

ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS

FINAL

Quarterly Status Report No. 10

For the Period 1 January - 31 March 1997

Contractor

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Alternative Fuels and Chemicals from Synthesis Gas

Quarterly Technical Progress Report

1 January - 31 March 1997

Contract Objectives

The overall objectives of this program are to investigate potential technologies for the conversion of synthesis gas to oxygenated and hydrocarbon fuels and industrial chemicals, and to demonstrate the most promising technologies at DOE's LaPorte, Texas, Slurry Phase Alternative Fuels Development Unit (AFDU). The program will involve a continuation of the work performed under the Alternative Fuels from Coal-Derived Synthesis Gas Program and will draw upon information and technologies generated in parallel current and future DOE-funded contracts.

RESULTS AND DISCUSSION

TASK 1: ENGINEERING AND MODIFICATIONS

1.1 Liquid Phase Fischer-Tropsch Demonstration

A meeting was held with Sundstrand personnel on 9 January to discuss their post Fischer-Tropsch III run observations of the slurry pump and develop a plan to improve its performance. Following is a summary of the discussion:

- The throat can be opened up from 0.328 in. to a maximum of 0.446 in. This will reduce the throat velocity by almost a factor of 2: from 83.5 ft/sec to 45.2 ft/sec at 22 gpm (9 ft/sec in the filter element). We can reduce the throat velocity further to 30.1 ft/sec by operating at 14.7 gpm (6 ft/sec in the filter element). A larger throat diameter would require us to operate at lower pump speed, which would decrease the efficiency. This is not a problem at LaPorte, because we have enough HP. According to Sundstrand, our application involves too low a flow for the head requirement. Scaleup to higher flow for commercial application would improve efficiency.
- There is no need to increase the impeller clearances at the top or bottom from a bowl erosion point of view. The clearance between the impeller and the bottom bowl was measured at 0.055 in., which is within specification. The clearance may have opened up about 0.004 in. The clearance between the impeller and the top cover was measured at 0.050 in., which is within the normal range of 0.040-0.060 in.
- Sundstrand asked us to consider alternative harder materials for pump internals instead of the current 316 SS (ASTM A351 grade CF8M - both bowl and impeller are made of this material): either duplex steel (CD4MCU) or heat-treated carbon-steel. The current pump had no coating on the internals. Sundstrand does not favor coating because if the coating is broken through, it leaves a rough surface for significant erosion.

- Sundstrand suggested use of bellow seals in the lower position to prevent leakage during the operation. Other suggestions included use of a differential pressure regulator to maintain the seal pressure 50 psi above the suction pressure; pressure rating of the lower seal at full pressure; and use of a block valve to stop process fluid from going into the buffer system. The valve can trip on a buffer pump trip or a differential pressure trip. A normally closed solenoid valve connected with the pump circuit can be used. We already have a check valve to prevent pressure on the buffer pump.
- There was no evidence of damage in the largest diameter of the bottom bowl. All damage was on the angled portion, where it was close to the spinning impeller. Sundstrand was surprised at the extent of damage on the bottom bowl and that only one scratch was found on the top cover. Typically, they observe a lot more damage at the top compared to the bottom.

Sundstrand agreed to prepare a proposal based on our discussion. Shell is currently reviewing Sundstrand's suggestions.

A meeting was held with Shell International personnel to define scope and develop a run plan consistent with available funding for a Fischer-Tropsch (IV) demonstration run. Shell has been following up several possible causes of filter problems during F-T III: (1) The strength of their proprietary catalyst used in F-T III vs. the strength of their improved proprietary catalyst; (2) the effect of liquid medium on catalyst attrition; (3) the effect of pumping velocity on attrition; (4) the use of a different type of filter element. So far, laboratory test results have been inconclusive for (1), (2) and (3). The improved catalyst appears to be stronger when slurried with water. However, in oil, the two catalysts show similar attrition. Also, surprisingly, Shell did not see an effect of pumping velocity on attrition. Next, they plan to test three types of filter elements (sintered metal, ceramic membrane and woven metal) in parallel with activated improved catalyst in wax. A Sundstrand centrifugal pump will be used in these tests to evaluate erosion. The testing is expected to be complete by the end of May. This leaves a narrow window for design and engineering because the desired start-up time is mid October. In addition to the pump and the filters, the modifications will include redesign of the product wax system to improve filtration control and inclusion of a molecular sieve bed to accelerate catalyst activation. A tentative plan for a 20-day run was developed with Shell's input. The run will include five different process conditions (16 days), 3 days for a tracer study and 1 day for dynamic gas disengagement tests.

A rough cost estimate of about \$600,000 was made for the F-T IV modifications described above. This was higher than anticipated because even with a smaller scope, we still need to perform tasks such as equipment and instrument specification, flowsheet changes, piping design, operability/safety review and installation. The \$600,000 estimate includes new filters, modifications to the Sundstrand pump, four control valves and associated piping. The molecular sieve vessel (\$100,000) was excluded, since the costs exceeded the benefits. Instead, it was decided to eliminate one process condition and shorten the run time to 18 days to allow 2 extra days for reduction. To be cost-effective, the project will be kicked off only after the scope is well defined. During March, Shell continued commissioning of the filter loop in its pilot plant. The

main cause of the delay was mechanical problems encountered with the slurry pump. The testing will be completed by mid June. If the tests are successful, we will begin the modifications immediately and plan for an October-November run.

1.2 Liquid Phase DME Demonstration

Discussions continued with R&D to develop a run plan to demonstrate DME synthesis at LaPorte. Since the timing of the demonstration is not critical, it was decided to postpone the run until February 1998. This will give R&D six months to improve the catalyst system further and six months to scale up the preparation and make batches for LaPorte. The most important objective for the next run will be to demonstrate improved stability over the 1991 catalyst system. A key question is what run duration at LaPorte is required to achieve this objective. Data from the 1988-89 4-month LPMEOH™ LaPorte run (E-7) were statistically analyzed to answer that question. Standard errors for deactivation rates were calculated for different on-stream times, as shown Table 1.1.

Table 1.1
Analysis of 4-Month LPMEOH™ Life Run at LaPorte

Days On-Stream	Deact. Rate (a) of k0, %/day	2*Std Error of (a)	2*% Std Error of (a)
113	-0.38	0.01	3
60	-0.36	0.04	11
45	-0.29	0.06	21
30	-0.44	0.10	24
22	-0.52	0.18	34
15	-0.25	0.26	106
7	0.44	0.59	132

Days On-Stream	Deact. Rate (b) of Productivity, %/day	# of Days needed to see a 2% drop
113	-0.17	12

The data indicate that we need minimum data for ~15 days to check stability if the DME catalyst system is as stable as the LPMEOH™ system. Data for more than 3 weeks on stream will be required to quantify the deactivation rate. Data for 60 days on stream are enough to obtain a fairly accurate deactivation rate. LPMEOH™ life data from Kingsport will be analyzed as they become available before the LaPorte DME run.

A preliminary run plan for the DME demonstration is given in Table 1.2. With emphasis on catalyst life, the DME run duration was extended to 40 days. We have retained some time for LPMEOH™ studies, as current laboratory water injection results are inconclusive. The plan allows 15 days for the life study; however, we will have to be flexible and adjust the duration, depending upon the results. Two different catalyst ratios will be evaluated for DME synthesis. A process variable study will evaluate performance at higher pressure (up to 1800 psi), higher superficial velocity (1-1.2 ft/sec) and water injection. A variety of gas compositions such as Shell, Texaco, and Kingsport gas will be tested. The run will also include a 3-day tracer study.

**Table 1.2
Preliminary Run Plan for a DME Demonstration Run at LaPorte**

OBJECTIVE	CATALYST	FEED GAS	DURATION, DAYS
METHANOL WATER INJECTION STUDY	MEOH	TEXACO	7
DME LIFE STUDY	MEOH + X% DEHY.	SHELL	15
DME PROCESS VARIABLE STUDY: - HIGHER PRESSURE - HIGHER SUPERFICIAL VELOCITY - WATER INJECTION	MEOH + X% DEHY.	SHELL	7
DIFFERENT FEED GAS COMPOSITIONS	MEOH + X% DEHY.	TEXACO KINGSPORT	4
TRACER STUDY	MEOH + X% DEHY.	SHELL	3
HIGHER PROPORTION OF DEHY. CATALYST	MEOH + Y% DEHY.	SHELL	4
TOTAL			40

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

3.1.1 Improved Synthesis of Aluminum Phosphate

The aluminum phosphate dehydration catalyst has shown the best performance thus far. This catalyst displays sufficient sustained activity to give acceptable economic performance in the IGCC-coupled scenarios, and will be used in the next plant trial. Thus, it is important to understand this catalyst and the factors affecting its performance. Efforts were continued to understand the key parameters in the preparation of the aluminum phosphate catalyst.

Two parameters, which were suggested by the work leading to the successful preparation of AP05C, are the time spent for the precipitate to mature and the pH at which the filtrate is washed. A set of experiments was conducted to study these parameters. Two good aluminum phosphate samples, designated AP05D and AP07, were obtained from this set of experiments. The common thread between these two samples is long maturing time. Further experiments are under way to confirm this observation and to prepare more active catalysts based on this finding.

Three modified aluminum phosphates were tested in LPDME™ runs under standard conditions. These catalysts were prepared by treating a standard material (called AP05C) with a base at 800°C for varying times. The objective was to learn whether there was an optimum duration of the base treatment in producing adequate stability of the methanol synthesis activity without sacrificing dehydration activity. The results are summarized in Table 3.1.1, and key points are discussed below.

Table 3.1.1 Performance of Modified AP05-C Materials*

Sample	Amount of Treatment	Atomic % Base on Surface**	Duration of Dehydration Activity Rise (hrs)	Methanol Activity Loss (%/hr)***	Maximum Dehydration Rate Constant	Methanol Productivity Maximum (gmol/kg,hr)
Base AP05C	None	---	250	0.10	8.2	27.5
1427X1-3x6	3 hours	1.1	350	0.07	6.2	26.7
1427X1-3x5	5 hours	1.4	150	0.14	5.8	26.4
1427X1-3x3	8 hours	2.2	550	0.05	6	25.5

*All experiments were performed in the AFDU using Texaco gas at 6000 GHSV, 250°C and 750 psig. The catalyst charge was composed of BASF S3-86 methanol synthesis catalyst (80%) and the respective aluminum phosphate (20%). The run with -3x5 used 30 grams of catalyst (20 wt % in the slurry); all other runs used 10 grams (6.7 wt %). 120 grams of Drakeol-10 mineral oil were used in each run. In the run Base AP05C, which employed the standard aluminum phosphate, S3-86

was reduced in the presence of the aluminum phosphate. In the other three runs, the S3-86 was pre-reduced before the aluminum phosphate was introduced.

**Surface base concentration obtained by X-Ray Photoelectron Spectroscopy

***Based on methanol synthesis rate constant

The results showed that:

1. The methanol synthesis activity of the S3-86 was significantly more stable in the presence of the 8-hour modified material than it was when used with the base AP05C. The 3- and 5-hour materials also showed enhanced stability, although not as clearly as the 8-hour material.
2. The results obtained with the 5-hour modified material were not consistent with the other data. Methanol catalyst deactivation was faster, and the period of development of dehydration activity was shorter. This could be due to the fact that this run was performed with a 20 wt % slurry loading, compared with 6.7 wt % for the other runs. If the weight percent really influences performance, then this run is an anomaly.
3. All three modified materials had approximately the same dehydration activity, 25% lower than that of the base AP05C.
4. The run using the 8-hour modified catalyst showed no acceleration in methanol catalyst deactivation rate with time on stream over the course of a 900-hour run. The other runs were not long enough to probe this effect adequately.
5. For the first 50-80 hours of each run using a modified dehydration catalyst, the methanol synthesis activity was suppressed. The magnitude and duration of this suppression increased with increasing time of modification. It is postulated that during this period, some of the methanol is lost to reactions with the basic moieties on the aluminum phosphate.

3.1.2 Improved Dehydration Catalysts

A more active dehydration catalyst would, of course, be desirable. Thus, efforts continued in development of a second-generation stable catalyst.

Two strong Brønsted acid zeolite catalysts deactivated when used in LPDME™ experiments. This deactivation occurred primarily through hydrocarbon deposition, although interaction with the methanol catalyst, S3-86, contributed. S3-86 activity was shown to be less stable in the presence of these materials than had been hoped from the results of previous tests. We conclude that strong Brønsted acids are not appropriate for methanol dehydration at these temperatures. Future work in the molecular sieve area will focus on more weakly acidic materials or materials containing Lewis acidity.

In a promising development, a LPDME™ run using an ion-exchanged γ -alumina with S3-86 displayed improved stability over the baseline system using unmodified γ -alumina, while sacrificing only 10% of the methanol equivalent productivity.

Two samples of zirconium phosphate were tested as methanol dehydration catalysts. Neither provided acceptable activity and stability. Work on phosphates will continue.

Eta alumina showed similar deactivation to gamma alumina when tested in the LPDME™ reaction. The activity was also lower. The potential of higher activity of eta alumina did not translate into a process improvement. We plan no further work on this material.

3.1.3 Process Variable Studies

Effect of Space Velocity

It is important to ascertain the stability of the aluminum phosphate catalyst under varied conditions. One condition of interest is low GHSV, which allows high selectivity to DME. The following experiments were designed to study the effect of reduced space velocity.

- While the methanol catalyst in the dual catalyst system containing AP05D showed a stability similar to the LPMEOH™ baseline under the standard test conditions (250 °C, 750 psig, 6,000 GHSV), deactivation rate increased when the space velocity was decreased to 2,000. In additional experiments rapid deactivation of both methanol synthesis and dehydration catalysts at 2,000 GHSV was observed using Shell gas. A more robust dehydration catalyst, e.g., AP05C treated with base for 8 hours, was used this time.
- An LPDME™ run using S3-86 with a modified AP05C did not show accelerated deactivation when the GHSV was lowered from 6000 to 2000. The key differences in this run (compared with previous experiments which have shown the GHSV effect) were: (1) a change in the reduction of the S3-86 prior to addition of the aluminum phosphate and (2) Texaco-type syngas rather than Shell.

Some physical factors, such as agglomeration, may play an important role in this rapid deactivation. It is also possible that the change in the chemical nature of the catalyst environment are responsible for the increased aging. Our understanding of deactivation at low GHSV is incomplete. Experiments are being conducted to pin point the cause and develop solutions.

Long Life Run

- The LPDME™ run using AP05-C continued up to 1027 hours on stream. The acceleration in the deactivation of the methanol catalyst with time on stream we saw in the previous long aging test using AP05 was again observed. However, this time the acceleration was not accompanied by the increase in the water concentration. We hypothesize that accelerated aging at the end of long-term runs may be due to some physical causes such as agglomeration of catalyst particles. The recent result of particle size analysis supports this interpretation - agglomerates were indeed observed in the spent slurry from the second 1000-hour LPDME™ experiment. Efforts to understand the cause of this acceleration are continuing.

Task 3.2 New Fuels from Dimethyl Ether (DME)

3.2.1 Overall 2QF97 Objectives

The following set of objectives appeared in Task 3.2 of the previous Quarterly Technical Progress Report No. 9:

- Continue to screen immobilized catalyst candidates for hydrocarbonylation of dimethyl ether to ethylidene diacetate and reach productivity targets set for the Rh heterogeneous catalyst.
- Continue catalyst development work on the cracking of ethylidene diacetate to vinyl acetate and acetic acid.
- Complete cetane testing at Southwest Research Institute on linear and branched dimethoxy derivatives.

3.2.2 Background

The overall objective for this project is to define a commercial process from synthesis gas to vinyl acetate (VAM) using dimethyl ether as a chemical building block. The three chemical step process is:

syngas \rightarrow dimethyl ether (DME)

DME + 4CO + H₂ \rightarrow ethylidene diacetate (EDA) + acetic acid (HOAc)

EDA \rightarrow vinyl acetate (VAM) + HOAc

The overall economics of the proposed process are to be compared with the existing VAM process based on ethylene and acetic acid.

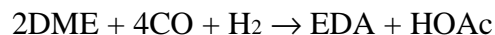
3.2.3 Chemistry and Catalyst Development

(i) Ethylidene Diacetate (EDA) Productivity

In most carbonylation or hydrocarbonylation reactions, a homogeneous Rh catalyst is employed in the chemical process. Loss of Rh through deactivation or separation of product is minimum when the product is volatile. EDA is a less volatile product than acetic acid, acetic anhydride or n-butylaldehyde (products from commercially practiced homogeneous Rh-catalyzed carbonylation reactions).

The Rh complex, which is a precursor to the active catalyst under reaction conditions, has been successfully anchored onto a commercially available organic polymer. The organic polymer is thermally stable up to approximately 225°C.

In the hydrocarbonylation of DME to EDA, the overall reaction is a carbonylation followed by a hydrogenation step, both occurring in the same reactor.



Preliminary economics has set a productivity target of 328 g EDA per liter of solution per hr to keep the reactor made from Hastelloy C to a minimum expense.

Initially the carbonylation of DME to acetic anhydride and subsequent hydrogenation of acetic anhydride to EDA and HOAc was studied independently. With the Rh complex anchored to the organic polymer, acetic anhydride was hydrogenated at 180°C to EDA with 65% selectivity at 70% acetic anhydride conversion with an EDA productivity of 642 g EDA per liter solution per hr. The syngas composition was $\text{CO}/\text{H}_2 = 20/80$.

The individual sequential intermediates from DME to EDA consist of methyl acetate and acetic anhydride. Examination of each separate reaction under different CO-rich or H₂-rich syngas established that the carbonylation rates are similar to the hydrogenation rate. Therefore, the best conditions for hydrogenation of acetic anhydride are not the optimal for DME and methyl acetate carbonylation. The carbonylation step may thus have to be separated from the hydrogenation step unless the overall productivity target is decreased. This was verified further because the hydrocarbonylation of DME to EDA has an EDA productivity of 131 g EDA per liter solution per hr, with a EDA selectivity of 22% at 190°C using a $\text{CO}/\text{H}_2 = 80/20$.

The heterogenous Rh catalyst must have physical integrity and constant activity (no Rh loss) under typical process conditions. The hydrogenation of acetic anhydride was selected for the model reaction. The experimental protocol selected allows for solution analysis for organic products and Rh content (if leaching occurs from heterogeneous catalyst). In addition, the heterogeneous catalyst can be further characterized for Rh content and C¹³ NMR to monitor chemical change within the polymer. A series of 20 recycle experiments using the same Rh catalyst throughout has been carried out. Complete analyses of data is to be reported next quarter.

(ii) Ethylidene Diacetate (EDA) to Vinyl Acetate

The third chemical step in the overall syngas to vinyl acetate is shown below:



This reaction is actually an equilibrium with retro-reaction of EDA to acetic anhydride and acetaldehyde (AcH).



Therefore, the conversion of EDA to VAM requires the cracking to be conducted with an excess of Ac₂O to suppress the EDA retro-reaction to Ac₂O and AcH. Commercially available

heterogeneous sulfonic catalysts are being screened to test their feasibility in the cracking step. These catalysts are required to be thermally stable at 140°C, the reaction temperature of the cracking. The productivity target is 238 g VAM per liter solution per hour. With a 10/1 mole ratio of Ac₂O/EDA, the cracking by heterogeneous catalyst "A" gave a 58% conversion of EDA, however, with only a 2.6% selectivity to VAM. Productivity was 1.2 g VAM per liter solution per hour. Carbon mass balance was 99% and oxygen mass balance was 101%.

The concept of adding an oxygenated compound or a blend of oxygenated compounds to diesel fuel in order to enhance the cetane value of the fuel is being investigated. A family of ethers has been identified and tested at SwRI for cetane number (CN). Synthetic methodologies to economically manufacture these oxygenated compounds are being evaluated in order to initiate an experimental program.

3QFY97 Objectives

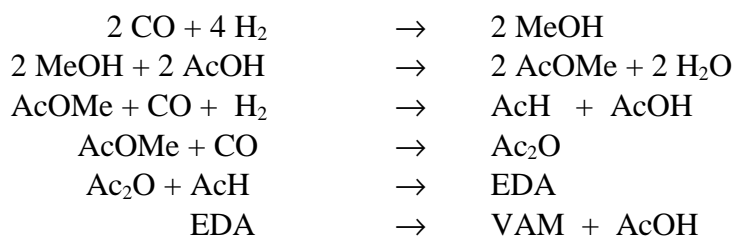
Future plans for Task 3.2 will focus on the following areas:

- Determine the leaching rate of Rh and any chemical modification to the organic polymer when the heterogeneous Rh catalyst is used in the hydrocarbonylation of DME to EDA and the hydrogenation of acetic anhydride to EDA.
- Continue to define a heterogeneous catalyst for the cracking of EDA to VAM and acetic acid.
- Continue to define the family of oxygenated compounds to be used as cetane enhancers for diesel fuel.

Value Added Acetyls from Syngas (Eastman Chemical Company)

A. Introduction/Background

The overall objective of this project is to produce a commercially viable process for the generation of vinyl acetate monomer (VAM) based entirely upon coal-generated syngas. Previous attempts at this objective have generally involved the combination of acetic anhydride (generated by carbonylation of either dimethyl ether or methyl acetate) with acetaldehyde (generated by either hydrogenation of acetic anhydride (Ac₂O) or hydrocarbonylation of either methanol (MeOH) or a methyl ester) to generate ethylidene diacetate (EDA). The EDA is subsequently cracked to form VAM in a separate step. An exemplary process is shown below:



AcH = acetaldehyde

AcOMe = methyl acetate

These efforts have failed to generate a commercially viable process to date. One of the key reasons for this failure was the very large quantities of recycled acetic acid (and consequently large commercial facilities) inherent in the earlier proposed processes.

Eastman's proposal was to circumvent the recycle problem by generating AcH via hydrogenation of acetic acid (AcOH) instead of by reductive carbonylation. Unfortunately, this process is thermodynamically disfavored and, even if acetic acid is hydrogenated, the conditions required generally favor further hydrogenation to form ethanol and ethyl acetate, which are the thermodynamically favored products. Currently, any processes that have successfully hydrogenated a carboxylic acid circumvent this problem by operating at unacceptably high pressures and temperatures to overcome the thermodynamic constrictions and by operating at low conversion to minimize over-hydrogenation to the alcohol.

Given these obstacles, Eastman initially proposed a conversion of the acetic acid to ketene (a very well known process) and planned to utilize the high energy content of the unstable ketene intermediate to overcome the thermodynamic constrictions to hydrogenation. Past reports detailed their success in pursuing this goal using palladium-based catalysts at 98°C and 1 atmosphere of hydrogen pressure. However, several problems still remained.

In the hydrogenation of ketene, carbon monoxide, a natural small by-product resulting from the generation of ketene, was a significant reversible poison. However, when operated at slightly higher temperatures, the catalyst was still capable of fulfilling its function as a hydrogenation catalyst, and the situation was readily resolved. Similar problems of catalyst deactivation were addressed successfully as well.

Unfortunately, the last problem is less easily resolvable. The initial economics indicated that the generation of ketene in these volumes, while achievable, was likely to be too capital intensive to be supported by the current vinyl acetate price. (This was particularly true if the subsequent esterification of acetaldehyde to vinyl acetate needed to be accomplished with ketene, as well.)

Therefore, the direct hydrogenation of acetic acid to acetaldehyde (without the generation of activated intermediate) had to be achieved despite its likely challenges and shortcomings. This transformation has occupied most of Eastman's attention over the last quarter. A catalyst has now been identified that meets the criteria of high selectivity and rates at moderate pressure, and will be discussed in this report.

The success of this transformation, which appeared so unlikely at the outset of the investigation, has shifted Eastman's attention toward processes incorporating acetic acid hydrogenation.

B. Results and Discussion

Task 1.2. Direct Hydrogenation of Acetic Acid to Acetaldehyde

The key barriers to the hydrogenation of acetic acid to acetaldehyde are that the reaction:

- is mildly endothermic ($\Delta G_{300C} = 2.51$ kcal/mol),

- must compete with a parallel (and thermodynamically favorable) dimerization reaction of acetic acid to acetone (with coproduction of water and carbon dioxide), and
- is subject to a subsequent (also thermodynamically favorable) hydrogenation of acetaldehyde to ethanol.

Given these difficulties, this transformation appeared unlikely at the outset, and our initial research was directed toward the hydrogenation of ketene. Nevertheless, as indicated in the October - December 1996 quarterly report, we have been encouraged by the results obtained using several new catalysts.

We recently completed a preliminary study of the preferred catalyst. A microreactor with on-line gas chromatography was installed and used for the study. Acetic acid was delivered to the reactor along with metered streams of hydrogen and nitrogen. The catalyst was activated by reduction in hydrogen. The acetic acid hydrogen study was performed over a total time of 254 hours. After a partial initial decline in activity, the average activity of this catalyst leveled out, and it appears that this type of catalyst may have a very long lifetime (weeks, months or maybe even years). Kinetic experiments were often complicated by a “hysteresis” that caused a temporary change in activity during the experiments. Since the activity later returned to normal, it appeared that some of the changes in reaction conditions slowly altered the oxidation state or other catalyst structural aspect in a slowly reversible manner. Hydrogenation of the catalyst overnight generally returned the activity to its previous level. In the kinetic studies summarized in the sections below, efforts were made to insure that the studies were being performed at below equilibrium conversion levels, both by calculation and by deliberately reducing the space velocity to determine if a corresponding increase in conversion occurred.

First Activation Energy Study

Conditions: Run under slightly hydrogen-deficient conditions to limit conversion. HOAc accountability during run = 96-100%, HOAc conversion ~0-4% and HAc selectivity = 82-89%.

Results: Hysteresis observed with catalyst deactivation during temperature rise, giving nearly zero activation energy. However, with a return to the lower temperature, deactivation was sufficiently low to provide the following activation energies:

For acetaldehyde = 15.5 kcal/mole

For acetone = 9.3 kcal/mole.

The conditions used in this run were sufficient to place the catalyst in an oxidized state, which favors acetone production.

Second Activation Energy Study

Conditions: Operated in a more hydrogen-rich mode at lower space velocity. HOAc accountability during run = 90-102%, HOAc conversion ~5-41% and HAc selectivity = 82-95%.

Results: No hysteresis observed (data track is reproducible with either an decrease or increase in temperature). The following activation energies were found:

For acetaldehyde = 17.8 kcal/mole

For acetone = 32 kcal/mole

For ethanol = 28.5 kcal/mole.

The conditions used in this run were sufficient to keep the catalyst in a reduced state, as reflected in the higher activation energy for acetone than seen in the first study. In spite of the fact that this experiment was run at higher than desirable conversions, the activation energy value for acetaldehyde compared well with the value obtained in the first study.

Hydrogen Reaction Order Study

Conditions: HOAc rate constant, hydrogen varied with nitrogen diluent present, nearly constant space velocity. HOAc accountability during run = 96-106%, HOAc conversion = 3-11% and HAc selectivity = 82-95%.

Results: Hysteresis observed, consistent with reducing the amount of hydrogen present in a relatively large amount of acetic acid, thereby changing the nature of the catalyst. The reaction orders found for the first pass (decreasing the level of hydrogen) and then upon increasing the hydrogen back to the original level (second pass) were:

For acetaldehyde = 0.98 (1st pass) and 0.79 (2nd pass)

For acetone = -0.08 (1st pass) and -0.32 (2nd pass)

For ethanol = 1.76 (1st pass) and 1.40 (2nd pass).

Acetic Acid Reaction Order Study

Conditions: Hydrogen held constant, HOAc varied with nitrogen diluent present, and held at nearly constant space velocity. HOAc accountability during run = 81-99%, HOAc conversion = 13-33% (higher than desirable) and HAc selectivity = 93-95%.

Results: Some hysteresis observed, but it was possible to reverse the sequence without significantly affecting the kinetic results. The results were consistent with those expected for a reaction in which one component (acetic acid in this case) is very strongly adsorbed on the catalyst surface, causing the apparent reaction order to change as the partial pressure is changed. Thus, for all products, the rate increased and then decreased as the partial pressure of acetic acid was increased. For acetaldehyde, the average reaction order in acetic acid at low partial pressure was 0.66, whereas at higher partial pressure it was -0.77. The overall trend for acetaldehyde was approximately 0.04. For acetone, the approximate overall trend was 0.2 order (not linear). For ethanol, the approximate overall trend was -0.3 order (not linear). This interesting kinetic behavior is possibly responsible for the encouraging effect of total pressure described in the next section.

Effect of Total Pressure

Conditions: Performed at a fixed hydrogen-to-HOAc ratio with added nitrogen at constant space velocity. Partial pressure of hydrogen - HOAc was decreased and then subsequently increased. HOAc accountability during run = 73-105%, HOAc conversion = 66-71% (1st pass), = 22-61% (2nd pass) and HAc selectivity = 77-93%.

Results: The hysteresis for the rate was less on the second pass. This observation is consistent with the change in the nature of the catalyst caused by operating in a hydrogen-deficient atmosphere. However, in spite of the hysteresis, the same behavior trend was observed with both passes: the rate increased with an increase in pressure without significantly affecting selectivity.

Effect of Conversion

These results were obtained under a wide variety of conditions and illustrate that, regardless of the means used to cause an increase in acetic acid conversion, this increase in conversion causes an increase in the selectivity to ethanol. These results are to be expected with consecutive reactions. Acetone selectivity does not really follow this trend, and the higher levels sometimes seen at low conversions are often the result of reaction conditions that oxidize the catalyst. At about 30% acetic acid conversion, the selectivity to acetaldehyde is about 90%.

Conclusions, Current and Future Work

The availability of on-line GC has allowed us to acquire a large amount of data in a fairly short time. We now have calibration gases for methane, ethane and ethylene, and, since our GC column separates these gases, we will be able to retrofit the data to improve mass balances. Although hysteresis has complicated our kinetic studies somewhat, we are encouraged by the long catalyst lifetime and the high acetaldehyde production rates achievable. The thermodynamic restrictions on the reaction no longer appear to be a matter of great concern: it is relatively easy to achieve high conversion, even at fairly low hydrogen-to-acetic acid ratios. More important is the effect of conversion on selectivity, and this would be important regardless of the thermodynamics of the reactions. Excellent selectivity to acetaldehyde is possible at moderate conversions. The by-product (ethanol or, ultimately, ethyl acetate) may have value as well. We are investigating ways to efficiently recover the acetaldehyde from the product stream.

Task 3.1 Preliminary Economic Estimates

Eastman has been making progress on the preliminary economic estimates. Initial estimates have been obtained for key reactors and first pass models for the various purification trains. At present, Eastman is integrating the units. (Several synergistic interactions within the production system that allow cost reductions, particularly in the purification stream, need to be evaluated.)

Current focus is on obtaining economic models for processes incorporating the new acetic acid hydrogenation.

Task 7.2. Reductive Carbonylation of Methanol

Several mixed metal heterogeneous catalysts have been tested for the vapor phase reductive carbonylation of methanol to acetaldehyde (Equation [7]). Unfortunately, we have yet to identify a viable catalyst for this transformation in the vapor phase.



However, part of the problem is operational. Our initial methodology entailed capturing the acetaldehyde by condensation in a dry ice trap. However, given the gas flows in this process, we have determined that we would only trap a portion of the acetaldehyde by this method if it was formed and probably not at all if it was at low to moderate conversion. To overcome this problem, Eastman installed on-line GC capabilities on these units. These are currently being calibrated, after which this study will commence again.

C. Summary

Over the last quarter, Eastman has:

1. investigated direct hydrogenation of acetic acid in detail,
2. continued to develop an economic model for the process, and
3. installed upgraded equipment on the reductive carbonylation unit.

D. Future Plans

Over the next quarter, Eastman's goals are to:

1. complete the economic models,
2. continue studies on the direct hydrogenation of acetic acid to acetaldehyde, and
3. continue to examine processes for the reductive carbonylation of methanol.

Task 3.3 New Processes for Alcohols and Oxygenated Fuel Additives

3.3.1 Development of a Catalyst for Isobutanol Synthesis from Syngas (Institute for Technical Chemistry and Petrol Chemistry, RWTH, Aachen-Germany)

Introduction

We are taking a new course in our attempt to find a catalyst for isobutanol production in a slurry application. The primary focus of this investigation is aimed at determining the catalytic behavior of different compositions with changes in pressure and temperature. This preliminary work should set the framework for the development of a catalyst system operating at moderate pressure (12.5 MPa) and temperature (325-385°C).

Building on the high activity of copper catalysts at mild reaction conditions, four copper-containing catalysts have been synthesized. The first catalyst is a well-known cesium-doped Cu/ZnO/Cr₂O₃ catalyst system which was tested for comparison. A Cu/ZrO₂/ZnO/MnO/CoO catalytic system was synthesized as a reference catalyst. In order to investigate the influence of copper on the ZrO₂/ZnO/MnO system, a potassium-promoted Cu/ZrO₂/ZnO/MnO catalyst was tested, following earlier results of our own catalyst development with Cu/ZrO₂/ZnO catalysts¹. Building upon results obtained with cerium oxide containing catalysts, a Cu/ZrO₂/ZnO/Ce₂O₃ was tested.

The results obtained with these catalysts were compared to those reached over a potassium-doped ZnO/Cr₂O₃ catalyst. Following the positive influence palladium has shown on isobutanol synthesis, a palladium-promoted sample of the ZnO/Cr₂O₃ catalyst was also tested.

Catalyst Preparation

The tested catalysts were synthesized using different methods. The cesium-doped Cu/ZnO/Cr₂O₃ catalyst (LG 5) was synthesized following a report of K. Klier et al. by coprecipitation from an aqueous nitrate solution (Table 3.3.1). The Cu/ZrO₂/ZnO/MnO/CoO catalyst (LG 7) was

synthesized following a synthesis procedure by Foley et al. by coprecipitation from an aqueous nitrate solution.

The systems in our own catalyst development program, a Cu/ZrO₂/ZnO/Ce₂O₃ catalyst (LG 6), a Cu/ZrO₂/ZnO/MnO catalyst (LG 10) and a ZrO₂/ZnO/MnO-Pd catalyst (LG 11), were synthesized by a supercritical drying method for a methanolic nitrate solution.

The potassium-promoted ZnO/Cr₂O₃ catalyst (LG 9) was used in its original form as "BASF-Isobutylöl" catalyst. The palladium promotion of this catalyst (LG 8) was done by impregnation with 0.25 wt % Pd (from Pd(acac)₂).

Table 3.3.1
Specifications of Synthesized Catalysts

Catalyst	LG 5	LG 6	LG 7	
Composition	Cu/Zn/Cr-Cs	Cu/Zr/Zn/Ce-K	Cu/Zr/Zn/Mn/Co-K	
	1.2/1.8/1.0/0.02	1/3/1/0.02/0.02	2/4/1/1/0.002/0.02	
Synthesis Method	coprecipitation	aerogel	coprecipitation	
Calcination	3 h, 350°C	5 h, 450°C	6 h, 415°C ¹	
Reduction	16 h, 225°C	16 h, 250°C	16 h, 260°C	
V_{Cat} [ml]	4.0	4.0	4.0	
m_{Cat} [g]	4.5	6.2	6.0	

Catalyst	LG 8	LG 9	LG 10	LG 11
Composition	Zn/Cr-K/Pd ^b	Zn/Cr-K	Cu/Zr/Zn/Mn-K	Zr/Zn/Mn-K/Pd ^b
			2/4/1/1/0.02	1:1:1:0.02
Synthesis Method	-	-	aerogel	aerogel
Calcination	6 h, 450°C	6 h, 450°C	6 h, 415°C ^a	6h, 450°C
Reduction	16 h, 250°C	16 h, 250°C	16 h, 260°C	16 h, 250°C
V_{Cat} [ml]	4.0	4.0	4.0	4.0
m_{Cat} [g]	4.9	4.9	5.1	5.7

^a Calcined under nitrogen.

^b Promoted with 0.25 wt % Pd from Pd(acac)₂.

The catalysts were calcined and reduced ex situ. For calcination, synthetic air was used, and for reduction of the catalysts, a mixture of 5% H₂ in N₂ was employed. The heating rate of the calcination and reduction procedures was 1°C/min.

Summary

Several catalysts have been tested for isobutanol synthesis. A potassium-doped, low-temperature Cu/ZnO/Cr₂O₃ catalyst was found to be highly active, but unselective in isobutanol production (Table 3.3.2). Methanol was by far the favored product at all reaction conditions. Increasing pressure or GHSV did not improve isobutanol selectivity.

A potassium-promoted Cu/ZrO₂/ZnO/Ce₂O₃ catalyst was compared to a potassium-impregnated Cu/ZrO₂/ZnO/MnO and ZrO₂/ZnO/MnO-Pd catalysts. The Cu/ZrO₂/ZnO/Ce₂O₃ catalyst showed a fairly high activity to isobutanol. Unfortunately, methanization was too high over this catalyst. The ZrO₂/ZnO/MnO-Pd catalyst appeared to need higher temperature and pressure to yield high isobutanol activity.

The best results in isobutanol activity at 385°C and 12.5 MPa were reached with a Cu/ZrO₂/ZnO/MnO/CoO catalyst. However, methanization over this catalyst was also too high. Copper-cobalt containing catalysts will be further investigated in order to reduce methanization while maintaining isobutanol activity.

The potassium-promoted ZnO/Cr₂O₃ catalyst showed a moderate activity at low pressure and temperature. Promotion of this catalyst with palladium increased the overall activity, but favored the formation of branched alcohols. Over the palladium-doped ZnO/Cr₂O₃ catalyst, isobutanol activity more than doubled, whereas activity to linear alcohols remained unaltered, and methanol activity was raised to a significantly smaller extent than isobutanol activity.

Table 3.3.2

Survey of Tested Catalysts at 385°C and 12.5 MPa^a

catalyst^b	LG	methane	methanol	ethanol	isobutanol	2-methyl- butanol-1
Cu/Zn/Cr/Cs ^c	5	112	3169	147	147	57
Cu/Zr/Zn/Ce/K	6	175	337	6	77	13
Cu/Zr/Zn/Mn/Co/K	7	499	235	22	174	53
Zn/Cr/Pd/K	8	82	353	8	41	12
Zn/Cr/K	9	< 10	282	7	17	4
Zr/Zn/Mn/Pd/K	11	< 10	462	7	58	< 3

^a STY in g/(l_{cat}·h), syngas 1:1, GHSV = 11,000 h⁻¹, V_{cat} = 4 ml, particle size = 0.63-0.71 mm.

^b Stated as metals.

^c T = 325°C.

Task 5: PROJECT MANAGEMENT

5.1 Planning - No progress to report this quarter.

5.2 Liquid Phase Fluid Dynamic (Methanol) Run

A draft of a topical report on the results of the 1995 Fluid Dynamic/Methanol LaPorte run was completed. The report includes both catalyst and fluid dynamic results. The draft is currently being reviewed internally.

A paper, co-authored by Air Products, Shell and DOE personnel on the F-T III results, was presented by D. M. Brown of Air Products at the AIChE spring meeting in Houston.
