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ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS

Quarterly Status Report No. 1

For the Period 1 October - 31 December 1994

Contractor

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

Prepared for the United States Department of Energy
Under Contract No. DE-FC22-95PC93052
Contract Period 29 December 1994 - 28 December 1997

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DISCLAIMER

Alternative Fuels and Chemicals from Synthesis Gas

Quarterly Technical Progress Report

1 October - 31 December 1994

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

- At the end of the quarter, DOE approved the Cooperative Agreement for the new Alternative Fuels and Chemicals program. The program was funded in full for FY95: $8.8 million in total. Air Products and its industrial partners, Eastman Chemical and Bechtel, will contribute a 20% cost share ensuring us of all technology rights. We will now move to institute the subcontracts with Eastman and Bechtel, and the several universities who have been working with us. Next year promises to be a much more difficult time for fossil energy R&D funding.

- Work began on modifications for the hydrodynamic/methanol run scheduled for June 1995. Discussions were held with Piping Design for changes in the heater/cooler sequence in the utility oil system. Moving the heater downstream of the cooler is expected to improve the reactor temperature control. After a field inspection, it was decided to install additional piping instead of physically moving the equipment. Installing the piping would be cheaper than moving the equipment, and the oil pump has enough capacity to handle the additional pressure drop caused by the piping. Discussions have also begun for installation of a sump and a pad in the trailer area. This will improve our ability to handle spills. Air permit requirements for the hydrodynamic/methanol run were discussed between Process Engineering, Environmental Engineering, and Radian Corporation personnel. Radian will evaluate the proposed modifications and different operational options to determine whether we need a new air permit exemption.

- A confidentiality agreement was signed between Air Products and Syncrude Technology (STI). Technical discussions were held in a series of meetings between Air Products, STI, and DOE-PETC personnel for a proposed F-T run at La Porte. The objective of the run would be to evaluate performance of catalyst-reactor systems to confirm the design basis. A preliminary process flow diagram has been developed based on STI's desired operational envelope. The total cost of the run was initially expected to be $2,028,000. A meeting was held in early November to further discuss the run plan and conduct a tour of the LaPorte facility. Several potential investors of STI also joined for part of the meeting. Later discussions with STI indicated that the ~$2 MM estimate for the run exceeded their current budget.

Another meeting was held with STI in December to discuss their goals and technical data base in detail. It appears that their catalyst requires a high level of inerts (~50% N_2) in the feed for activity maintenance. To accommodate the inerts, the operating pressure and flow were doubled from the original design basis. They also want to maintain a high wax (dry) recycle to avoid catalyst agglomeration at the bottom of the reactor as well as maintain catalyst stability. STI would like to use Mott's sintered porous metal elements for catalyst-wax separation as they are unable to have their wire screen elements fabricated in a timely fashion. They have not done any commercial economic study since 1990 and would rely on an Engineering and Construction Contractor to update it. Air Products has decided not to kick off project work until economics from an ECC are updated and appear promising.

- A visit to Institut Francais du Petrole (IFP) revealed that they have stopped work on their (linear) higher alcohols process because of the unfavorable economics relative to MTBE production. They have switched their syngas work over to Fischer-Tropsch chemistry.

- A cesium doped copper/zinc oxide/chromia catalyst was tested at Lehigh University yielding isobutanol at a rate of 48 gm per hour per kilogram of catalyst. This yield almost meets the previous target for isobutanol set in the Alternative Fuels I program. Today's target is at least 400 gm/hour per kilogram of catalyst.

- The Ag/SrO catalyst for converting methanol to isobutanol has been modified with Cs. This modification has increased the lifetime of the catalyst and changed the mol % selectivity to oxygenates. The catalyst has been stable for 55 hours, and the combined isobutyraldehyde and isobutanol selectivity is 23-24 mol %. The catalyst Ag/Cs/SrO is very good at converting a C_1 to a C_2.

  To date the effect of Cs on extending the lifetime of the Ag on SrO catalyst for the conversion of methanol to isobutanol and isobutanol precursors appears to be a unique combination. Rapid deactivation occurs with other control catalyst systems: Cs on SrO; Ag, K on SrO; and Ir, Cs on SrO.

- The University of Aachen reports that their initial attempts to reproduce "Falter-type" catalysts have resulted in adequate activity with lower than expected selectivity to isobutanol.

  TGA analysis of used Falter-type catalyst did not reveal any reasons for our lack of success in reproducing the previous Aachen results. The spent catalyst showed a higher degree of reduction and lost zinc at high temperatures, but neither of these phenomena were responsible for poor performance. Replacement of potassium with lithium in the Falter catalyst improved performance incrementally. This trend was the same as seen by Falter at Aachen. However, rate of reaction was still much lower than in the original Aachen work.

A visit to Aachen confirmed that the original Falter reactor was not isothermal. In addition, the reactor had both radial and axial gradients. It may be that the reactor characteristics had a great deal to do with the success of the original Falter catalyst. However, the deliberate imposition of steep axial temperature gradients in the packed bed reactor, like those observed in the previous work of Falter at Aachen did not improve the performance of the Li/Mn/Zn/Zr-based catalyst in syngas or syngas-plus-methanol conversion to isobutanol. The result, derived from experiments in a packed bed reactor designed like the one used in the original work, indicates that the most likely reason for our failure to reproduce the pre-performance results lies in the catalyst itself and not the testing method. Analytical measurement of the catalyst also indicates differences in catalyst.

- The University of Delaware has completed analysis of the factorial design based on the previous work of Styles. Some trends have been identified. Additional variables (e.g., alkalies and transition metals) will be screened.

- The cause of the rapid aging of the syngas to dimethyl ether catalyst system has finally been identified. Rapid aging of the mixed catalyst system is caused by an interaction between the methanol catalyst and the dehydration catalyst. Holding methanol catalyst and alumina under reducing conditions, with no reaction resulted in loss of activity, while the same conditions with no dehydration catalyst gave an active methanol catalyst. The exact nature of the interaction will be investigated further, since this understanding should hold the key to solving the problem.

  In a parallel effort, we are testing new dehydration catalysts. None of the dehydration catalysts screened under LPDME conditions this month showed improved aging over the standard catalyst system. Tested were CuO-doped Catapal g-alumina, magnesium exchanged zeolite Y, and TiO_2.

- A catalyst system consisting of BASF S3-86 methanol catalyst and silicon modified Catapal B g-alumina exhibited a 30% lower deactivation rate than that of the standard system (S3-86 plus virgin Catapal B alumina). While the initial activity is lower than the standard system, the new system demonstrated higher methanol equivalent productivity than the standard system after 50 hours on stream. Although the stability of the system is not completely satisfactory, the potential of improving the stability of LPDME catalyst systems by selecting proper dehydration catalysts has been demonstrated.

RESULTS AND DISCUSSION

TASK 1: ENGINEERING AND MODIFICATIONS

1.1 Liquid Phase Hydrodynamic Run

Air permit requirements for the hydrodynamic/methanol run were discussed among Process Engineering, Environmental Engineering and Radian Corporation personnel. Radian Corporation, contracted to evaluate air permit requirements, will review the proposed modifications and different operational options to determine whether we need a new air permit exemption.

Work began on modifications for the run scheduled for June 95. Discussions were held with Piping Design for changes in the heater/cooler sequence in the utility oil system. Moving the heater downstream of the cooler is expected to improve the reactor temperature control. After a field inspection, it was decided to install additional piping instead of physically moving the equipment. Installing the piping is cheaper than moving equipment, and the oil pump has enough capacity to handle the additional pressure drop caused by the piping. Discussions have also begun for installation of a sump and a pad in the trailer area to improve our ability to handle spills.

1.2 Liquid Phase Fischer-Tropsch Demonstration

A confidentiality agreement was signed between Air Products and Syncrude Technology (STI). Technical discussions were held at a meeting of Air Products, STI and DOE-PETC personnel for a proposed F-T run at LaPorte. The objective of the run is to evaluate performance of catalyst-reactor systems to confirm STI's design basis. A preliminary process flow diagram was developed based on STI's desired operational envelope. Four line specifications were generated for new equipment required at LaPorte. Equipment and materials costs for the modifications were estimated at $425,000, and the total cost of the run was estimated at $2,028,000.

A meeting was held in early November among Air Products, Syncrude Technology (STI) and DOE-PETC personnel to further discuss the run plan and conduct a tour of the LaPorte facility. Several potential investors in STI also joined for part of the meeting. The investors were impressed with our presentations and the facility. Later discussions with STI alone indicated that the ~ $2 MM estimate for the run exceeds their current budget. However, they cannot reduce the scope of the run as they do need to recycle dry wax to sustain catalyst activity and breakup catalyst agglomeration at the reactor bottom. Air Products and DOE personnel believe that STI will not be ready for a demonstration run in September 95. Confirmation of the recycle idea is needed in their laboratory which will not be operational till at least May 95. Also, catalyst preparation at a large scale can involve significant development work. Therefore the run schedule has now been pushed back to early 96. This schedule works well with PS Engineering's manpower situation, as a current estimate for a project completion without a high priority is about 12 months.

A two-day working meeting was held with Syncrude Technology (STI) to discuss their technical data base in detail. It appears that their catalyst requires a high level of inerts (~50% N_2) in the feed for activity maintenance. To accommodate the inerts, the operating pressure and flow were doubled from the original design basis. STI would like to use Mott's sintered porous metal elements for catalyst-wax separation as they are unable to have their wire wound screen elements fabricated in a timely fashion. They have not done any commercial economic study since 1990 and would rely on an Engineering & Construction Contractor to update it. Air Products has decided not to kick off the project until economics from an ECC appear promising.

Bogdan Slomka from Iowa State University visited LaPorte in early November. He and his team have been working on sonic-assisted cross-flow filtration, and for removal of solids from coal liquefaction products, they have demonstrated a 2.7 fold increase in filtrate flux with sonic treatment. They plan to evaluate the F-T spent slurry from LaPorte (F-T I) next.

TASK 2: AFDU SHAKEDOWN AND OPERATIONS

There is no progress to report this quarter.

TASK 3: RESEARCH AND DEVELOPMENT

3.1 DME Catalyst Activity Maintenance

In the last two quarterly reports from Contract No. DE-AC22-91PC90018 we have shown that DME and high water level are not directly responsible for the rapid aging of the catalyst system in the LPDME process. Since then, our focus has been on the effect of alumina on catalyst stability. Indeed, as shown below, an interaction between BASF S3-86 methanol catalyst and Catapal B g-alumina has been identified specifically as the cause of catalyst deactivation under LPDME conditions. The exact nature of this interaction is under investigation.

This finding shows that we need two catalysts that are compatible with each other. Considering the availability and the complex nature of methanol catalysts, alternative dehydration catalysts become an apparent solution. More efforts, therefore, have been directed at screening dehydration catalysts, an activity that had been started before the cause was found. Five dehydration catalysts have been tested in the past quarter. A catalyst system consisting of BASF S3-86 methanol catalyst and a silicon modified Catapal B g-alumina exhibited better stability and higher productivity (after 50 hours on stream) than that of the standard system (S3-86 plus virgin Catapal B alumina).

A literature review on the recent development (1990 to present) of the one step syngas-to-DME process has been conducted. The highlights include the following: 1) a novel catalyst has been developed by Eastman to convert syngas to methanol and DME, while all other catalyst systems are still some form of a mixture of a methanol synthesis and a dehydration component; 2) stable catalyst systems (up to 1000 hr) have been reported for syngas to DME under gas phase reaction conditions; 3) dehydration catalysts other than pure g-alumina appeared in the literature, providing leads for our catalyst screening; and 4) in terms of methanol equivalent productivity, there is no order-of-magnitude difference in the performance among the literature catalysts/processes and between them and the Air Products LPDME process.

3.1.1 Identifying the Cause of Catalyst Deactivation under LPDME Conditions

The effect of alumina on the stability of methanol catalysts was investigated using the following experimental scheme. Upon the standard catalyst reduction using 2% H_2 in N_2, a catalyst mixture consisting of 80 wt.% of BASF S3-86 methanol catalyst and 20 wt.% of Catapal B g-alumina was left under flowing reduction gas (2% H_2 in N_2, 50 sccm/min.) at 250°C for 117 hours. The activity of the catalyst system was then measured using Shell syngas to see if holding the two catalysts together at 250°C has any effect on their activity. This scheme avoids exposure of the catalyst system to syngas and reaction products during the holding period; therefore, any effect can be attributed to the mere presence of alumina.

Ideally, one would like to use a inert gas such as nitrogen or helium for the holding period. However, a previous experiment (13465-60) has shown that the methanol catalyst, when loaded by itself, deactivates under flowing nitrogen (APCI zero grade) at 250°C. In contrast, holding the methanol catalyst by itself at 250°C under 2% H_2 in N_2, as shown below, exhibits little effect on its activity. Therefore, the reduction gas was used in the current alumina impact study to provide an inert medium.

The activity of this catalyst mixture (14045-26) is compared in Table 3.1.1 with that of similar catalyst mixtures from two previous LPDME life studies (11782-3 and 13467-11). Note that the initial activity of the current catalyst mixture, i.e., within 30 hours after the standard reduction, was not measured. This was done to avoid the complication that heavy products might be introduced from the initial activity check and remain in the slurry to deactivate the catalysts. We have confidence in catalyst reduction due to excellent reproducibility in the past. The hydrogen uptake during the current reduction was also found to be in the normal range. Therefore, it is assumed that the initial activity of the catalyst in the current run is similar to the other two DME life runs listed in the table, i.e., about 30 mol/kg-hr in productivity.

Table 3.1.1 - Comparison of the Catalyst Activity of Different LPDME and LPMEOH Runs
Reaction Conditions: 250°C, 750 psig, 6,000 sl/kg-hr, Shell gas

Run	Catalyst S3-86:Al2O3	Time on Stream (hr)			MEOH Equiv. Prod. (mol/kg-hr)	Concentration (%)		Rate Constant	
		Rdctn gas	Syngas	Total		MEOH	DME	k_m^a	k_d^b
LPDME									
14045-26	**80:20**	**117**	**26**	**143**	**13.7**	**0.27**	**2.66**	**0.84**	**6.4**
11782-3	81.3:18.7	0	20	20	30.7	1.01	6.95	2.61	17.0
			139	139	22.9	0.85	4.71	1.65	10.5
13467-11	81.3:18.7	0	25	25	30.7	1.02	6.85	2.60	12.5
			140	140	21.6	0.78	4.37	1.66	8.7
14045-36	**80:20**	**120**	**29**	**149**	**13.9**	**0.28**	**3.52**	**0.89**	**7.3**
LPMEOH									
14045-28	**100:0**	**17**	**7**	**24**	**15.7**	**6.80**	**0.006**	**1.51**	
		128	**14**	**142**	**14.8**	**6.28**	**0.006**	**1.29**	
		128	**39**	**167**	**15.0**	**6.34**	**0.004**	**1.32**	

Table 3.1.1 - (continued)

Run	Catalyst S3-86:Al2O3	Time on Stream (hr) Rdctn gas	Syngas	Total	MEOH Equiv. Prod. (mol/kg-hr)	Concentration (%) MEOH	DME	Rate Constant k_m^a	k_d^b
13467-90	100:0	0	24	24	14.4	5.9	0.08	1.81	
		0	140	140	15.0	6.2	0.03	1.74	

a: Methanol synthesis rate constant calculated from $R_m = k_m k_{co_2} f_{H_2}^{2/3} f_{CO}^{1/3}(1-appr.)$, based on methanol catalyst weight.

b: Methanol dehydration rate constant calculated from $R_d = k_d f_{CO_2}^{-0.33} f_{MEOH}^{0.11} f_{CO}^{0.70}(1-appr.)$, based on alumina weight.

Table 3.1.1 shows that holding the methanol catalyst together with Catapal B alumina at 250°C for 117 hours results in a 55% drop in methanol equivalent productivity. Judging by the rate constants calculated from our current methanol synthesis kinetic model (with some confidence) and methanol dehydration kinetic model (with little confidence), their presence together causes both catalysts to deactivate. Since this observation of incompatibility of the two catalysts is important for the direction of our future work, the above experiment was repeated. As shown in Table 3.1.1, (Run 14045-36), the observation is reproducible.

In order to ensure that the presence of the reduction gas does not have any negative effect on catalyst stability, a similar holding-under-reduction-gas experiment was conducted with only the methanol catalyst loaded in the reactor. The results from this control experiment are also shown in Table 3.1.1 (14045-28), along with the results from a normal LPMEOH run under similar reaction conditions (13467-90). It can be seen that holding under the reduction gas for 128 hr has little effect on methanol catalyst activity. The small drop in activity between the first two measurements (15.7 mol/kg-hr at 7 hours under syngas to 14.8 at 14 hours) is expected when the catalyst burned out its initial hyperactivity under syngas. Upon exposure to the reduction gas for 128 hours, the catalyst has an activity similar to that under normal LPMEOH conditions. (The difference between two measurements in Run 13467-90 is within the noise level in that experiment.)

These results clearly indicate that there is a strong interaction between the methanol catalyst and the Catapal B g-alumina that deteriorates both catalysts. It is not clear what effect of syngas and reaction products would have on this interaction. However, the greater drop in activity under the reduction gas (55% in methanol equivalent productivity) than that under LPDME conditions for a similar length of time (33%) suggests that the interaction is more severe in the absence of syngas and LPDME products.

3.1.2 Understanding the Nature of the Interaction

Working Hypotheses

Understanding the exact nature of the detrimental interaction between the two catalysts is important for the development of stable catalyst systems for the LPDME process. The possible mechanisms are either chemical or physical. Chemically, there may exist spontaneous migration of active component(s) from the methanol catalyst to the alumina, since alumina is known as a good support material for metals, metal oxides and metal salts, i.e., a good chemical potential sink. In many cases, a monolayer coverage of metal compounds on the alumina surface can be achieved spontaneously. Second, ion exchange can occur between metal ions in the methanol catalysts (e.g., Cu^+) and certain specific sites on alumina (e.g., Bronsted acid sites). Third, solid state reaction may take place between two catalysts, e.g., between ZnO (basic) and alumina (acidic), forming chemically bound agglomerates. Fourth, contaminants can be brought into the system by the alumina that poison the methanol catalyst. All of these mechanisms will result in the deactivation of both catalysts (except the fourth one) and can be categorized as *inter-catalyst mass transfer* or *inter-catalyst solid state reaction.*

Physically, agglomerates can be formed from the two catalysts, resulting in thermal sintering or a change in the sedimentation properties of the solids. The formation of fines as a result of the collision between the two catalyst powders in the slurry is another harmful factor . Would large surface area and the porous structure of alumina have any negative effects? What is the role of the mineral oil, serving as slurry fluid, in catalyst deactivation? Some of these physical processes may deactivate catalysts directly (e.g., thermal sintering and a change in sedimentation properties). Some may operate along with the chemical processes mentioned above. For example, formation of physical agglomerates will provide the long contact time necessary for intercatalyst mass transfer or reaction. The mineral oil can provide a good mass transfer medium.

Even with this short list, a considerable number of parameters need to be examined to shed light on the development of stable catalyst systems. If alternative dehydration catalysts are chosen to be the solution, one needs to look at the following properties of dehydration catalysts:

— Acid types and strength
— Dispersing ability as a support material
— Hardness
— Pore structure and surface area
— Hydrophilic vs. hydrophobic

Thus there are many areas in catalyst screening that need to be explored. Understanding the nature of the interaction will decrease the number of catalyst candidates to be screened. Several possible mechanisms have been investigated in the last quarter.

Gas Phase DME Life Study

A gas phase DME life study has been carried out to shed light on the mechanism of possible mass transfer between the two catalysts. Some of the ways in which migration of material from one catalyst component to the other catalyst component could occur are:

(1) transport of a soluble species through the slurry liquid
(2) transport of a volatile species through the gas phase
(3) surface diffusion when the catalyst particles are in direct contact

Any of these transport mechanisms could occur in a slurry reactor. However, for a packed bed reactor the situation is different; only routes (2) and (3) are possible. Route (2) could certainly be operative in any situation where the two catalysts are in the same packed bed reactor, but route (3) could only be operative if the two components were in close contact.

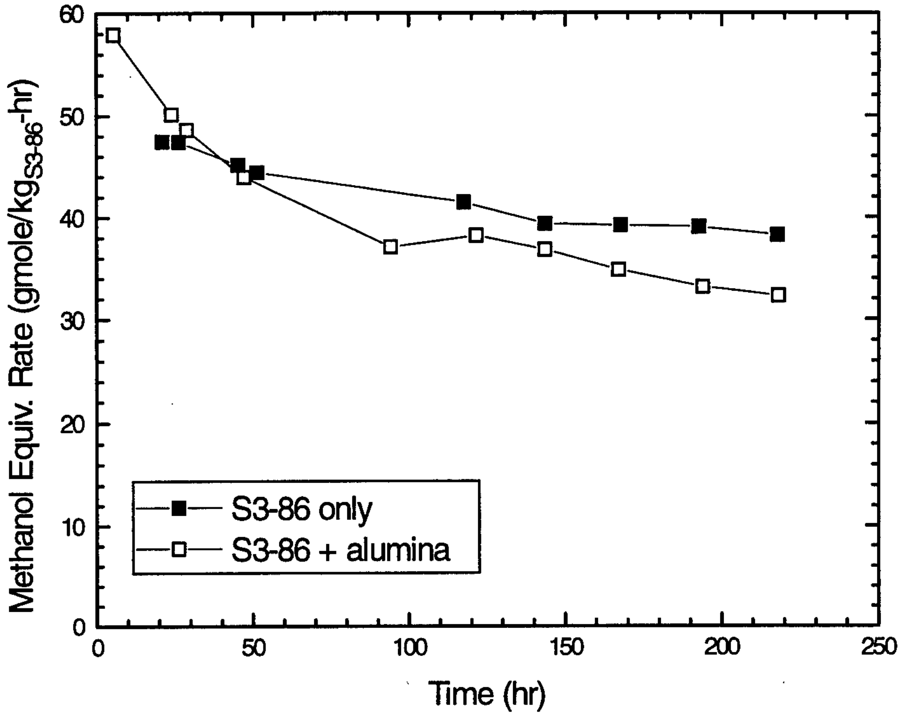
Thus, to test the hypothesis of inter-catalyst mass transfer and to narrow the field of possibilities on mechanisms of transport, deactivation studies were done using a packed bed reactor. Two packed bed life test runs were conducted: one with S3-86 alone to establish a deactivation baseline and the other with an intimate physical mixture of S3-86 and alumina powders. Both tests were run at differential reaction conditions, i.e., very low CO conversion. In this case, the DME productivity is very low for the S3-86/alumina mixture. Thus, the effect of alumina on the S3-86 component is observed, in the absence of appreciable concentrations of products from the alumina and also in the absence of a liquid phase. Specifically, the goal of this experiment was to test whether alumina provides a sink for Cu and/or Zn transported from the S3-86 by one or more of the above mechanisms.

For each run, powder was pressed into pellets approximately 0.5 mm in diameter. The same quantity of S3-86, 0.11 g, was used in each case. To minimize the exotherm (and the concentration of DME) in the packed bed, the conversion was kept very low (<2% CO) by operating at high GHSV (130,000 sl/kg-hr in each case). The calculated adiabatic temperature rise is 32°C at 2% CO conversion. Because of constraints imposed by the reactor configuration and the extremely small bed size, it was not possible to measure the actual temperature of the catalyst particles. Instead the temperature a short distance upstream from the catalyst particles was maintained at 250°C. Due to the very high GHSV the DME productivity for the S3-86/alumina mixture was approximately 5% of the methanol productivity. In fact, the reactor exit DME concentration was comparable to that observed in methanol synthesis over S3-86 alone at typical integral conversions of CO. (For S3-86 alone under differential conversion, the DME productivity and exit concentration was zero.)

The methanol production rates (methanol equivalent rate for the S3-86 plus alumina mixture) as a function of time on stream for both cases are shown in Figure 3.1.1. Initial rates are comparable for both cases. The deactivation rate for the S3-86 alone is higher than typically observed in a LPMEOH run at integral conversion at 250°C. This is likely due to the fact that the catalyst particles in the packed bed experiment are probably at a temperature higher than 250°C because of the reaction exotherm. The deactivation rate for S3-86 is known to increase with increasing temperature. The deactivation rate for the S3-86/alumina mixture appears to be slightly greater than that for S3-86 alone, but the magnitude of the apparent difference is small. In fact, it is not possible to conclude with any confidence that there is a significant difference between the two rates of deactivation. The current experiment does not demonstrate that alumina provides a sink for Cu and/or Zn from the S3-86 component transported by the mechanisms appropriate for a packed bed reactor.

An experiment utilizing Robinson-Mahoney basket internals in a 300 CC autoclave is now being conducted. The liquid phase reaction can run isothermally, thus avoiding the complications involved with reaction exotherms in the packed bed. This experiment uses pellets of S3-86 and alumina, thus making possible several studies which cannot currently be done in the slurry reactor. For example, analysis of the individual catalyst components that have been used in reaction will be possible. Also, spatial separation of the two catalyst components is possible to provide information as to whether inter-catalyst transport of Cu, Zn, or Al is operative.

Figure 3.1.1 - Methanol Synthesis Life Tests using a Differential, Packed Bed Reactor



Effects of Large Surface Area Materials

To find out if the large surface area (265 m^2/g) and porous structure (average pore diameter 100 A) of the Catapal alumina are responsible for the deactivation of the catalyst mixture, a holding-under-reduction-gas experiment was conducted using a silica gel (Davison grade 55, SA=300 m^2/g, average pore diameter = 150 A) mixed with S3-86 methanol catalyst. The initial activity of the mixture was measured using syngas upon reduction. As shown in Figure 3.1.2, the initial methanol synthesis activity of the mixture is similar to that of a pure methanol catalyst. Judging by the product distribution, the activity is solely due to the methanol catalyst, and the silica gel is completely inert under the reaction conditions. The activity of the methanol catalyst was checked again after the system was maintained under 2% H_2 in N_2 for 117 hr (250°C, 750 psig, 50 sccm). In contrast to the S3-86/Catapal B g-alumina system, no significant drop in the activity was observed. This indicates that a high surface area material is not solely the problem.

The above catalyst system was left under syngas for an additional 173 hr, and a continuous decrease in the activity was observed (Fig. 3.1.2). Figure 3.1.3 shows the normalized methanol synthesis rate constant, calculated from the process engineer's model, as a function of time on syngas stream for this run, along with the constant when pure S3-86 or a S3-86/Catapal B mixture was used. It can be seen that the silica gel causes deactivation of the methanol catalyst under LPMEOH conditions, but at a much slower rate than Catapal B alumina under LPDME conditions. The results shown in Figures 3.1.2 and 3.1.3 indicate that silica may be more compatible to the methanol catalyst than alumina. Therefore, more silica-based dehydration catalysts will be examined.

Figure 3.1.2 - Compatibility Study of S3-86 and Silica Gel System

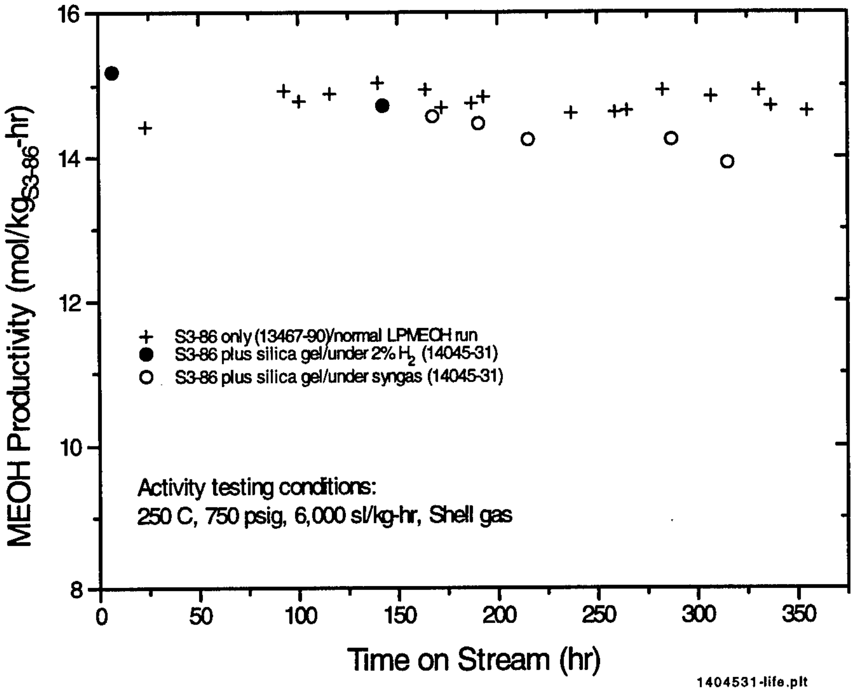
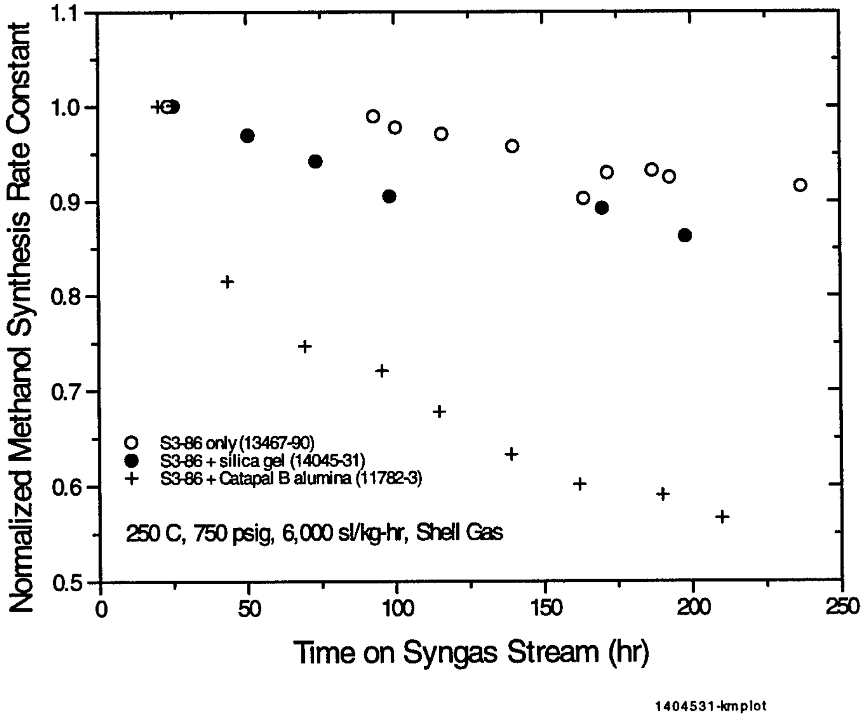


Figure 3.1.3 - Methanol Catalyst Stability with Different Dehydration Catalysts



Possibility of Sediment Formation

The possibility of sediment formation was also examined. Scanning electron micrographs have shown that many fine methanol catalyst and alumina particles are formed under LPDME conditions, apparently due to the collision between catalyst particles. It is possible that the formation of these fines changes the sedimentation properties of the slurry system. For example, large agglomerates with poor dispersing properties could be formed, or the fines themselves may stick to the walls of the reactor, therefore, reducing the activity of the system. Should sedimentation be the cause of catalyst deactivation, increasing stirring rate would bring some of the sediments back into the slurry, resulting in higher activity. Based on this thinking, the activity of a deactivated catalyst system consisting of BASF S3-86 methanol catalyst and a Si-modified Catapal B g-alumina (see Run 14191-36 in the next section) was measured after the stir rate was changed from the normal rate at 1,600 rpm to 2,500 rpm. However, little effect on the activity was observed. This simple experiment rules out the sedimentation hypothesis.

Contamination from Alumina?

Another possible effect of the Catapal B alumina on the methanol catalyst is that the impurities in the alumina, including known methanol catalyst poisons such as Fe, Ni, S and Cl, may migrate onto the methanol catalyst, leading to its deactivation. To check this possibility, bulk elemental analysis of the Catapal B alumina was conducted, and the results are shown in Table 3.1.2 below. Also included in the table is the bulk composition of the methanol catalyst. It can be seen that the level of poisonous elements in the alumina sample is very low, actually lower or comparable to that in the methanol catalyst. Therefore it is unlikely the alumina is a source of contamination to the methanol catalyst. The high purity of Catapal alumina is due to its production method (ethoxide route).

Table 3.1.2 - Elemental Analysis of Catapal B g-Alumina and S3-86 Methanol Catalyst
(in ppmw)

Sample	Fe	Ni	Cu	Zn	Ti	Ca	Mg	S	Cl
Catapal B alumina (LaPorte 91 run)	<7.3	<10	<1	<5	840	<8.3	<1.4	<100	<100
S3-86 (91/14638)	100	11							33

The surface composition of a deactivated sample of S3-86 and Catapal alumina mixture (S3-86:alumina = 81:19, 500 hr on stream, #13467-11) was analyzed using XPS, and the result is compared in Table 3.1.3 with the surface composition of a pure methanol catalyst of normal activity (#13467-90). No conclusion can be drawn from this analysis because the concentrations of Cl, Fe and Ni in both samples are below the detecting limit of the instrument.

Table 3.1.3 - XPS Analysis of the Surface Composition of Methanol Catalyst Samples*

Sample ID	Cu	Zn	C	O	Al	Cl	Ni	Fe
13467-11	4.2	5.3	33.1	34.2	23.2	ND	ND	ND
13467-90	3.9	5.2	36.0	33.0	21.9	ND	ND	ND

* Composition in atomic percentage; ND: not detected; detection limit: 0.1 atomic%.

Plan for the Coming Quarter

In addition to the study utilizing Robinson-Mahoney internals, efforts are being made 1) to characterize the surface composition of Catapal alumina before and after deactivation under LPDME conditions, and 2) to understand the effect of the acid properties of a dehydration catalyst (type and strength) on the aging of a catalyst system. The first investigation, primarily using scanning electron microscopy (SEM), will reveal if there is mass transfer between the two catalysts; and if true, what species is transferred. The second study, assisted by IR characterization, will hopefully demonstrate if catalyst deactivation is specifically related to certain acid sites on a dehydration catalyst.

3.1.3 Catalyst Screening

Even before the detrimental interaction between the two catalysts was identified, efforts had been started to search for stable catalyst systems based on the hypothesis of mass transfer or reaction between two catalysts. The approaches included stabilizing the methanol catalyst and examining alternative dehydration catalysts. It was soon realized that the temperature ceiling (ca. 300°C) for a stable methanol catalyst leaves little room for modification of a commercial methanol catalyst, and the methanol catalyst is too delicate a system to manipulate. Therefore, primary efforts have been on screening alternative dehydration catalysts. In the past quarter, a modified methanol catalyst and five alternative dehydration materials have been tested.

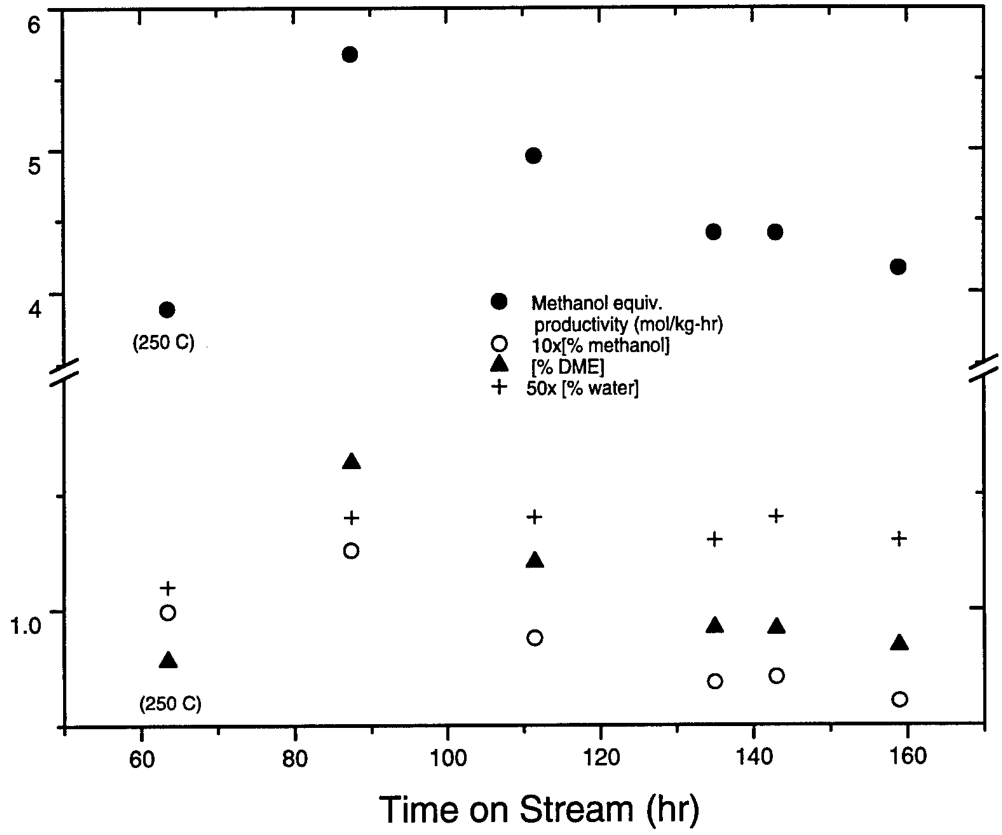
Cr_2O_3 -Modified S3-86

The BASF S3-86 methanol catalyst was modified by Cr_2O_3 according to a literature method [P. G. Bondar et al., US Patent 4,107,089, 15 August 1978]. This modification reportedly should result in high thermal stability. The modified catalyst, combined with Catapal B g-alumina, was tested using Shell gas. As shown in Figure 3.1.4, the activity of the methanol catalyst is very low at 250°C, an initial methanol equivalent productivity of 4 mol/kg-hr. A previous run using virgin BASF S3-86 under similar conditions (13467-11) shows an initial methanol equivalent productivity of 30.7 mol/kg-hr. The activity of the modified S3-86 catalyst is also an order of magnitude lower than that of the Cr_2O_3 -modified catalyst reported in the original patent, indicative of the difficulty in reproducing the literature preparation. Nevertheless, we proceeded to test the stability of the catalyst system. In order to start at a reasonable activity, the test was conducted at 270°C. Aside from the low activity, the figure shows that this Cr_2O_3-modified catalyst does not have good stability.

Si-Modified Catapal B g-Alumina

A 1979 patent by Snamprogetti [G. Manara, et al., US Patent 4,177,167 (1979)] shows that the stability of a mixture of methanol catalyst and g-alumina for a *gas phase* one step syngas-to-DME process can be greatly improved if the alumina is treated with a silicon compound. We prepared a silicon-modified Catapal B alumina sample (Si-Catapal B) according to the patent. A LPDME life test using the Si-Catapal B sample and S3-86 methanol catalyst was conducted at 250°C and 750 psig using Shell gas, and the results (14191-25) are shown in Figure 3.1.5 along with the results from a previous LPDME run using S3-86 and virgin Catapal B alumina (11782-3).

Figure 3.1.4 - Catalyst Screening Run Using Cr_2O_3-Modified S3-86 (14191-2)
Conditions: 270 C, 750 psig, 5,000 sl/kg-hr, Shell Gas
Catalysts: Cr_2O_3-Modified BASF S3-86 (13467-77) plus Catapal Alumina (4:1)



The methanol equivalent productivity of the Si-Catapal B system is fairly low initially. However, it increases with time on stream, reaches a maximum at ca. 50 hours, and then continuously decreases. The induction behavior in the first 50 hours can be attributed to the conditioning of the dehydration catalyst under the reaction conditions. As shown in Figure 3.1.6, the methanol concentration drops rapidly in this period, accompanied by an increase in DME concentration, indicating that the dehydration catalyst is activated in this period. This is understandable because the highest temperature seen by the Si-Catapal B sample during preparation is 200°C, 50°C lower than the reaction temperature. In order to reduce this induction behavior and to see if better stability can be obtained, another Si-Catapal B sample was calcined at 500°C for 5 hours and tested in a separate run (14191-36). As shown in Figure 3.1.5, this calcined Si-Catapal B sample still exhibits an induction period (ca. 115 hr), during which the activity increases slightly. The catalyst system containing the calcined Si-Catapal B sample does not show a better stability than the one without calcination. The activities of the two systems actually become similar to each other upon 200 hr on stream.

The system consisting of S3-86 and Si-Catapal B appears to be more stable than that of S3-86 and virgin Catapal B alumina. As shown in Figure 3.1.5, the methanol equivalent productivity of the Si-Catapal B system becomes higher than that of the virgin Catapal B system after 50 hr on stream, partly due to rapid deactivation of the latter system.

Figure 3.1.5 - LPDME Life Study Using S3-86 and Si-Modified Catapal B Alumina

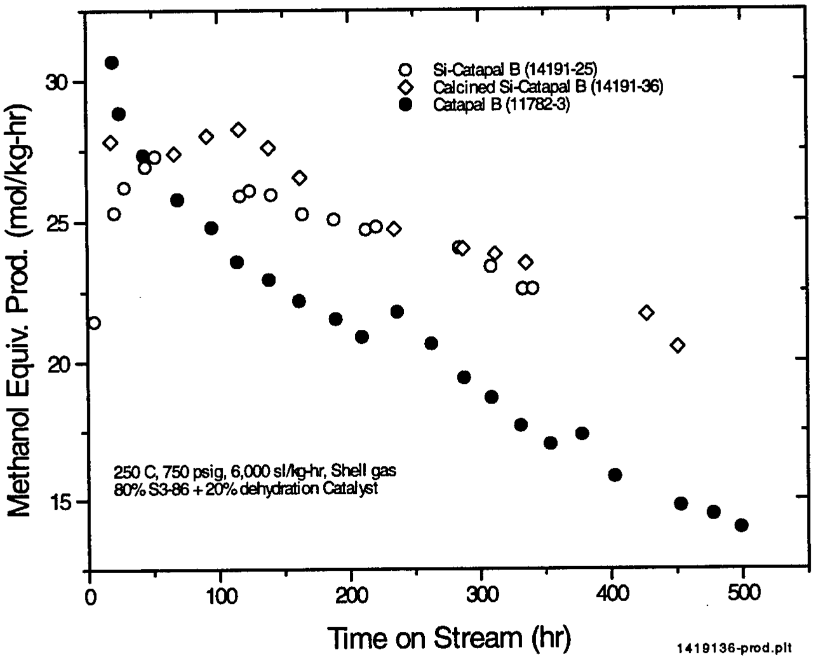
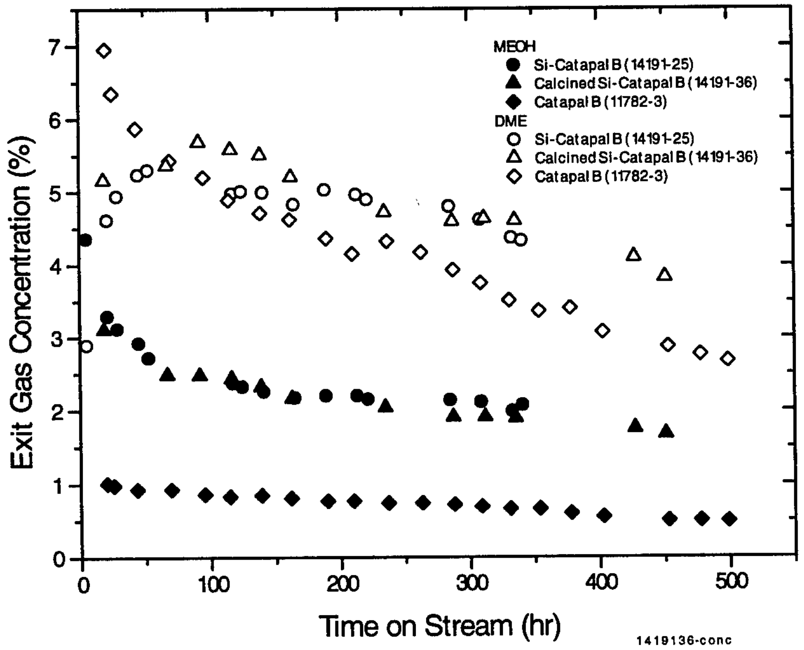


Figure 3.1.6 - Methanol and DME Concentration in the Effluent as a Function of Time on Stream

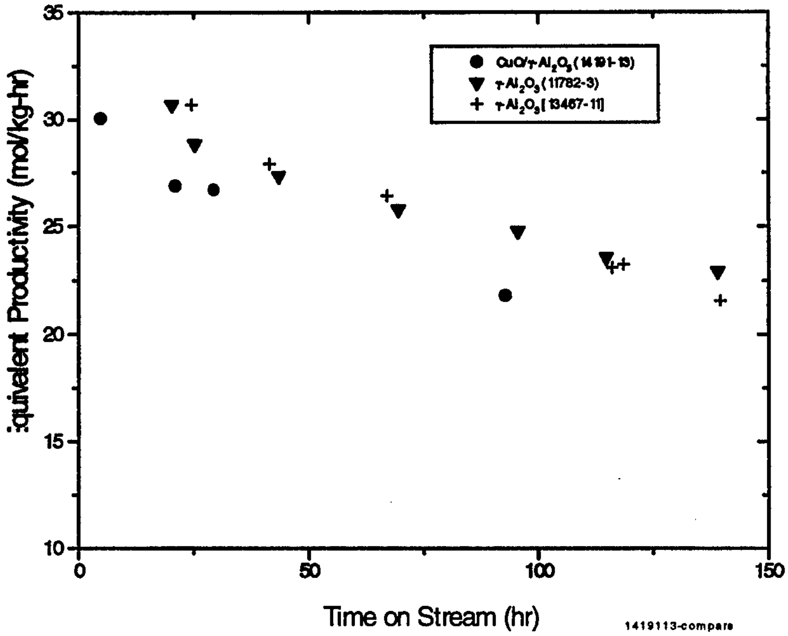


The difference between the two systems becomes larger with increasing time on stream because the deactivation rate of the Si-Catapal B system is smaller by a factor of 0.7. This result is encouraging because it shows the potential of improving the stability of LPDME catalyst systems by selecting proper dehydration catalysts.

CuO-Doped Catapal B g-Alumina

CuO doped g-alumina was tested as a dehydration catalyst for the following two reasons. First, it is reported [K. Fujimoto et al., EP patent 591,538 (1994)] that CuO doped g-alumina is more active than pure g-alumina for one-step syngas-to-DME process. Second, if the migration of the active components from the methanol catalyst to alumina (especially, a Cu-containing species) would be the cause of the catalyst deactivation under LPDME conditions, doping with CuO might make the alumina a lesser acceptor, therefore reducing the migration/deactivation process. A CuO doped g-alumina was prepared in this lab from the Catapal B alumina. The catalyst contains 6.2 wt.% of CuO and exhibits no CuO XRD powder pattern, indicative of perfect dispersion. This loading corresponds to a 20% monolayer CuO coverage on the alumina surface. This catalyst and S3-86 methanol catalyst were loaded into a 300 cc autoclave, and the test result (14191-13) is shown in Figure 3.1.7, along with two previous LPDME life runs under similar conditions (11782-3 and 13467-11) using virgin Catapal B alumina. It can be seen that the deactivation pattern of the catalyst mixture containing CuO-doped alumina is similar to that of virgin alumina. Contrary to the literature report, the methanol equivalent productivity of the system containing CuO-doped g-alumina is slightly lower than that of virgin alumina.

Figure 3.1.7 LPDME Runs Using Different Dehydration Catalysts
250°C, 750°C, 6,000 sl/kg-hr, Shell gas, S3-86:alumina=80:20



Chabazite

A chabazite dehydration catalyst developed at Air Products for a commercial methyl amine process was tested along with S3-86. The chabazite catalyst was chosen because it is a weaker acid than many other zeolites such as H-ZSM5 and Y-zeolite. (Strong acidity reportedly results