ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS

FINAL

Quarterly Status Report No. 15

For the Period 1 July - 30 September 1997

Contractor

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DISCLAIMER

Alternative Fuels and Chemicals from Synthesis Gas

Quarterly Technical Progress Report

1 July - 30 September 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 indus0trial 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 DOE personnel on 10 July to discuss LaPorte plans. DOE agreed with Air Products' plan for the Fischer-Tropsch IV run, as described in the previous quarterly report. They expressed their interest in obtaining Fischer-Tropsch as well as DME products for engine testing.

A cost estimate was prepared at ENI's (Eniricerche's) request, for demonstration of their Fischer-Tropsch technology at LaPorte. A preliminary estimate of \$2.5 MM for a 30-day and \$4 MM for a 60-day run was obtained. Due to permitting limitations, the 30-day run is preferred.

1.2 Liquid Phase DME Demonstration

To follow up on Akzo Nobel's request, an equipment specification package was prepared for the production of 99.9% pure DME by methanol dehydration at the LaPorte AFDU. Since the methanol dehydration process produces no CO_2, the purification of DME does not require an expensive refrigeration system. The design uses the 27.20 slurry column to produce 10.0 TPD of DME from a fresh feed of 37 lb-mol/hr of methanol. The reactor effluent is cooled and sent to a single distillation column, where pure DME is recovered as overhead, by-product water is removed in the bottoms, and unreacted methanol is recovered as a side stream and recycled to the reactor. The proposed new column is also suitable for use as one of the two columns required for producing pure DME from syngas. The capital cost estimate for the design, including storage, was \$2.5 MM. Discussions with Akzo Nobel indicated that this was still more than they had available.

DOE's interest in obtaining DME for engine testing led to the idea of cost-splitting the investment necessary for producing DME from syngas at LaPorte between Akzo Nobel, DOE, and Air Products. As a result, the draft equipment specification package for DME production from syngas at LaPorte, described last quarter, was completed and released for cost estimation. The design produces 8.8 TPD of 99.9% pure DME from a fresh feed of 160 lb-mol/hr of balanced gas in a once-through mode. A cost estimate of $3.2MM was obtained for the design, which requires two new columns. This design minimizes capital cost by eliminating the need for refrigeration in the purification of DME from CO_2. However, 25% of the DME produced ends up in the purge.

A meeting was held with representatives from Akzo Nobel on 26 August to discuss our design results for the production of DME at LaPorte. In addition to the above design, a design discussed in the previous quarterly was also presented, in which 13.6 TPD of 99.9% pure DME is produced with a capital investment of $6.0MM. The operating costs for the two designs were determined to be $1.10/lb for the 8.8-TPD design and $0.80/lb for the 13.6-TPD design. Akzo indicated that these costs were far above their target cost of $0.40/lb. However, they did show an interest in a proposal for replacing their Rotterdam methanol dehydration unit with a single-step syngas-to-DME slurry column.

1.3 Oxidative Coupling of DME

A meeting was held with Corporate Science and Technology Center (CSTC) personnel to discuss the demonstration of oxidative coupling (OC) of DME at LaPorte. The reaction will need a new fixed-bed reactor, as it cannot be carried out in a slurry reactor due to the explosion potential of a O_2/oil mixture. Additionally, an O_2 feed gas system, a cooling water heat exchanger, a vapor-liquid separator, and liquid storage are required. It was decided to stay with the original $2.5MM budget number for this modification. In terms of timing, we are estimating early 2000 for operations. CSTC needs till the end of FY98 to develop the chemistry. Permitting and installation will require an additional 15 months.

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

TASK 3: RESEARCH AND DEVELOPMENT

Task 3.1 Improved Processes for DME

3.1.1 Investigation of the Effect of Additives and Alternate Solvents on the Stability of LPDME™ Catalysts

- A LPDME™ run using an additive resulted in very good catalyst stability. The dehydration activity suffered somewhat. Further studies in this direction are underway.

- An ether-based solvent (tetraglyme) was tested in a LPMEOH™ run as an alternate slurry oil. The performance was poorer than our current slurry fluid and unacceptable.

3.1.2 Investigation of the Cause of More Rapid Catalyst Deactivation at Low Space Velocity in LPDME™

- LPDME™ runs using different feed gases are being carried out to establish the correlation between gas phase composition and catalyst deactivation. Different deactivation patterns were observed under Kingsport gas.

- A LPDME™ run entirely at 2000 GHSV was conducted. The spent sample from this run will be analyzed to help understand the deactivation mechanism at low space velocity. Parallel LPDME™ runs at the standard space velocity (6000 GHSV) were also conducted to generate comparative samples.

3.1.3 Scaleup of LPDME™ Catalyst

- In June Air Products personnel visited two catalyst manufacturers. Early this past quarter we selected one of these to partner with us in the scaleup and development of Air Products' aluminum phosphate LPDME™ catalyst. The immediate goal of this effort will be to supply 800 pounds of material for our LaPorte trial slated for summer 1998.

- Air Products finalized a lab recipe for scaleup. This recipe was then prepared in our labs, and the entire procedure was videotaped to provide a record for internal use and for our scaleup partner. This sample was tested in Air Products' lab 300-mL reactor using S3-86 methanol catalyst and our standard test conditions. The activity of the mixed catalyst was found to be very stable, but the dehydration activity of the aluminum phosphate was somewhat lower than is typical.

- We repeated the preparation of the standard recipe, but substituted commercial-grade reagents supplied by our partner for the analytical grade reagents we had used previously. The resulting LPDME™ run using this sample showed typical activity, but was slightly less stable than our specification (the methanol rate constant declined -0.07% per hour versus -0.05% per hour for LPMEOH™). While this difference may not be significant, we will pay close attention to the stability results from subsequent batches using commercial-grade reagents.

- Our partner has prepared two 30-gallon batches of our material. These will be sent to us for testing early this coming quarter.

3.1.4 Development of LPDME™ Catalysts

- *Aluminum Phosphate*: Air Products clearly showed that the faster deactivation at lower space velocity of the LPDME™ process using aluminum phosphate is due to the difference in the bulk gas composition in the reactor. This rules out physical causes due to the change in actual gas flow rate. The experiment was to use a feed gas composition at 6000 GHSV, which would result in the same exit gas composition observed when Shell-type syngas is run at 2000 GHSV. Upon switching to this special feed gas from Shell-type syngas in the middle of a run, we observed very rapid deactivation of both the S3-86 and the aluminum phosphate. We are conducting a series of follow-up experiments to understand the regime of stable performance and the nature of this deactivation.

- *Developmental Dehydration Catalysts*: We continued our work in testing zeolites that have been ion-exchanged to remove Brønsted acid sites (which cause deactivation), but that retain Lewis sites active for methanol dehydration. Lanthanum-exchanged Zeolite Ultrastable Y (USY) showed improved stability for methanol conversion to DME at 250°C and 750 psig. The level of activity was about 75% that of gamma alumina. Cobalt-exchanged USY also demonstrated very stable activity for methanol dehydration to DME, and had higher activity than the lanthanum-exchanged USY. However, when the Co/USY was used with S3-86 in a standard LPDME run, most of the activity for methanol dehydration was quickly lost. The steady-state methanol equivalent productivity of this system was only 17 gmol/kg,hr. The cobalt ions may be too weakly held and therefore may migrate to the S3-86, creating Brønsted sites on the USY which rapidly deactivate. We intend to test several more modified zeolites before closing out this effort.

3.1.5 Miscellaneous

- A paper entitled "Progress in Development of LPDME™ Process: Kinetics and Catalysts," was prepared and presented at the 1997 DOE Coal Liquefaction & Solid Fuels Contractors Review Conference.

Task 3.2 New Fuels from Dimethyl Ether (DME)

3.2.1 Overall 4QF97 Objectives

The following set of objectives appeared in Task 3.2 of the previous Quarterly Technical Progress Report No. 11:

- Evaluate the process parameters that influence the leaching rate of Rh from heterogeneous catalyst.

- Continue defining a heterogeneous catalyst for the cracking of EDA to VAM and acetic acid.

- Continue to define a synthetic methodology to economically manufacture cetane enhancers.

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 (DME) as a chemical building block. The three chemical step process is:

syngas → dimethyl ether (DME)

2DME + 4CO + H_2 → ethylidene diacetate (EDA) + acetic acid (HOAc)

EDA → 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) Studies on the Robustness of the Heterogeneous Catalyst

The Reillex polymer that anchors the active catalyst $[Rh(CO)2ICl]^{\ominus}$ for the hydrocarbonylation of DME to EDA and HOAc or the hydrogenation of acetic anhydride to EDA and HOAc is being tested for attrition, Rh loss and polymer modification through hydrogenation.

Experimentally an autoclave is charged with the heterogeneous catalyst, and the reactants are added through a high-pressure Isco pump. The system is pressurized with syngas, and after it is held at reaction temperature for 30 minutes, the autoclave is cooled and the liquid content is removed without opening the autoclave. New reactants are added to the heterogeneous catalyst remaining behind in the autoclave. The reaction sequence is repeated. At the end of the recycle experiment sequence (15-20 individual runs on the same initial charge of heterogeneous catalyst), the catalyst is removed for Rh analysis. Each solution is analyzed by GC for product, and then the solutions are grouped into batches of three or seven for concentration and finally analyzed for any soluble Rh.

(i)a. Study 4: 180°C, 1500 psi 30/70: H_2/CO Mixture - Hydrogenation of Acetic Anhydride to EDA and HOAc

A plot of molarity (M) of EDA verses recycle number shows that the average EDA concentration is 0.3M from the first catalyst recycle until the 16th recycle. An elemental Rh analysis of the recovered catalyst from the reactor showed that approximately 50% of the rhodium is removed from the solid polymer. The solutions were analyzed for Rh and any pyridine (from the polymer support) containing fragments. ^{1}H NMR did not detect any pyridine fragment. Also some of the dissolved Rh was isolated as a carbonyl specie by stirring with dried Reillex. The results of this experiment should be compared with Study 3 in Quarterly Technical Progress Report No. 11.

1b. Study 5: 180°C, 1500 psi N_2 - Control

The ionically bound $[Rh(CO)_2ICl]^{\ominus}$ on Reillex was treated with a premix solution of acetic anhydride, HOAc, ethylidene diacetate (EDA), and MeI for 1 hr. The amount of Rh on the polymer before and after the static test was the same. This suggests that any leaching of Rh is a chemical problem and not due to physical attrition of the catalyst.

1c. Study 6: 190°C, 750 psi 5/95: H_2/CO Mixture - Carbonylation of Methyl Acetate to Acetic Anhydride (Ac_2O)

A plot of molarity (M) of Ac_2O verses recycle number showed that the average Ac_2O concentration is 2M from the first catalyst recycle until the 14th recycle. An elemental Rh analysis of the recovered catalyst from the reactor showed that only 20% of rhodium is lost from the solid polymer. The Rh leaching rate is a fairly constant value of 0.7 mg per hr over the 14 recycles of the catalyst.

1d. Study 4-5 Summary

The leaching of Rh from the organic polymer support appears to be a result of chemistry, not the physical attrition of the catalyst. Some of the Rh in solution is associated with CO carbonyls as detected by IR, and this material can be scavenged by Reillex. ^{1}H NMR of the solutions did not detect any pyridine fragments from the organic polymer.

(ii) Ethylidene Diacetate (EDA) to Vinyl Acetate

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

$$\text{EDA} \rightarrow \text{VAM} + \text{HOAc}$$

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

$$Ac_2O + \text{AcH} \rightleftharpoons \text{EDA} \rightleftharpoons \text{VAM} + \text{HOAc}$$

Therefore, the conversion of EDA to VAM requires the cracking to be conducted with an excess of Ac_2O to suppress the EDA retro-reaction to Ac_2O and AcH.

A series of 10/1 mole ratio of Ac_2O/EDA cracking experiments done under distillation conditions was compared when the EDA/catalyst ratio was varied from 1.2/1 to 3.6/1. The catalyst was Amerlyst 15, a sulfonic acid type in exchange resin. The best cracking occurred at an EDA/catalyst ratio of 1.2/1, with an EDA conversion of 48% and a VAM selectivity of 44%. Mass balance on carbon and oxygen was approximately 100%.

(iii) Economic Process Evaluation

Dr. R. Colberg of Eastman Chemical Company and R. Moore of Air Products compared independent economic evaluations for the chemical processes under investigation by Air Products and Eastman. The route under investigation by Eastman is outlined below, and preliminary economic conclusions are summarized.

$$\text{DME} + \text{CO} \rightarrow Ac_2O$$

$$\text{HOAc} + H_2 \rightarrow \text{AcH} + H_2O$$

$$Ac_2O + \text{AcH} \rightarrow \text{VAM} + \text{HOAc}$$

1) The analyses by both Air Products and Eastman indicate that the cost of VAM from a 450 MM-lb/yr facility would need to sell at $0.42 to 0.44/lb to achieve a reasonable return on investment.

2) A new stand-alone 450 MM-lb/yr facility for a conventional VAM via ethylene with its own 330 MM-lb/yr acetic acid facility could produce VAM at about $0.39/lb. With imported acetic acid from a world-scale, 1,000 MM-lb/yr facility, the VAM might sell as low as $0.35/lb. Thus, with the assumed feedstock costs and financial constraints, the conventional VAM process has the more favorable economics.

It was agreed to complete the economics, and write a final topical report summarizing the Eastman and Air Products approaches to VAM. Each partner has agreed to bring to a conclusion the cooperative program on syngas routes to VAM at the end of September 1997.

(iv) Cetane Blending Components

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. Based on external testing by SwRI, a family of ethers has been identified as cetane enhancers. The blend of oxygenated compounds is potentially accessible from the oxidative coupling of DME. A patent has been filed on the family of ethers.

A literature survey has revealed only one substance that is a catalyst for selective oxidative coupling to 1,2-dimethoxyethane (DMET). Reports of catalysts that are selective for oxidative coupling of methane to ethane are much more abundant, and the most promising ones will be evaluated for DME oxidation. Three such catalysts were synthesized: Na_2WO_4/CeO_2, $SrSnO_3$, and a Bi-Mo-Fe mixed oxide. Modifications to the catalysis evaluation unit and design hazards review paperwork are nearing completion, with an initial hazards review planned for the beginning of October.

3.2.4 1QFY97 Objectives

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

- Continue to define synthetic methodology to economically manufacture cetane enhancers.
- Document in a topical report the syngas to VAM routes.

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.

$$\begin{aligned}
2\,\mathrm{CO} + 4\,\mathrm{H_2} &\Rightarrow 2\,\mathrm{MeOH} \\
2\,\mathrm{MeOH} + 2\,\mathrm{AcOH} &\Rightarrow 2\,\mathrm{AcOMe} + 2\,\mathrm{H_2O} \\
\mathrm{AcOMe} + \mathrm{CO} + \mathrm{H_2} &\Rightarrow \mathrm{AcH} + \mathrm{AcOH} \\
\mathrm{AcOMe} + \mathrm{CO} &\Rightarrow \mathrm{Ac2O} \\
\mathrm{Ac2O} + \mathrm{AcH} &\Rightarrow \mathrm{EDA} \\
\mathrm{EDA} &\Rightarrow \mathrm{VAM} + \mathrm{AcOH}
\end{aligned}$$

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 operate 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 Eastman's 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 cost of generating ketene in these volumes, while achievable, was likely 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. A catalyst was identified in the first quarter of 1997 that meets the criteria of high selectivity and rates at moderate pressure. 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, and most of Eastman's experimental efforts over the last two quarters have been devoted to optimizing this critical process.

In addition, Eastman completed its assessment of the economics for the process involving acetic acid hydrogenation. The conclusion was that the best all-syngas-based process (which is the process involving the hydrogenation of acetic acid) is marginally (ca. 15%) disadvantaged when compared to existing technology for a process sited on the Gulf Coast. The estimates are close enough that scenarios involving other locations may favor a syngas-based process. Details of the acetic acid hydrogenation studies (Task 1.2 in the Statement of Work) and a summary of the economic assessments (Tasks 3 and 5.2 in the Statement of Work) appear below.

B. Results and Discussion

Task 1.2 Direct Hydrogenation of Acetic Acid to Acetaldehyde

In the April - June 1997 quarterly report, Eastman described a series of catalysts that hydrogenated acetic acid to acetaldehyde. The proprietary catalysts used in the acetic acid hydrogenation process consisted of an essential component (A) and a promoting component (B). A series of catalysts had been prepared and evaluated, for which the amounts of components A and B were varied. Catalysts studied contained in wt %: 100A-0B, 97.5A-2.5B, 95A-5B, 90A-10B, 80A-20B, 60A-40B, 20A-80B and 0A-100B. Eastman also indicated that it was investigating ways to recover the acetaldehyde from the product stream. One method that was investigated was to reduce the amount of hydrogen present to the minimum levels required to reach equilibrium conversion. Since the reaction is mildly endothermic, a hydrogen/acetic acid ratio = 5/1 allows a theoretical equilibrium conversion of acetic acid to acetaldehyde in the range of 40-50%. Optimum performance using the 5/1 hydrogen/acetic acid ratio was found with the 90A-10B catalyst. During the last quarter Eastman continued to explore additional ways to recover the volatile acetaldehyde product from the reaction product. We believed that it would be necessary to increase the reaction pressure from the 1 atmosphere conditions used previously to about 250 psig in order to recover the acetaldehyde in an economical manner.

A medium-pressure vapor phase reactor was constructed from a 12-inch length of Hastelloy C tubing having an outer diameter of ¼ inch. All gas flow, pressure and temperature control devices were controlled by a Camile® Model 3300 process monitoring and control system interfaced with an IBM Model 750-P90 computer. Hydrogen flow was provided by a Brooks mass flow controller, and acetic acid was fed using dual ISCO high-pressure syringe pumps. The device was fitted with a relief valve set for 500 psig. Pressure was controlled by a modified Research Control Valve with a pressure transducer located between the flow controller and the reactor. A 2-micron filter was placed between the reactor and the Research Control Valve. The product exiting the Research Control Valve was fed to a Valco Industries 6-port gas chromatographic sampling valve containing a 1-mL sample loop. The gas chromatographic sampling valve was interfaced to a Hewlett-Packard Model 3790A gas chromatograph fitted with a 6 foot x 1/8 inch stainless steel column containing 80/120 Carbopack B/6.6% Carbowax® 20M. Products were analyzed by this on-line gas chromatograph with the column programmed for 80°C for 0 minutes, 4°C/minute to 150°C and 150°C for 0 minute using a flame ionization detector. The transfer lines, filter, and Research Control Valve connecting the reactor to the gas chromatographic sampling valve were heated to 200°C by a temperature-controlled heating tape. The gas chromatographic sampling valve and the transfer line connecting it to the gas chromatograph were maintained to 150°C. The reactor tube was loaded to position the catalyst charge in the middle of the reactor. Quartz fines (1-inch layer), 12 x 20 mesh quartz chips (3.5-inch layer) and quartz wool plugs were placed on both sides of the catalyst charge. The entire length of the reactor was heated with a temperature-controlled heating tape. The acetic acid was delivered to the reactor via a line passing concentrically through the reactor head and about an inch into the upper portion of the heated portion of the reactor. The hydrogen delivery line and the relief valve were also fitted to the reactor head. Thus the upper portion of the heated reactor acted as an acetic acid vaporization and vapor mixing zone.

The on-line gas chromatography technique that had been so useful in Eastman's previous work at 1 atmosphere has become a more qualitative technique when used with the medium-pressure reactor. The main reason for this is related to the action of the Research Control Valve, which acts more like an on/off valve than a true back-pressure regulator. Thus the flow across the catalyst is in pulses rather than steady and smooth. This causes periods when the flow of gas across the catalyst is essentially static (when the valve is closed, leading to very high conversions) and other periods when the flow is extremely fast (when the valve is open, leading to very low conversions). Pressure variation in the reactor set for 250 psig is ±10-15 psig as the valve opens and closes. Since the on-line sampling is an instantaneous sampling technique, conversions and selectivities for a given catalyst vary considerably, depending upon the particular time within the valve cycle that the sample happens to be taken. Recently we began to analyze the product mixture by condensing the vented products over a timed period in two traps connected in series and held at 0 and –78°C. These products were then combined, weighed and analyzed by gas chromatography. However, most of the results (especially those obtained with the more selective catalysts) have been obtained using the on-line gas chromatography as the sole means of analysis, and therefore these results should be considered very qualitative. Nevertheless, the on-line gas chromatographic technique is still very useful for comparing the performance of different catalysts.

The 90A-10B catalyst, which had been the best catalyst when operating at 1 atmosphere with a 5/1 hydrogen/acetic acid ratio, performed rather poorly at 250 psig. Both the rate and the selectivity deteriorated rapidly with time on stream, and the selectivity to acetone, ethanol and ethyl acetate increased while the selectivity to acetaldehyde decreased (ethyl acetate is normally not seen at 1 atmosphere operation, but can become a major component at higher pressure conditions). However, excellent selectivity with steady performance has been attained using a 60A-40B catalyst with a 7/1 hydrogen/acetic acid ratio at 250 psig. Under these conditions, the on-line gas chromatography technique indicated that acetaldehyde was produced at a rate of 2000 g/l-hr at about 48% acetic acid conversion and in about 87% selectivity. Other products in order of decreasing amounts were ethanol, ethyl acetate, acetone, methane and C_2 hydrocarbons.

Reduction of the hydrogen/acetic acid ratio to 5/1 lowered the acetaldehyde selectivity to 75-80%. These performance data need to be confirmed by the condensed bulk liquid sampling technique mentioned above. Although these results are quite qualitative at this time, Eastman is very encouraged about the ability of these A-B type catalysts to produce acetaldehyde under conditions that may be practical commercially.

Tasks 3 and 5.2 Economic Assessments

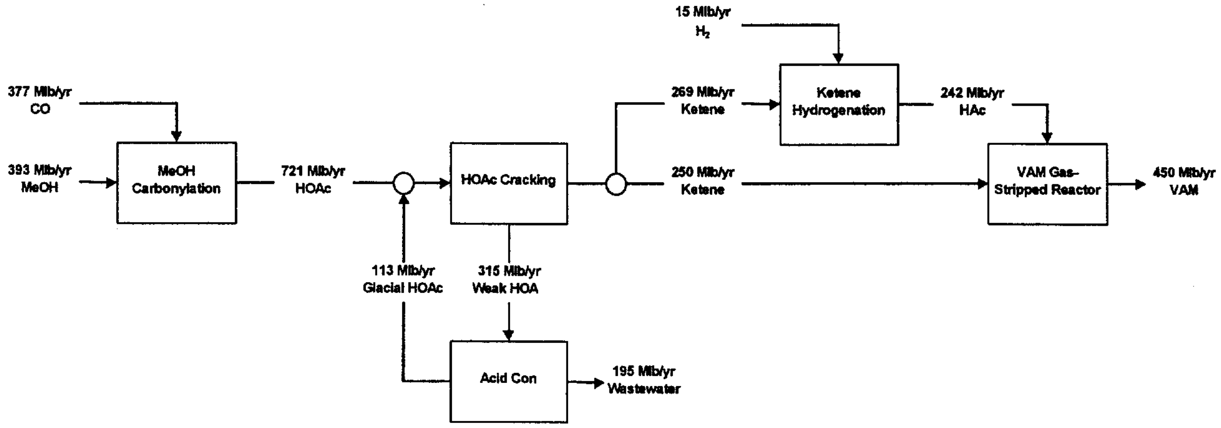
During the past quarter, Eastman has completed its economic evaluation comparing the following routes for making VAM:

- "No-Ketene Route" whose key steps include:
    - -- Hydrogenation of acetic acid (HOAc) to acetaldehyde (HAc)
    - -- Esterification of HAc with Ac2O to produce VAM (by reactive distillation)

(Note: The remaining steps, their arrangement in a process, and the block flow diagram for this process are not included within this quarterly report because they are subject to a patent hold. However, they will appear in the final report.)

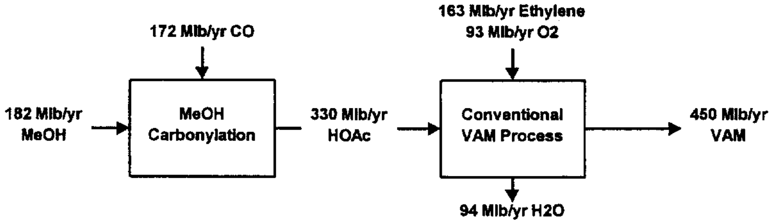
- "All-Ketene Route"
    - -- Carbonylation of methanol (MeOH) to acetic acid (HOAc)
    - -- Thermal cracking of HOAc to ketene
    - -- Hydrogenation of ketene to acetaldehyde (HAc)
    - -- Esterification of HAc with ketene to produce VAM (in a gas-stripped reactor)
    - -- "Acid Con" to recover unconverted HOAc from HOAc cracking (ketene production)

"All-Ketene" Route—Block Flow Diagram



- Conventional Route
    - -- Carbonylation of methanol (MeOH) to acetic acid (HOAc) in a dedicated plant
    - -- Oxyacetylation of ethylene with HOAc and oxygen to produce VAM

“Conventional” Route—Block Flow Diagram



Compared to a conventional VAM process with a (small) dedicated HOAc plant, the no-ketene route suffers a ~17% cost disadvantage—44.1¢/lb vs. 37.5¢/lb product value at 15% return on investment (ROI)—in spite of a 2.5¢/lb raw material cost advantage (including an EtOAc by-product credit). (See tables below.) This cost disadvantage is mostly due to higher capital (especially for DME carbonylation, which constitutes half the battery limits capital) and utilities (especially for VAM reactive distillation). Sensitivity analysis indicates that the no-ketene route can compete with the conventional VAM process at a combination of historically high U.S. ethylene and low U.S. MeOH prices (or at locations in the world with relatively expensive ethylene). At current U.S. ethylene and MeOH prices, large (~35%) reductions in battery limits capital (e.g., breakthroughs to reduce DME carbonylation capital) could make the no-ketene route competitive with the conventional VAM process. The all-ketene route is ~8¢/lb more expensive than the no-ketene route (product value at 15% ROI) due to 22% higher battery limits capital, and higher raw material and utility usages.

VAM Product Value Comparison (SRI-Style Economics, 450 MLb/Yr VAM)

	Conventional VAM	**No-Ketene Route**	**All-Ketene Route**
Raw Material Costs			
Methanol @ 9.1¢/lb	0.036	0.079	0.079
CO @ 5.4¢/lb	0.021	0.044	0.045
H_2 @ 37.7¢/lb		0.014	0.013
Ethylene @ 20¢/lb	0.072		
Oxygen @ 1.9¢/lb	0.004		
Other	0.004		
Total Raw Material Cost	**0.138**	**0.137**	**0.138**
HOAc Credit @ 12¢/lb		(0.002)	
EtOAc Credit @ 38¢/lb		(0.021)	
Net Raw Material Cost	**0.138**	**0.113**	**0.138**
Utility Costs	0.015	0.027	0.033
Labor Costs	0.011	0.015	0.016
Maint. & Oper. Matls.	0.006	0.009	0.011
Plant Overhead	0.009	0.012	0.013
Taxes & Insurance	0.013	0.018	0.022
10% Depreciation	0.066	0.092	0.109
Gen. & Adm., Sales, Res.	0.017	0.017	0.017
15% ROI (before taxes)	0.099	0.139	0.164
Product Value (fob)	**0.375**	**0.441**	**0.523**

VAM Capital Cost Comparison (SRI-Style Economics, 450 MLb/Yr VAM)

Process Block	**Product**	**Conventional VAM**	**No-Ketene Route**	**All-Ketene Route**
MeOH Dehydration	DME		20	
DME or MeOH Carbonylation	Ac2O or HOAc	76	136	128
HOAc Cracking	Ketene			68
HOAc or Ketene Hydrogenation	Hac		39	55
Acid Con	HOAc/EtOAc		14	30
Oxyacetylation or Esterification	VAM	103	38	21
Total Battery Limits Capital		**179**	**248**	**303**

C. Summary

Over the last quarter, Eastman Chemical Company continued to reduce the hydrogenation of acetic acid to acetaldehyde from a laboratory-scale success to a process that is industrially practicable. This has entailed operating at reasonably high conversions using elevated hydrogen pressures. These conditions generally lead to over-reduction of acetic acid to ethanol and ethyl acetate. However, by optimizing the catalyst composition, Eastman Chemical Company has achieved these objectives.

Eastman has also completed its economic evaluation, which indicated that, despite the raw material advantage inherent in syngas-based routes, the best route envisioned to date is still disadvantaged by about 6.5 cents/lb when compared to the conventional approach using a U.S. Gulf Coast based site. The disadvantage is attributable to both higher capital and utilities for the syngas-based process. However, the difference is sufficiently small that economic situations that vary significantly from those on the U.S. Gulf Coast or technical advances that reduce the capital cost of the syngas-based process may make the syngas-based route preferred.

D. Future Work

This is the final quarterly report for this project. However, Eastman Chemical Company will spend the next quarter completing documentation and will submit a final report before the end of the calendar year. In addition, invention reports and patent applications will be filed covering the hydrogenation of acetic acid to acetaldehyde and the overall process for the generation of vinyl acetate from syngas incorporating this technology.

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)

On-Line Product Analysis

The on-line GC product analysis used in Unit I functions with two VICI six-way valves. The first valve separates the on-line GC from the unit and reduces the pressure of the injected product sample to atmospheric pressure. The second six-way valve injects the sample into the GC column. To verify the accuracy with which the first valve keeps the injected volume constant by relieving pressure to atmospheric pressure, calibration runs are executed before and after every experiment with a 10% methane mixture in argon. It was observed that these calibration runs no longer correlated. Therefore, the entire GC on-line system was thoroughly examined. Both VICI valves, as well as the GC split valve, were replaced, and all capillaries were cleaned or replaced. After extensive testing of the on-line GC, catalyst testing in Unit I has resumed.

Catalyst Preparation

The $ZrO_2/ZnO/MnO/K_2O$-catalyst was impregnated with copper and cobalt acetylacetonate to investigate the influence of these metals on isobutanol synthesis over the $ZrO_2/ZnO/MnO/K_2O$ system. As previously explained, these metals are expected to enhance formation of linear alcohols, even at the lower reaction conditions investigated here. This again is expected to enhance isobutanol formation (Quarterly Status Report No. 2, 1997).

As a starting point, a molar load of copper and cobalt of 0.024 mmol/g_{cat} was used, which is identical to the 0.25 wt % load of palladium employed in prior investigations. In addition to this 0.024 mmol/g_{cat} load, the ZrO_2/ZnO/MnO/K_2O catalyst was impregnated with a 0.10 mmol/g_{cat} load of copper, cobalt and rhodium. Details of the preparation method are provided in Table 3.3.1.

Table 3.3.1

Preparation of the Tested Catalysts

Composition	ZrO_2/ZnO/MnO
Synthesis method	Coprecipitation (at 353 K and pH 9) of the nitrates (1:1:1) with KOH
Impregnation method	Incipient wetness
Promoter load	0.024 – 0.10 mmol/g_{cat}
Calcination	6 hr at 723 K (1 K/min)
Reduction	8 hr at 548 K (1 K/min) with 5% H_2 in N_2

Catalyst Screening

The catalyst screening was executed in Unit II. Heating rates used in the experiments were 1°C/min. After a stabilization period of 18 hr at the reaction temperature, a product sample was taken over a 90-minute period. All experiments were executed at a pressure of 12.5 MPa, a GHSV of 11,600 hr^{-1} and a reaction temperature of 623 and 658 K. The results obtained over the impregnated catalysts are compared to those obtained over the unimpregnated ZrO_2/ZnO/MnO/K_2O-catalyst (Tables 3.3.2 and 3.3.3).

At 623 K the ZrO_2/ZnO/MnO/K_2O catalyst showed only minor activity towards isobutanol, the main product being methanol (Table 3.3.2). Impregnation does not increase isobutanol activity at this temperature.

Table 3.3.2

Product Distribution and STY over Three Different $ZrO_2/ZnO/MnO/K_2O$-Catalysts; Unit II, p = 12.5 MPa, GHSV = 11600 hr^{-1}, V_{cat} = 3.0 ml, D_{cat} = 0.25-0.50 mm, Syngas 1:1

	623°K					
Promoter M[a]	**-**	**Cu I**	**Cu II**	**Co I**	**Co II**	**Rh II**
Liquid product distribution						
% methanol	86	90	90	90	88	90
% ethanol	<1	1	1	<1	1	1
% n-propanol	<1	1	1	<1	1	1
% i-butanol	3	2	1	1	1	2
% 2-methylbutanol-1	<1	<1	<1	<1	<1	<1
STY [g/(l_{cat}·hr)]						
methane	<10	<10	18	<10	16	<10
methanol	420	480	480	434	427	384
ethanol	<3	3	3	<3	4	3
n-propanol	<3	3	3	<3	3	3
i-butanol	13	11	7	5	6	8
2-methylbutanol-1	<3	<3	<3	<3	<3	<3

[a] Promoter M I: 0.024 mmol M/g_{cat}, M II: 0.10 mmol M/g_{cat}.

At the higher temperature, the addition of 0.024 mmol/g_{cat} copper to the $ZrO_2/ZnO/MnO/K_2O$ catalyst leads to an increase in all products except methanol (Table 3.3.3). The higher load of copper does not lead to improved results towards isobutanol. However, over both copper-promoted catalysts, methane activity is also enhanced. The addition of cobalt or rhodium to the $ZrO_2/ZnO/MnO/K_2O$ system only seems to benefit methanol production, the product distribution being similar to the one obtained over the unpromoted catalyst. A slight increase in linear alcohol formation over copper-, cobalt- or rhodium-containing catalysts could be observed, but this did not increase isobutanol formation.

Table 3.3.3

Product Distribution and STY over Three Different $ZrO_2/ZnO/MnO/K_2O$-Catalysts; Unit II, p = 12.5 MPa, GHSV = 11600 hr^{-1}, V_{cat} = 3.0 ml, D_{cat} = 0.25-0.50 mm, Syngas 1:1

	658°K					
Promoter M[a]	**-**	**Cu I**	**Cu II**	**Co I**	**Co II**	**Rh II**
Liquid product distribution						
% methanol	71	63	61	77	71	76
% ethanol	<1	1	1	1	1	1
% n-propanol	<1	1	1	<1	1	1
% i-butanol	8	11	8	6	7	7
% 2-methylbutanol-1	<1	1	1	1	1	1
STY [g/(l_{cat}·hr)]						
methane	31	77	71	37	47	29
methanol	365	351	334	386	383	406
ethanol	<3	6	7	3	6	4
n-propanol	<3	5	4	<3	3	<3
i-butanol	42	62	41	30	36	37
2-methylbutanol-1	4	7	4	3	3	3

[a] Promoter M I: 0.024 mmol M/g_{cat}, M II: 0.10 mmol M/g_{cat}.

Conclusions

The results obtained with the copper-, cobalt- or rhodium-impregnated catalysts show that promotion with these metals does not lead to an increase in isobutanol yield at the applied lower temperatures. Only the $ZrO_2/ZnO/MnO/K_2O$ catalyst with a 0.024 mmol/g_{cat} copper load showed an improved isobutanol yield. This first series of experiments in improving the activity of the $ZrO_2/ZnO/MnO/K_2O$ catalyst at moderate reaction conditions will be continued with palladium- and platinum-promoted samples. Additionally, tests with higher loads and combinations of different metals are planned.

TASK 4: PROGRAM SUPPORT - No progress to report this quarter.

TASK 5: PROJECT MANAGEMENT

Liquid Phase Fischer-Tropsch III Run

A paper entitled “Fischer-Tropsch Run III at the LaPorte Alternative Fuels Development Unit" was presented at the Coal Liquefaction and Solid Fuels Contractors Review Conference on September 3-4, 1997. The paper, co-authored by Air Products, DOE and Shell personnel, was well received.