

# **Alternative Fuels and Chemicals From Synthesis Gas**

## **Quarterly Report January 1 - March 31, 1998**

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For  
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# **ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS**

Draft

## **Quarterly Status Report No. 14**

For the Period 1 January - 31 March 1998

Contractor

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# **Alternative Fuels and Chemicals from Synthesis Gas**

## **Quarterly Technical Progress Report**

**1 January - 31 March 1998**

### **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**

Preparations continued for the Fischer-Tropsch IV run at LaPorte, scheduled to start on March 16<sup>th</sup>.

- A hazards review was conducted in January. Safety analysis and documentation were completed to support the Flowsheet Change Notices (FCNs) required for the process hazards review.
- A meeting was held between ICI Tracerco, Air Products and Washington University personnel to discuss improvements in tracer techniques and to plan for a study during F-T IV. Tracerco agreed to several suggestions to improve the quantitative methods.
- An alternate oil was evaluated for the utility oil system to improve heat transfer. Better heat transfer in the reactor tubes translates into improved reactor temperature control. Therminol-59, a heat transfer fluid used in the Kingsport reduction vessel, was found to be superior to the current Drakeol-10. The log mean delta T (LMTD) decreased by about ~15%. The improvement is due to better heat transfer properties: higher thermal conductivity, lower viscosity and higher density. Lower heat capacity is the only negative. After consultation with Shell Synthetic Fuels, Inc. (SSFI), it was decided to switch the oil at the cost of ~\$9,000.
- Kinetic information was received from SSFI, and the LaPorte flow sheet was simulated to generate mass balances.
- Meetings were held with DOE and SSFI personnel to finalize the run plan. The plan (see the attached table), which includes 18 days of syngas operation, was approved by all participants.

## **1.2 Liquid Phase DME Demonstration**

An application for an air permit exemption for a DME run at LaPorte was prepared by GEG Environmental. Two cases with a maximum DME production rate of about 14 TPD (LaPorte limit) were simulated. A meeting was held between Air Products' Process Engineering and R&D departments to discuss the catalyst operating window, scaleup and commercially desired operating regime for DME synthesis. To allow more time for catalyst development and scaleup, the run was delayed until October 1998. The catalyst delivery date was relaxed to 1 July. The effect of iron contaminant in the commercial-grade reagent on catalyst life will be further explored. Additional dispersant experiments are also planned to determine if the stable operating range can be broadened. The commercial operating conditions provided by Process Engineering will be checked against catalyst limitations correlations. In addition, Process Engineering will review the effect on economics of operating at space velocities higher than 2000. Also, water injection experiments for both MeOH and DME synthesis will be scheduled in the autoclave.

## **TASK 2: AFDU SHAKEDOW, OPERATIONS, DEACTIVATION AND DISPOSAL**

### **2.1 Liquid Phase Fischer-Tropsch Demonstration**

Initial setup and calibration activities for the F-T IV demonstration began at LaPorte in February. This included the analytical setup, the data-acquisition system and the nuclear density measurements. Final preparations were completed in March. The new DCS control stations were programmed, and communications between the distributed control system (DCS) and the data acquisition system (DAS) were successfully tested. Nuclear density gauge calibration on the reactor was completed, and calibration of a radial nuclear density device for chordal scans was performed. A hot function test of the unit without catalyst was performed on 21-22 March. This test was conducted with both nitrogen and synthesis gas at the conditions for reactor operation, and provided a final check of the equipment and instrumentation systems.

Shell's improved proprietary catalyst (MDC), start-up wax (Callista-158) and some flush Durasyn-164 oil were mixed in the prep tank to make a 26.8 wt % slurry. The slurry was then transferred to the reactor, and catalyst drying began at 19:00 hours on 23 March 1998. Reactor temperature was ramped up with a flow of 100% nitrogen to drive the physical water out of the catalyst. Water concentrations were monitored in the system using both instantaneous Panametric instruments and accumulated measurements via zeolite-5A tubes. Initially, plugging was experienced at a pressure regulator on the sample line for the reactor offgas. Start-up wax was found in the regulator upon cleaning. The problem was addressed by inserting a knock-out pot upstream of the regulator, as well as increasing the reactor operating pressure. The drying was essentially complete at 22:00 hours on 24 March 1998. At that point, hydrogen was introduced to begin catalyst activation. We continued to monitor the water concentration, but water measurements proved to be inaccurate due to wax/oil contamination of the analytical system. However, the activation appeared to proceed well, since the expected methane production was observed. The activation procedure was completed at 14:00 hours on 28 March 1998. The

activation was terminated after the onstream time required in the autoclave at the activation conditions was exceeded.

Syngas was introduced to the process at 14:15 on 28 March 1998. The start-up with syngas included a series of intermediate steps to reach the first operating condition (Run AF-R16.1, see the attached run plan). Over Day 1 of the start-up, the plant was stabilized at approximately half the target productivity. Temperature control was satisfactory at stable operating conditions and low productivity, but proved challenging during transient moves to higher productivity conditions. As a result, we relied on the automatic temperature control scheme, with some tuning modifications, and made a series of small steps to the operating conditions. During this period, the productivity increased from about 65 g HC/hr-lit. of reactor volume to above 120 g HC/hr-lit. of reactor volume. Reactor operation was hydrodynamically stable, with uniform temperature and gas holdups. The catalyst/wax filters performed well, producing a clean wax product. For the most part, we needed only one of the four filter housings for catalyst/wax. The plant lined out at condition AF-R16.1 at midnight on 01 April, with a productivity of approximately 140 g HC/hr-lit. of reactor volume. At that point the heat load in the reactor caused the automatic temperature control to oscillate just enough to discourage any further increases in productivity. As a result, the baseline condition was defined, and a steady data collection period began. The operations will continue through the first half of April, as we execute the run plan.

FISCHER-TROPSCH IV DEMONSTRATION RUN PLAN								
<b>Shell's Proprietary Catalyst Charge:</b>	500	lbs			<b>Plant CO Conv:</b>		80	mole%
<b>Shell's SX-70 Wax + Durasyn-164 Oil:</b>	1350	lbs			<b>Reactor Productivity:</b>		150	g HC/lit-hr
					<b>Total Production:</b>			
<b>Reactor Pressure:</b>	710	psig		strm 1	<b>Heavy Wax (C14+):</b>		11500	gallons
<b>Reactor Temp:</b>	250-260	deg C		strm 1	<b>Light Wax (C11 - C26):</b>		2600	gallons
<b>Slurry Conc.:</b>	24-25	wt%		strm 2	<b>Hydrocarbons (C4 - C21):</b>		14900	gallons
<b>Slurry Height:</b>	20	ft		strm 2	<b>Water:</b>		31100	gallons
Run No.	Description	H2/CO in Fresh Feed	H2/CO in Reactor Feed	Recycle Ratio	Space Velocity sl/hr-kg cat	Days on-stream	Sup. Gas Vel (in), ft/sec	CO Conv. per Pass mole%
AF-R16.1	Mid H2/CO in Fresh Feed, Low Recycle (Baseline)	1.85	1.21	1.19	13460	4	0.41	33.7
AF-R16.2	Low H2/CO in Fresh Feed, Low Recycle	1.78	1.01	1.20	13103	3	0.40	31.7
AF-R16.3	Low H2/CO in Fresh Feed, High Recycle	1.80	0.81	3.01	23950	3	0.72	17.0

<b>FISCHER-TROPSCH IV DEMONSTRATION RUN PLAN</b>								
<b>AF-R16.4</b>	<b>High H<sub>2</sub>/CO in Fresh Feed, Mid Recycle</b>	2.18	2.11	1.99	20346	2	0.62	31.2
<b>AF-R16.5</b>	<b>Activity Check, Repeat Baseline (AF-R16.1)</b>	1.85	1.21	1.19	13460	2	0.41	33.7
<b>AF-R16.6</b>	<b>Tracer Study at Low Velocity (AF-R16.1)</b>	1.85	1.21	1.19	13460	1.5	0.41	33.7
<b>AF-R16.7</b>	<b>Tracer Study at High Velocity (AF-R16.3)</b>	1.8	0.81	3.01	23950	1.5	0.72	17.0
<b>AF-R16.8</b>	<b>Dynamic Gas Disengagement Test at High Velocity (AF-R16.3)</b>	1.8	0.81	3.01	23950	1	0.72	17.0
<b>TOTAL</b>						<b>18</b>		



## TASK 3: RESEARCH AND DEVELOPMENT

### 3.1 Improved Processes for DME

#### 3.1.1 Investigation of the Dependence of the Methanol Catalyst Deactivation Rate on Gas Phase Composition

- Efforts have been made to correlate the deactivation rate of the methanol catalyst under LPDME™ conditions with the gas composition in the reactor. Four phenomenological correlations were obtained. Although our current data base could not distinguish which one was real or the best, all four suggested a trend in the dependence of the deactivation rate on certain species.
- The trend suggested by the correlations was confirmed by four LPDME™ experiments with a modified process scheme. The table below lists the deactivation rate of the methanol catalyst with and without this modification, along with the rate calculated from the correlations. Efforts are continuing in this direction to broaden the window of stable LPDME™ operation and to better understand the correlation.
- Three more LPDME™ experiments using an additive did not result in the stable operation we have observed previously. This could be due to seemingly small changes in the operating conditions or procedures. We will continue to investigate this approach and probe its potential in stabilizing LPDME™ catalyst systems.

Feed Gas	Feed Comp. (mol%) H <sub>2</sub> CO CO <sub>2</sub> N <sub>2</sub>	GHSV	Modification	Deact. Rate of MSC (%/hr) Experimental Correlation
Shell	30 66 3 1	2000	no	0.14 0.18
			yes	0.05 0.04
Texaco	35 51 13 1	6000	no	0.11 0.15
			yes	0.06 0.03
CO <sub>2</sub> -free	40 59 0 1	1600	no	0.16 0.10
			yes	0.04 0.04
CO-rich	16 74 6 4	6000	no	0.20 0.27

\*: 250 C, 750 psig, 80:20 catalyst ratio.

### 3.1.2 Scaleup of Aluminum Phosphate for the LaPorte LPDME™ Trial

- Trace iron contamination (200 ppm) was shown to be a significant cause of substandard performance of the aluminum phosphate samples prepared by our commercial scaleup partner. The presence of the iron was shown to have an adverse affect on the stability of the methanol catalyst in an experiment using a batch of aluminum phosphate that was artificially spiked with 774 ppm iron. Our commercial scaleup partner has identified other sources of aluminum nitrate with lower iron content. A batch with 108 ppm iron did not show any stability improvement, indicating that there are other factors that can affect aluminum phosphate performance. Our commercial partner has recently prepared its first 500-gallon batch, using an aluminum nitrate of still higher purity. The final catalyst contains only 25 ppm iron. We will test this material this month. Our partner is developing revised pricing to include the use of this higher purity reagent.
- A standard LPDME™ experiment using methanol catalyst and uncalcined aluminum phosphate from our scaleup partner had surprisingly high activity and excellent stability. This level of activity is probably too low to be commercially viable, but it provides new insights into the nature of the active sites of the catalyst, since we would have expected the uncalcined material to have little activity at all. We have characterized aluminum phosphate samples before and after calcination by <sup>1</sup>H, <sup>27</sup>Al and <sup>31</sup>P nmr, as well as TGA/ir, to clarify how the structure of the catalyst changes during calcination.
- When the aluminum phosphate was calcined even at temperatures as low as 250°C – the same temperature that the material is exposed to in the LPDME™ reaction – the stability was lost. Apparently, the conditions of heat treatment are important in determining how the aluminum phosphate will affect the methanol catalyst. However, since the poor stability of the calcined material has been attributed to the presence of iron, this may not be true for a low-iron catalyst.

## 3.2 New Fuels from Dimethyl Ether (DME)

### 3.2.1 Overall 2QF98 Objectives

The following set of objectives appeared in Section 3.2 of the previous Quarterly Technical Progress Report No. 13:

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

### 3.2.2 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 Southwest Research Institute (SwRI), a family of ethers has been identified as cetane enhancers. The blend of oxygenated compounds is called CETANER™ and is potentially accessible from the oxidative coupling of DME.

#### *Catalyst Testing for Oxidative Coupling*

Five materials were evaluated as oxidative coupling catalysts at temperatures between 200 and 400°C and with a DME/O<sub>2</sub>/N<sub>2</sub> feed at near ambient pressure. Four of these showed no evidence of DME coupling. Only the C1 species CO, CO<sub>2</sub>, and CH<sub>4</sub>, were observed as products. Reaction of DME/O<sub>2</sub> over a 3-component mixed oxide catalyst at 300°C resulted in formation of the oxidative coupling products 1,2 dimethoxyethane, 2-methoxyethanol, and diglyme. A catalyst that shows oxidative coupling reactivity at low pressures would be expected to be significantly more reactive and selective at high pressure.

Three oxides were evaluated as oxidative coupling catalysts between 200 and 400°C and with a DME/O<sub>2</sub>/N<sub>2</sub> feed near ambient pressure. These oxides are various combinations of the 3-component catalysts found active for oxidative coupling of DME. Two oxides showed no evidence of oxidative coupling products. The third resulted in trace amounts of the coupling product 1,2-dimethoxyethane, along with larger concentrations of CO<sub>2</sub>, CO and CH<sub>4</sub>.

An earlier evaluation of the 3-component oxide showed trace production of the coupling products 1,2-dimethoxyethane (monoglyme) and diglyme. However, when the catalyst was re-evaluated at a lower reactor pressure, 6 psig, only C1 products were observed. Increasing the reactor pressure to 20 psig at 325 and 350°C resulted in traces of 1,2-dimethoxyethane and diglyme, **respectively**. The temperature required to observe coupling in the current run, 325°C, was greater than that required in the previous run, 300°C.

#### *Peroxide Testing of CETANERÔ*

The tendency of 1,2-dimethoxyethane and other components of CETANER™ to form peroxides when blended with diesel fuel is being evaluated. Various CETANER™/diesel blends will be stored in steel cylinders under 1 atm air at ambient temperature. The contents of each cylinder will be examined monthly (at least initially) to determine the extent of peroxide formation. A literature method will be used to determine the concentration of hydroperoxides (ROOH), but not dialkylperoxides (ROOR) present in a hydrocarbon sample [Anal. Chem. 33, 1423 (1961)]. Hydroperoxides are the most likely product based on the known chemistry of ethers.

A series of diesel fuel blends (Table 3.2.1) was prepared for evaluation of peroxide formation. These consisted of diesel fuel blended with two CETANER™ compositions (Table 3.2.2). The composition of Additive A was consistent with that reported in the literature for oxidative coupling of DME to CETANER™ product. Additive B represented a composition that might be obtained by a substantial improvement in catalyst selectivity for 1,2-dimethoxyethane (DMET) or monoglyme.

**Table 3.2.1 Diesel Fuel-Additive Blend Compositions for Peroxide Testing**

	Volume Diesel Fuel, mL	Volume Additive A, mL	Volume Additive B, mL
Blend 1	900	600	0
Blend 2	1050	450	0
Blend 3	900	0	600
Blend 4	1050	0	450
Blend 5	1500	0	0

**Table 3.2.2 Compositions of CETANER™ Additives A and B**

	-----volume %-----		
	1,2-dimethoxy ethane	dimethoxy methane	methanol
Additive A	72.9	24.2	2.9
Additive B	91.9	4.2	3.9

Each of the five blends was tested for the presence of hydroperoxide. Results are summarized in Table 3.2.3. For all five samples, the absorbance difference was less than 0.004. No peak was observed at 406 nm in the spectrum of any of the samples, suggesting that absorbance differences of this magnitude are equivalent to near zero peroxide.

**Table 3.2.3 Results for Initial Peroxide Testing of Fuel Blends**

	Blend Density, g/mL	Absorbance Difference at 406 nm	Concentration H <sub>2</sub> O <sub>2</sub> , ppm (by wt.)
Blend 1	0.846	0.0019	1.5
Blend 2	0.842	0.0007	1.2
Blend 3	0.842	-0.0004	0
Blend 4	0.842	0.0007	1.2
Blend 5	0.826	0.0031	1.9

Following peroxide testing, the remaining 1.4 L of each blend were transferred into D1-size steel cylinders with an internal volume of 2.1 L and stored under 1 atmosphere of air.

After storage for 1-month intervals, an aliquot of each blend was tested, and the results are listed in Table 3.2.4. No significant concentrations of peroxide were detected. All values were near the zero level of peroxides.

**Table 3.2.4 Results for Peroxide Testing of Fuel Blends**

	Concentrations, Volume %				H <sub>2</sub> O <sub>2</sub> Conc. in ppm (by wt.) on:	
	Diesel	DMET	DMM	MeOH	6 Feb 98*	6 Mar 98
Blend 1	60.0	29.2	9.68	1.16	1.4	1.6
Blend 2	70.0	21.9	7.26	0.87	1.8	3.4
Blend 3	60.0	36.8	1.68	1.56	2.9	1.4
Blend 4	70.0	27.6	1.26	1.17	1.4	0
Blend 5	100	0	0	0	1.1	0

\* Values for 6 Feb 1998 testing were slightly different than reported last month due to a change in the procedure for correcting blank absorbances.

To ensure that the absence of peroxides was not due to the method used, a diesel fuel-monoglyme blend was prepared from peroxide-containing monoglyme. The blend contained 40 volume % monoglyme, which had 15-25 ppm peroxide (determined using "Baker Teststrips" for peroxide). Testing using the Ti<sup>4+</sup>/H<sub>2</sub>SO<sub>4</sub> method indicated 29.8 ppm (by wt.) in the blend. Thus, if peroxides are present, the Ti<sup>4+</sup>/H<sub>2</sub>SO<sub>4</sub> method will detect them. However, the Ti<sup>4+</sup>/H<sub>2</sub>SO<sub>4</sub> method does give peroxide levels that are perhaps too large for neat monoglyme. Based on the peroxide concentration in the above blend, 75 ppm (by wt.) peroxide is expected in the neat monoglyme, a value significantly greater than that indicated by the test strips. Testing of neat monoglyme alone gave a value of 146 ppm. Similarly, testing of neat monoglyme from a new, unopened bottle gave 21 ppm peroxide.

Two possible reasons why peroxides were not detected in the fuel blend may be that the steel container catalyzes peroxides decomposition, or there is an antioxidant in the diesel fuel. Therefore, a blend consisting of 40% monoglyme (from a new, unopened bottle) and 60% diesel fuel was stored in a glass container under air. The headspace above the liquid was approximately the same as that of the samples in the steel cylinders. Initial peroxide testing (3/13/98) gave 0.3 wt ppm peroxide. The sample will be tested monthly. An additional sample having the same composition as blend 1 (see Table 3.2.3) will be prepared and stored in glass.

To ensure miscibility with diesel fuel, diglyme and triglyme fuel blends were prepared. As seen in Table 3.2.5, all blends consisted of only one phase.

**Table 3.2.5 Miscibility of Diesel Fuel with Diglyme or Triglyme**

Volume Diesel Fuel, mL	Volume Diglyme, mL (vol %)	Volume Triglyme, mL (vol %)	Number of Phases
5.0	0.88 (15%)	-	1
5.0	2.14 (30%)	-	1
5.0	4.10 (45%)	-	1
5.0	-	0.56 (10%)	1
5.0	-	1.25 (20%)	1
5.0	-	2.14 (30%)	1

***Cetane Determination of Oxygenates***

Preliminary cetane numbers for pure oxygenates were received from SwRI: diglyme, 282; triglyme, 190; dioctylether, 178; 2-methoxyethanol, 13. Because of the lack of suitable standards, differentiation of cetane numbers greater than 100 may not be wise.

***Potential Health Hazards***

A series of literature searches was conducted regarding the health hazards associated with 1,2-dimethoxyethane (monoglyme), diglyme, and triglyme. The literature implies that glymes are teratogens and reproductive toxins. Ferro Corporation, the sole known U.S. manufacturer of glymes, states in its product literature that the glymes exhibit only low to moderate toxicity. However, it is further stated that "concern regarding chronic exposure and reproductive effects indicate that glymes be used only in industrial applications." In a preliminary evaluation, C.E. Hamilton of Air Products' Corporate Toxicology department concluded that the health hazards of 1,2-dimethoxyethane are significant compared with those reported for the gasoline oxygenate MTBE. It appears that the adverse effects of the glyme family are related to its metabolism to 2-methoxyethanol (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH) and ultimately to methoxyacetic acid, CH<sub>3</sub>OCH<sub>2</sub>COOH, for which adverse health effects are well established. A literature search of the glyme metabolism found studies that conclude that diglyme is metabolized to methoxyacetic acid and that similar metabolism of triglyme is likely. No definitive studies for 1,2-dimethoxyethane were found, but its metabolism to methoxyacetic acid was implied based on the similarity of its effects as a reproductive toxin to those of methoxyacetic acid. A full summary of the metabolism literature of the glymes is available.

***External Contacts to Evaluate CETANERÔ***

***UOP***

A meeting was held with a "third party" representing UOP to share information on the manufacture of DME through LPDME™ and to manufacture liquid DME (now called CETANER™) as a cetane enhancer for diesel fuel. The "third party" sent a report to UOP based on his one-day visit to Air Products on 28 January.

## ENI

A meeting was held with the ENI Group in Milan, Italy on 23-24 February. The business purpose of the trip was to evaluate ENI's expertise in working with Air Products on the manufacture of ethers from the oxidative coupling of dimethyl ether; to tour their engine-testing facility and research laboratories; and to discuss a preliminary letter of intent between both parties. A trip report was issued summarizing the two-day visit.

### *Advanced Engine Technology (AET)*

The following is a brief summary of the expected outcome from AET's proposed statement of work evaluating CETANER™ in diesel fuel derived from Canadian tar sands:

*Task 1.* Determine the volume % of fuel blends as a function of cetane number. The blending stock will be two low-cetane fuels as base fuels and one reference fuel (EPA certification).

*Task 2.* Determine the following physical properties of two test fuel blends, two base fuels and one reference fuel:

distillation temp	sulfur content	water content
density	conductivity	cloud point temp
viscosity	calorific value	flash point temp

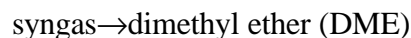
*Task 3.* Determine combustion and exhaust emission characteristics of two test fuel blends and one reference fuel. These emission characteristics are regulated exhaust emissions and particle size emissions.

*Task 4.* Determine lubricity for one fuel blend and each of the two base fuels and reference fuel.

*Task 5.* Write Final Report.

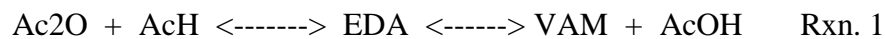
### **3.2.3 Vinyl Acetate from DME**

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:



### ***Background***

Ethylidene diacetate (EDA)  $\{\text{CH}_3\text{CH}(\text{O}_2\text{CCH}_3)_2\}$  can be cracked to vinyl acetate (VAM)  $\{\text{CH}_2=\text{CHO}_2\text{CCH}_3\}$  and acetic acid (AcOH)  $\{\text{CH}_3\text{CO}_2\text{H}\}$ . Ethylidene diacetate (EDA) can also react to yield acetic anhydride (Ac<sub>2</sub>O)  $\{(\text{CH}_3\text{CO})_2\text{O}\}$  and acetaldehyde (AcH)  $\{\text{CH}_3\text{C}(\text{O})\text{H}\}$ . Reaction 1 depicts this series.



### ***Supported Sulfonic Acids***

Previously, we reported on the use of supported sulfonic acid catalysts for cracking EDA. Varying the EDA/catalyst ratio was shown to influence the selectivity. Temperature stability was unknown. Additionally, like most other catalysts examined, the amount of AcOH produced was in excess of the predicted value. We believe the excess AcOH comes from VAM.

#### *10:1 Ac<sub>2</sub>O/EDA Feed*

Three different supported sulfonic acid (SSAC) catalysts were screened. The catalysts were wet as received, and were washed first with acetic acid, followed by acetic anhydride. This washing appeared to remove the water and leave the catalyst solvated. In all cases, a 3.3-gram sample of starting material was used, yielding a 1-gram sample of “dried” catalyst. A 1-gram sample of SSAC was loaded with a 10:1 mole ratio of Ac<sub>2</sub>O/EDA (17.5g Ac<sub>2</sub>O; 2.5g EDA) and distilled as described previously. Distillation time was about 0.3 hour. Determination of components was accomplished via gas chromatography using amyl acetate as an internal standard. Upon completion of distillation, the pot was recharged with a fresh Ac<sub>2</sub>O/EDA mixture and brought back to distillation conditions. This procedure was performed several additional times. The reason for attempting this recycle scenario was to test the catalysts’ temperature stability and recycle potential. Mass balances on carbon and oxygen approached 100%.

As can be seen from the summary in Table 3.2.6, conversion of EDA dropped while selectivity to both VAM and AcH fluctuated. This may be due to a buildup of reactants in the pot. The drop in conversion suggests that the catalyst is in fact losing activity. Interestingly, the amount of excess acetic acid produced drops at the same time.



**Table 3.2.6 Recycling SSAC**

SSAC	EDA Conv. (%)	VAM Sel (%)	C Mass Balance (%)	Throughput (g Prod)/(l sol'n)/hr
SSAC1	70.5	3.5	99	5.8
	62.3	2.3	100	3.3
	47.7	2.8	100	3.1
	34.3	6.1	100	4.9
	17.4	7.9	100	3.3
SSAC2	51.7	1.9	99	2.3
	33.4	1.9	100	1.5
	27.9	4.7	100	3.1
	34.8	2.3	100	1.9
SSAC3	48.2	5.2	100	5.9
	41.9	3.9	100	3.9
	35.7	0.3	100	0.3

*EDA-Only Feed*

A 1-gram sample of SSAC1 was loaded with a 20-gram sample of EDA and distilled as described previously. Distillation time was about 0.3 hour. Determination of components was accomplished via gas chromatography using amyl acetate as an internal standard. Carbon and oxygen balances approached 100%. The table below shows the initial and final compositions for this distillation. We already know that the absence of Ac<sub>2</sub>O will allow the retro-reaction to proceed to a significant extent.

Initial EDA fed = 136.8 mmole

Composition of distillate

EDA = 75.4 mmole  
 Ac<sub>2</sub>O = 56.7 mmole  
 VAM = 2.5 mmole  
 AcH = 42.9 mmole  
 AcOH = 6.8 mmole

As can be seen from the data above, 61.4 mmoles of EDA were consumed; 56.7 mmoles of Ac<sub>2</sub>O were formed and the corresponding AcH was present, to a first approximation. This indicates that 4.7 mmoles of VAM and 4.7 mmoles of AcOH should have been formed. Instead, 2.2 mmoles of VAM appeared to be missing, and approximately the same amount of excess AcOH produced. This suggests that VAM, under these conditions, was converted to AcOH by some undefined mechanism. Alternatively, VAM could be lost due to volatility, but this is less likely.

#### *Ac<sub>2</sub>O + VAM Feed*

A 1-gram sample of SSAC1 was charged with 19.2 grams of Ac<sub>2</sub>O and 0.8 grams of VAM. Distillation was typical, requiring about 20 minutes. The distillate was analyzed via gas chromatograph using amyl acetate as an internal standard. Results of this distillation were as follows:

Ac <sub>2</sub> O fed	=	188 mmole
VAM fed	=	9.4 mmole
EDA in distillate	=	0.5 mmole
Ac <sub>2</sub> O in distillate	=	162 mmole
VAM in distillate	=	8 mmole
AcH in distillate	=	0.4 mmole
AcOH in distillate	=	3.8 mmole

Because Ac<sub>2</sub>O can decompose in the presence of acid catalysts, and because of its apparent ability to decompose VAM, exact mathematical analysis of this product slate is difficult. The interesting observations are the formation of EDA and AcH.

#### **3.2.4 3QFY98 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.

### **3.3 New Processes for Alcohols and Oxygenates**

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

##### *Catalyst Performance*

As reported in the last Quarterly Status Report, in searching for activation of the Zr/Zn/Mn/K-oxide catalyst system at lower reaction conditions, we have found that impregnation with various hydrogenation metals (Table 3.3.1) leads to similar results in isobutanol synthesis over most catalysts (Figures 3.3.1 and 3.3.2).

**Table 3.3.1 Preparation and Impregnation of the Tested Catalysts**

Composition	ZrO <sub>2</sub> /ZnO/MnO
Synthesis method	Coprecipitation (at 353 K and pH 9) of the nitrates (1:1:1) with KOH
Impregnation method	Incipient wetness
Promoter	Cu, Ag, Co, Rh, Pd, Pt, Ru
Promoter load	0.024 (M 1)- 0.10 (M 2) mmol/g <sub>cat</sub>
Calcination	6 h at 703 K (1 K/min)
Reduction	8 h at 548 K (1 K/min) with 5% H <sub>2</sub> in N <sub>2</sub>

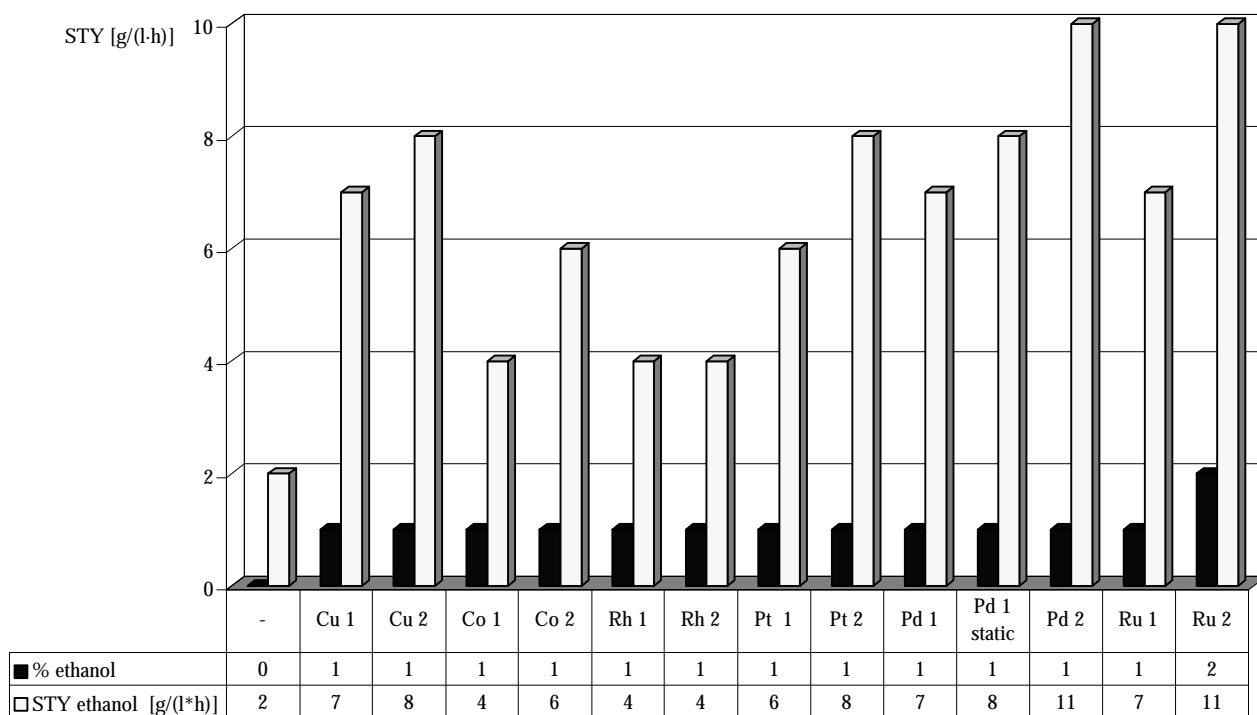
Although the propensity towards the linear alcohols is enhanced over all tested catalysts, isobutanol production is not increased by this tendency at the reaction conditions employed (385°C, 125 bar and 11,600 h<sup>-1</sup> GHSV).

However, a copper load of 0.024 mmol/g<sub>cat</sub> gives an improved result towards isobutanol. One can speculate about the mechanistic explanation for this behavior. The results from this investigation allow the presumption that it is not the hydrogenation activity of the copper promoter that benefits isobutanol production. Further investigations will be made concerning the function of copper in isobutanol synthesis.

#### ***Catalyst Preparation***

Normally our Zr/Zn/Mn/K-oxide catalyst is prepared as mentioned in Table 3.3.1. The catalyst synthesis is carried out in a 4l flask to yield only 20-30 gm of catalyst with the desired particle size distribution. Since we encountered difficulties in reproducing the Zr/Zn/Mn/K-oxide catalyst, we are scaling up the catalyst synthesis method. Various batches are being synthesized and investigated.

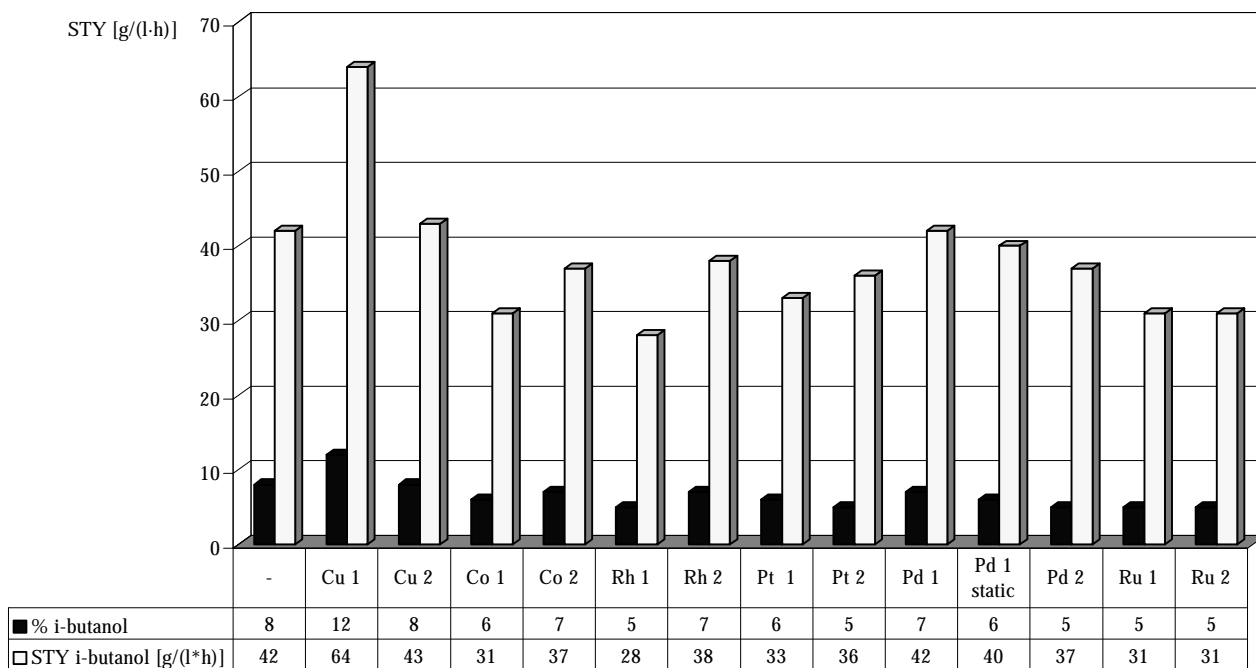
STY ethanol, 385 °C



**Figure 3.2.1 Influence of Hydrogenation Metals on Ethanol STY over the Zr/Zn/Mn/K-Oxide Catalyst**

(PFR, Unit II, 125 bar,  $V_{\text{cat}}=3 \text{ ml}$ ,  $\text{GHSV}=11,600\text{h}^{-1}$ )

STY isobutanol, 385 °C



**Figure 3.3.2 Influence of Hydrogenation Metals on Isobutanol STY over the Zr/Zn/Mn/K-Oxide Catalyst (PFR, Unit II, 125 bar,  $V_{cat}=3$  ml,  $GHSV=11,600$  h<sup>-1</sup>)**