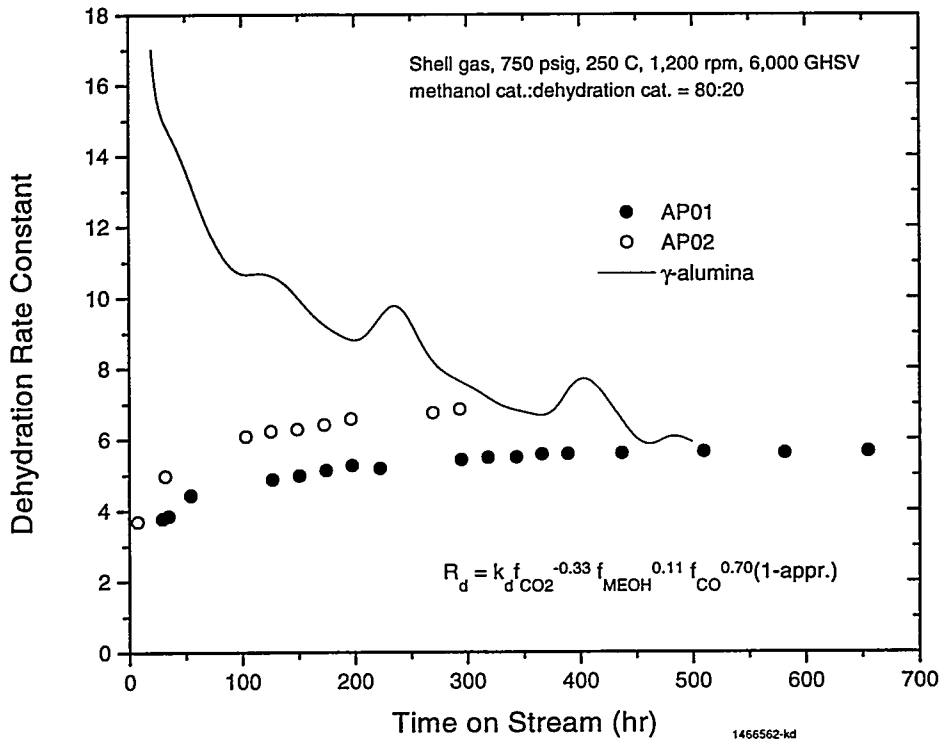


Figure 3.1.5 Normalized Methanol Synthesis Rate Constant as a Function of Time on Stream

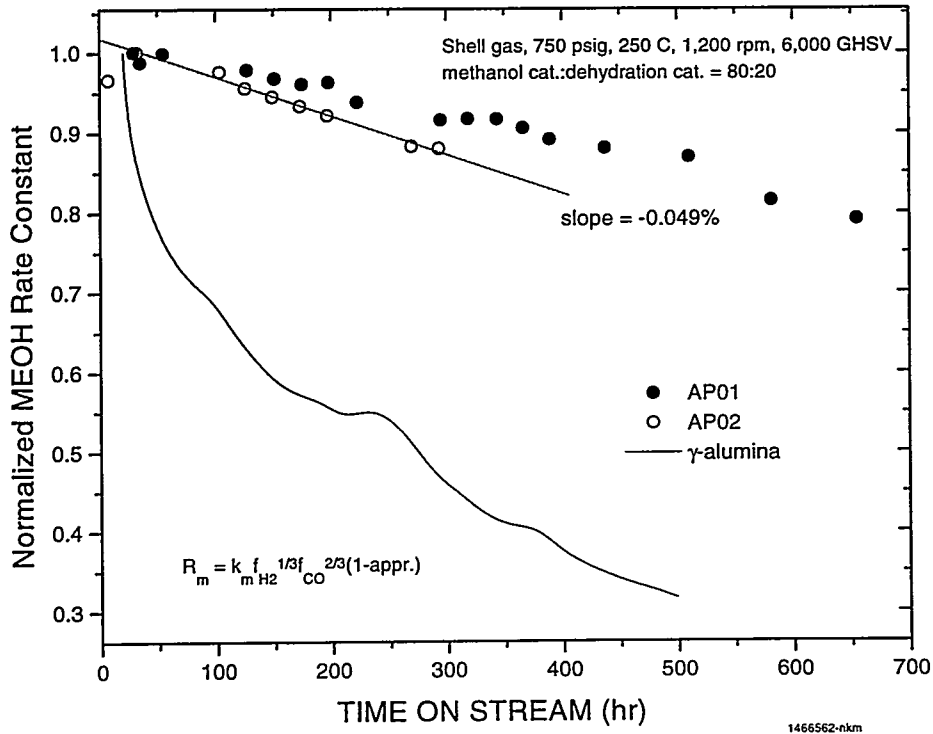
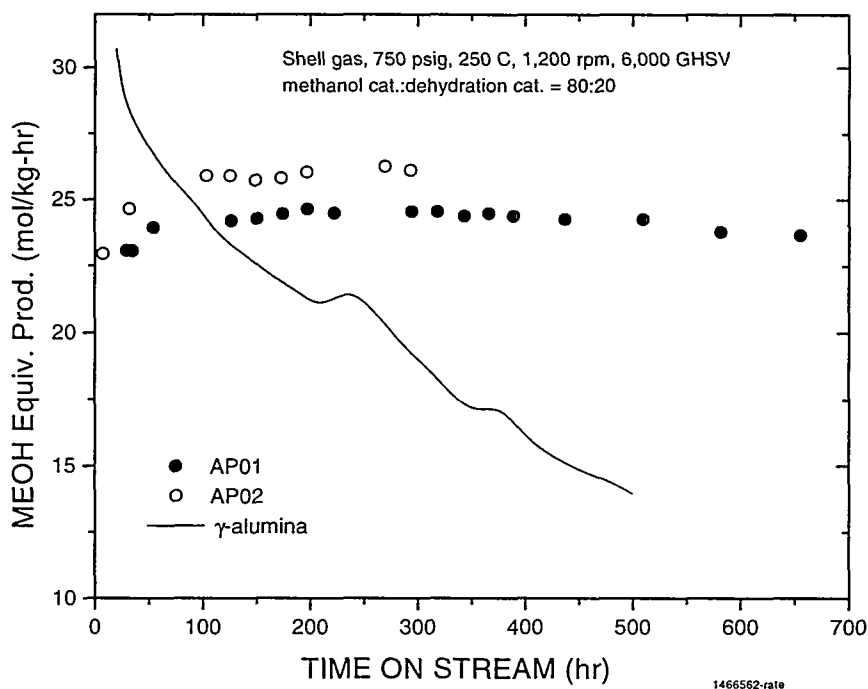


Figure 3.1.6 Methanol Equivalent Productivity as a Function of Time on Stream



2. Catalyst Performance as a Function of Preparation Parameters

The results above show that catalyst performance is sensitive to washing variables during catalyst preparation. Other preparation parameters also have a large effect. An aluminum phosphate sample with an Al/P ratio equal to 1.64 was prepared according to the standard procedures (Sample # 1427x1-1x1). This sample was tested along with BASF S3-86 methanol catalyst in a LPDME™ run (#14665-71) under the standard conditions (250°C, 750 psig, 6,000 GHSV, and 80:20 catalyst ratio) using Shell gas. As shown in Figures 3.1.7 to 3.1.9 by the open circles, the catalyst exhibited much higher dehydration activity than any other aluminum phosphate sample we have tested. In fact, the methanol equivalent productivity was similar to the initial productivity by the standard δ -alumina-containing dual catalyst system. However, this dehydration catalyst caused a 40% faster deactivation of the methanol catalyst. The dehydration catalyst itself is stable.

Figure 3.1.7 Methanol Dehydration Rate Constant as a Function of Time on Stream

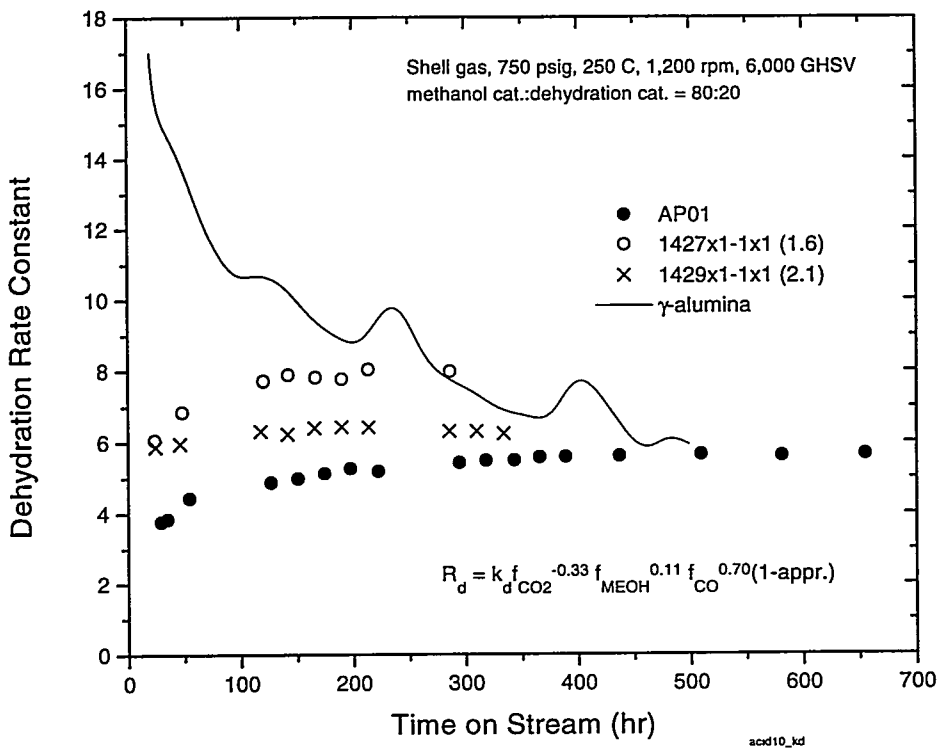


Figure 3.1.8 Methanol Equivalent Productivity as a Function of Time on Stream

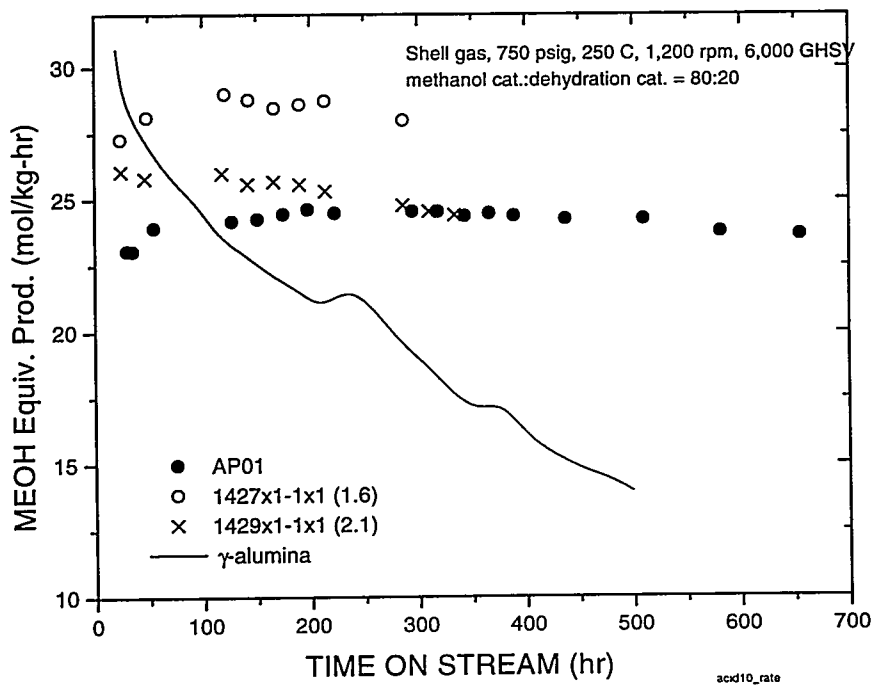
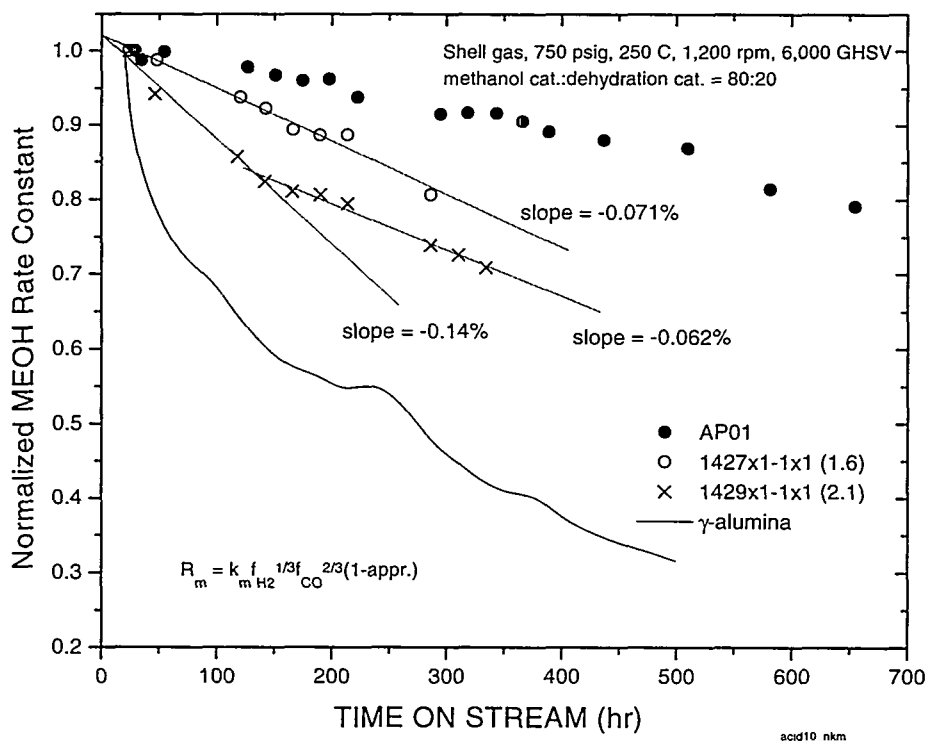


Figure 3.1.9 Normalized Methanol Synthesis Rate Constant as a Function of Time on Stream



A further increase in the Al/P ratio to 2.1:1 (Sample #1429x1-1x1) did not result in greater dehydration activity (Fig. 3.1.7), but caused more rapid deactivation of the methanol catalyst (Fig. 3.1.9). The negative effect on the methanol catalyst stability became smaller with increasing time on stream, stopping at a rate of $-0.062\% \text{ hr}^{-1}$, 24% higher than that of a LPMEOH™ run.

Table 3.1.1 summarizes dehydration activity, methanol equivalent productivity, and methanol catalyst stability as a function of Al/P ratio for three samples prepared using similar procedures. The dehydration activity of aluminum phosphate increased with increasing Al/P ratio initially, reached a maximum at a ratio of about 1.6, and then started to drop. The stability of the methanol catalyst decreased monotonically with increasing Al/P ratio. The dehydration catalyst itself was always stable, regardless of the Al/P ratio.

Table 3.1.1 Catalyst Performance as a Function of Al/P Ratio

Al/P Ratio	Dehydration activity, k_d	MEOH Equiv. Prod. (mol/kg-hr)	Stability of MEOH catalyst (slope)
1.22	6.8	26.2	- 0.049%
1.64	8.0	29.0	- 0.071%
2.12	6.3	26.0	- 0.14%

These results indicate that catalyst performance can be optimized by the following two approaches. First, we can work with the stable catalyst system containing aluminum phosphate samples with an Al/P ratio of about 1.2:1 and try to increase its dehydration activity, for example, by increasing the surface area. Second, we can work with the system with high activity (Al/P ratio about 1.6) and try to improve its stability. The fact that the dehydration catalyst itself is stable suggests that the active sites for dehydration are not involved in the accelerated deactivation of the methanol catalyst. Therefore, we can hopefully remove the sites on the phosphate sample that are harmful to the methanol catalyst without damaging the active sites for dehydration. Both approaches are being pursued along with other measures for optimization of the catalyst performance.

Three other phosphate samples were tested last quarter. The first was an aluminum phosphate with an Al/P ratio of 1:6, but prepared by reverse addition during precipitation (Sample #1430x1-1x1). This catalyst showed reasonable dehydration activity, but the stability of the methanol catalyst was worse. The second sample (1412x1-1x1) was prepared using $\text{Al}_2(\text{SO}_4)_3$ as the aluminum precursor, instead of the standard $\text{Al}(\text{NO}_3)_3$. The dehydration activity of this sample was low, one-half of that of AP01, and the methanol catalyst in this system was not stable. The last sample was a mixed aluminum and silicon phosphate (Sample #1425x1-1x1). Both the activity and the stability of the methanol catalyst from the dual catalyst system containing this sample were worse than pure aluminum phosphate samples of similar preparation.

3. Catalyst Stability as a Function of the Reaction Temperature

To determine if temperature ramping provides an additional means to maintain catalyst activity, or even a means to obtain higher productivity, we tested the dual-catalyst system containing AP01 at 270 and 290°C, following the two repeat runs carried out in two 300-cc autoclaves at 250°C. As shown in Figures 3.1.10 and 3.1.11, the activity of both catalysts increased when the temperature was raised to 270°C. However, both catalysts deactivated rapidly at this temperature. Similar behavior with a faster decrease in activity was observed for the run at 290°C (not shown).

Figure 3.1.10 The Stability of the Methanol Catalyst at Different Temperatures

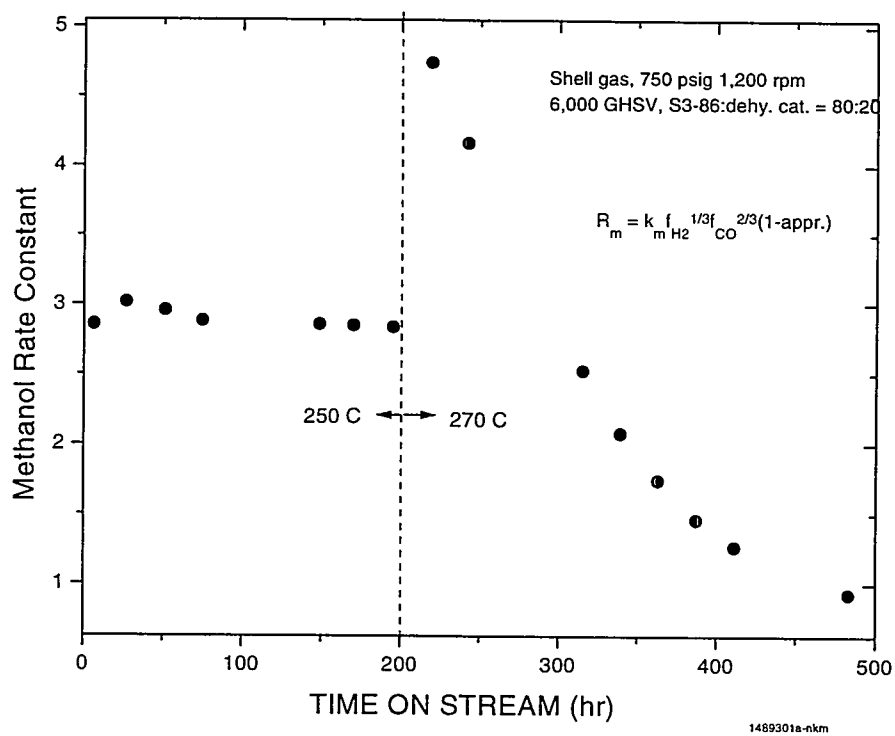
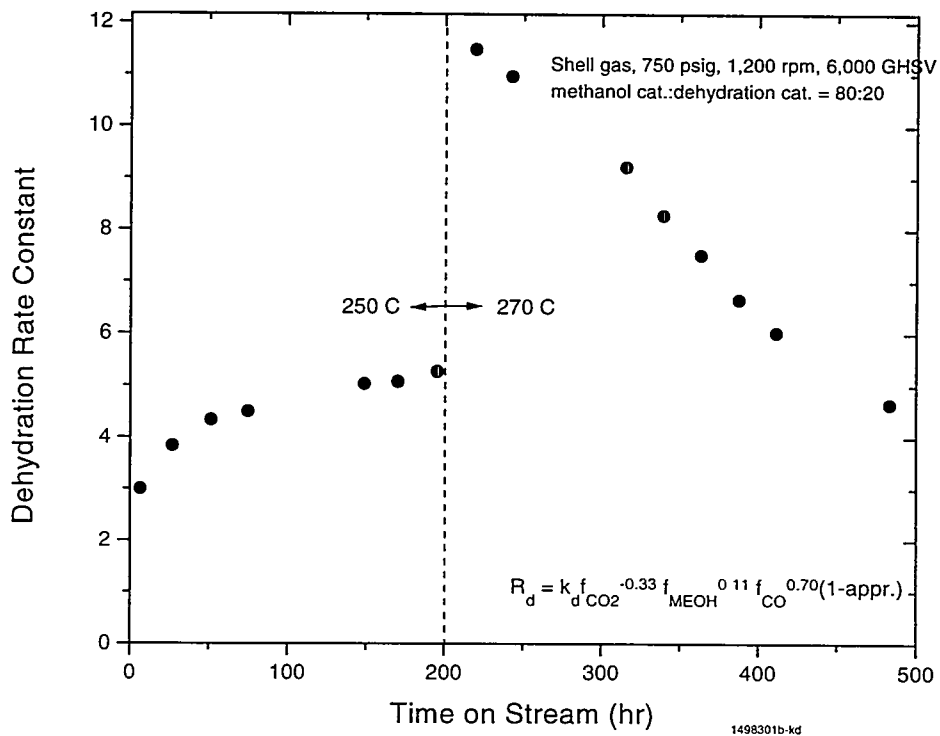


Figure 3.1.11 The Stability of the Dehydration Catalyst at Different Temperatures



The apparent activation energies for the deactivation of the two catalysts can be estimated by assuming zero-order deactivation kinetics and representing the deactivation rate by $-d(k/k_0)/dt$, where k is rate constant at any time t , and k_0 stands for the initial rate constant at a given temperature. They are summarized in Table 3.1.2.

Table 3.1.2 The Apparent Activation Energies for the Deactivation of the Methanol Synthesis Catalyst (S3-86) and AP01

Catalyst	Deactivation Rate at 250°C	Deactivation Rate at 270°C	Deactivation Rate at 290°C	Ea (kcal/mol)
S3-86	0.00044	0.00322	0.00712	40
AP01	0	0.00237	0.0044	90

Excluding the runs using AP01 and AP02 at 250°C, the runs thus far with aluminum phosphate dehydration catalysts exhibit two different patterns of accelerated catalyst deactivation. In the first pattern, only the methanol catalyst deactivates without simultaneous fast deactivation of the dehydration catalyst. This is the case for all phosphate samples we have tested at 250°C. One of the samples with very low dehydration activity (#7461-030.060) was even tested at 270°C and exhibited good stability (see October-December 1995 quarterly). The second pattern is the simultaneous deactivation of both catalysts as shown above in the runs using AP01 at 270 and 290°C. The first deactivation pattern suggests that there is no detrimental interaction between the methanol catalyst and the dehydration sites on aluminum phosphate — it is the other functional groups or impurities in aluminum phosphate that cause the deactivation of the methanol catalyst. While this may still be true for these specific cases, the second pattern we observed indicates that the dehydration sites in aluminum phosphate could be part of the deactivation mechanism, given the right conditions. It is possible that the interaction between the methanol catalyst and the dehydration sites becomes significant at higher temperature due to the higher acid strength of these sites. (Coking is an unlikely cause of the deactivation of the phosphate catalyst considering the low acid strength of the catalyst as shown by NH₃ adsorption experiments.) The data shown in the table above indicate that this is a highly activated process, that is, very sensitive to the reaction temperature.

We need to understand more about the deactivation mechanism for aluminum phosphate-containing dual catalyst systems and to develop catalysts that are not as sensitive to the reaction temperature. The strong dependence of catalyst stability on temperature could also be a practical issue considering that over-heating may occur for commercial scale operations.

4. A Single Particle, Dual Functional Catalyst — Pd on La₂O₃-Modified δ-Alumina

Palladium-based methanol catalysts have been reported in the literature. Although these catalysts in general are much less active than Cu-based methanol catalysts, they might offer alternative LPMEOH™ or LPDME™ catalysts with possibly better stability. It has been reported by Ryndin et al. (J. Catal. 70 (1981) 287) that the greatest specific activity is observed with palladium supported on La₂O₃. However, the overall productivity from this catalyst is low due to the small

surface area of the La₂O₃ support. We prepared an alumina support coated with a monolayer of La₂O₃, and impregnated the support with a Pd solution. In so doing, we hoped to obtain a large surface area support, as well as the desired synergism between Pd and La₂O₃. This Pd sample was tested in a 50-cc miniclave under the standard LPDME™ conditions (250°C, 750 psig, 6,000 GHSV) using Shell gas. Methanol and DME were the predominant products from this catalyst. A direct comparison between this catalyst and the ones reported in the literature could not be made because of the lack of a Pd dispersion measurement of our sample. Table 3.1.3 compares the performance of the Pd catalyst with that of our standard dual catalyst system (S3-86 plus δ-alumina).

Table 3.1.3 Productivity of Selected Catalyst Systems (gmol/kg-hr)

	Run ID	TOS (hr)	methanol	DME	methane
Pd/La ₂ O ₃ /g-Al ₂ O ₃	14667-18	15	0.73	0.35	0.03
S3-86 + g-Al ₂ O ₃ -	14047-61	19.7	2.76	14.69	0.017

The table shows that the activity of this Pd catalyst is an order of magnitude smaller than the standard dual catalyst system. The stability of this catalyst was poor; the methanol equivalent productivity dropped by 27% from 2 hours on stream to 15 hours on stream.

A commercial Pd catalyst (5% Pd on alumina) used in Air Products hydrogenation plants was also tested under LPDME™ conditions in this lab (Run 14656-40). No activity toward syngas conversion was detected.

5. Investigation of an Experimental Artifact

It was previously observed that, in LPMEOH™ runs, the methanol catalyst deactivates faster in lab 300-cc autoclaves than in the LaPorte bubble column reactor. It was also observed that, as shown in Figure 3.1.12, the catalyst system in LPMEOH™ and LPDME™ runs deactivated faster in a 50-cc microclave than in a 300-cc autoclave. This suggests the existence of an experimental artifact, or a deactivation mechanism, that becomes more pronounced in a reactor with a smaller volume-to-surface ratio. We continue to investigate the nature of this artifact or deactivation mechanism, and how much it contributes to the long-term deactivation in LPDME™ runs. The factors we have examined include: abrasion, attrition, loss of catalysts to the walls of the reactor internals, and poisons in the feed gas. As shown below, none of these appears to be responsible for the experimental artifact.