ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS

FINAL

Technical Progress Report No. 16

For the Period 1 July - 30 September 1998

Contractor

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Alternative Fuels and Chemicals from Synthesis Gas

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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 Dimethyl Ether (LPDME™) Demonstration
Heat and material balances were developed for a 40-day LPDME™ run at LaPorte, scheduled to begin in October 1998. The balances were compared with plant limitations and emission requirements to insure that the run plan was within plant constraints. In order to address catalyst stability concerns, the ratio of methanol catalyst to dehydration catalyst for the baseline condition was increased from 80:20 to 86:14. With the increased proportion of methanol catalyst, the higher concentration of methanol in the reactor was expected to decrease the deactivation rate of the catalysts. Correlations developed by the Reaction Engineering Group that relate the reactor outlet concentration to the catalyst deactivation rate were used to evaluate the deactivation rate at each process condition for the LaPorte trial.

A preliminary run plan was presented to DOE personnel at a meeting on 27 August. The main objective of the run is to demonstrate a stable, commercially viable process on a 10 T/D scale, using commercially produced catalysts. We also want to obtain information to correlate scaleup of catalyst aging from autoclave to bubble column. In addition, process variable testing including methanol and water injection as well as hydrodynamic experiments will be conducted. The run plan is summarized in the attached table. The scheduled start-up date for the run was October 19 (catalyst loading). The analytical and data acquisition system at LaPorte were set-up and checked out for the DME synthesis operating mode.

Due to delays experienced in producing the required 800 lb of dehydration catalyst at Engelhard, the run was postponed. The material produced at the larger scale appeared to be inferior to the laboratory-scale preparations. R&D is following up on certain leads and our expectation is to conduct the demonstration early next year.

Table 1.1 Preliminary Run Plan for DME/Methanol Run at the LaPorte AFDU – October/November 1998

Run No.	No. of Days	Comment	Gas Type	Reactor Pressure psia	Reactor Temp. deg F	Space Vel. sl/kg-hr	React. Fd. lbmol/hr	Inlet Sup. Vel. ft/sec	Slurry wt% oxide
MEOH CATALYST									
	1	Catalyst Loading							
AF-A13	1	Kingsport Reduction	4% CO in N2	67		615	32.3	0.62	40
AF-R17.1	5	Temperature Prog.	Kingsport	750	428-482	4000	210	0.48	40
AF-R17.2	2	Water Injection	Texaco	765	482	5000	263	0.60	40
Sub-total	9								
MEOH + DEHYDRATION CATALYST (MEOH CAT = 86%)									
	1	Catalyst Transfer							
AF-R18.1	15	Life Study	Shell	765	482	6000	319	0.72	40
AF-R18.2	2	High Pressure	Shell	1000	482	6000	319	0.55	40
AF-R18.3	2	High Velocity	Shell	765	482	8000	426	0.96	40
AF-R18.4	2	Texaco Gas	Texaco	765	482	6000	319	0.72	40
AF-R18.5	2	Low Vel. + MeOH Inj.	Shell	765	482	3000	165	0.37	40
AF-R18.6	1	Tracer (R18.5)	Shell	765	482	3000	165	0.37	40
AF-R18.7	2	Tracer (R18.3)	Shell	765	482	8000	426	0.96	40
AF-R18.8	1	Baseline	Shell	765	482	6000	319	0.72	40
Sub-total	28								
MEOH + DEHYDRATION CATALYST (MEOH CAT = 68%)									
	1	Catalyst Transfer							
AF-R19.1	2	Stoch. Feed+MeOH Inj.	1:1 H2/CO	1000	482	3000	173	0.30	40
AF-R19.2	2	Nat. Gas Based Feed	2.75:1 H2/CO	765	482	4000	210	0.48	40
AF-R19.3	2	Water Injection	Shell	765	482	6000	319	0.72	40
Sub-total	7								
TOTAL	44								

TASK 3: RESEARCH AND DEVELOPMENT

3.1 IMPROVED PROCESSES FOR DME

3.1.1 Improving DME Catalyst Activity
The understanding between the catalyst stability and reaction conditions obtained from an $AlPO_4$-containing dual catalyst system was applied to five LPDME™ catalyst systems we have studied in the lab. This analysis helped us to understand how much of the instability in these catalyst systems is due to the reaction condition and how much is due to the catalyst material itself. This understanding of the nature of the problem gives us some guidelines in developing LPDME™ catalysts.

3.1.2 Methanol Catalyst Research
- Reduction data showed that the new methanol synthesis catalyst we are qualifying differs considerably from the standard methanol synthesis catalyst. The standard catalyst undergoes strong interaction with aluminum phosphate during their initial contact, resulting in significant loss in both methanol synthesis and methanol dehydration activity. The new methanol catalyst does not have such initial, strong interaction with aluminum phosphate.

3.1.3 Understanding Liquid Phase Processes
- The alternate methanol catalyst sample received was tested under LPMEOH™ conditions. The activity of the methanol catalyst was comparable to or possibly better than that of the previous two alternate catalyst samples, as well as the standard methanol catalyst. The alternate methanol catalyst was stable during 146 hours on stream, showing a baseline rate of deactivation at 0.043% per hour.

- We have begun evaluating a number of methanol catalyst powders as candidates to replace the standard methanol synthesis catalyst in the LPMEOH™ and LPDME™ processes. Our first tests have looked at physical properties and slurry characteristics. None of the candidate catalysts approaches the uniquely high density of the standard catalyst. Several of the candidates exhibit much smaller initial particle size than the standard catalyst. These differences result in differences in slurry viscosity and settling characteristics, which in turn may impact process design constraints such as heat transfer, gas holdup and maximum slurry concentration. We will finish the physical characterization this quarter and begin performance testing of the more promising candidates.

- A research plan was prepared on a possible way to increase volumetric productivity in liquid phase processes. The plan explains why and how we want to achieve this increase and what the chances are that it would work. The results from a preliminary experiment looked promising.

- The surface tension of the slurry samples collected before and after the sudden decrease in the gas holdup in the Kingsport LPMEOH™ reactor on 28 June was analyzed. The results show that surface tension does not explain the change in gas holdup.

3.1.4 Scaleup of Aluminum Phosphate for an LPDME™ Trial at LaPorte

- Our commercial scaleup partner prepared eight 160-lb batches of uncalcined aluminum phosphate. This should yield roughly 1,000 lb of catalyst after calcination, a sufficient quantity to meet the requirements of one reactor charge plus one backup charge.

- Chemical analysis of the eight batches showed that the Al/P ratio varied significantly from batch to batch. Our partner agreed to make two more batches at one-half dilution, while also more carefully controlling the total amount of base added during the precipitation. This provided some insurance that we would have sufficient high-quality material to conduct the life-test portion of the run.

- Three of the batches were tested in the lab under conditions similar to those projected for the LaPorte life test. At least one, and perhaps all three, of the batches we tested are acceptable for the LaPorte LPDME™ trial. The criterion for acceptability is that the aluminum phosphate must have DME synthesis activity in line with our previous lab samples and must not cause the methanol catalyst to deactivate faster than it would in the absence of any aluminum phosphate. The acceptable batch was tested for 400 hours. The methanol catalyst stability between 150 and 400 hours on stream was acceptable, even though it had unacceptably high methanol catalyst deactivation rates over the first 150 hours on stream. From this we conclude that there is an initial 150-hour period of rapid methanol catalyst deactivation and that the aluminum phosphate provides acceptable LPDME™ performance thereafter. The other two batches tested showed similar behavior to the acceptable batch for the first 200 hours, after which the test was terminated. The overall process performance loss during the initial 150 hours was fairly small, and the LPDME™ productivity during the stable period was in line with the program goals of 28 gmol/kg-hr initial productivity and >14 gmol/kg-hr productivity after 1,000 hours.

- Our commercial scaleup partner also calcined a portion of the acceptable batch in its rotary calciner. We are currently testing this sample. If its performance is acceptable, our partner will proceed with the calcination of the remaining acceptable batches.

3.1.5 Characterization of Aluminum Phosphates by Nuclear Magnetic Resonance

- Solid-state NMR analysis has been applied to various aluminum phosphates, both from Air Products' labs and from those of our commercial scaleup partner. Aluminum and phosphorus NMRs have shown that there is considerable variety in the types of atomic bonding arrangements, which results from variations in the catalyst synthesis method. Some of these differences appear to be retained even after the catalyst is calcined. Proton NMR spectra of these materials has shown that a diversity of surface hydroxyl species is also present on these materials. We have further work planned to clarify these results and attempt to correlate them to one another and to the observed catalyst performance. From this we hope to elucidate both the causes of poor performance and the critical steps in the synthesis for producing good material.

Task 3.2 New Fuels from Dimethyl Ether (DME)

3.2.1 Overall 4QF98 Objectives
The following set of objectives appeared in Section III of the previous Quarterly Technical Progress Report No. 15:

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

- Document in a topical report the syngas to VAM routes.

3.2.2 Results

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 and other performance characteristics of the fuel is being investigated. Based on external testing by SwRI, a family of ethers has been identified as cetane enhancers. These blends of oxygenated compounds are called CETANER™ and are potentially accessible from the oxidative coupling of DME.

Oxidative Coupling Chemistry

1. Catalysis

Catalyst testing - importance of gas phase reactions. The methane oxidative coupling literature implies that increased reaction pressure does not yield increased conversion to coupled products. This is generally attributed to the relative importance of the catalytic versus gas phase reactions. At low pressure, the catalytic reaction dominates, while at high pressure the gas phase reaction does. Based on our results at near-ambient pressure and at elevated pressure, along with literature results at 235 psia, the same is not true for DME coupling; that is, coupling seems to be favored by high pressure.

Stability of monoglyme. The products of oxidative coupling of DME, like DME itself, are susceptible to unwanted oxidation reactions. To gauge this reactivity, a feed consisting of gaseous monoglyme, N_2, and air was passed through SnO_2/MgO, a literature catalyst. Gaseous monoglyme was obtained by pumping liquid monoglyme, 7.04 ml/hr, into a heated coil of tubing where it was vaporized. Before air was introduced, the thermal stability of monoglyme was evaluated. At 250°C, four products were observed (Table 3.2.1): trace amounts of DME, methyl formate, 2-methoxyethanol and more substantial amounts of methanol. Based on the ratio of methanol product to the initial monoglyme concentration, less than 1% monoglyme was decomposed at 250°C.

Table 3.2.1 Products from the Reaction of Monoglyme with O_2 over SnO_2/MgO
Feed: 25.0 sccm N_2, 23.9 sccm air, 25.2 sccm monoglyme except as noted; 20 psig feed;
0.704 g (1 cc) catalyst

Products (FID rt)	mmol products or monoglyme			
	250°C(no O_2)[a]	250°C	300°C	350°C
CO	0.0000	0.0547	0.1206	0.1262
CH_4	0.0000	0.0000	0.0000	0.0009
CO_2	0.0000	0.0830	0.1418	0.2338
DME (2.70)	0.0000	0.0005	0.0000	0.0010
MeOH (2.79)	0.0256	0.0660	0.0704	0.1097
methyl formate (2.98)	0.0001	0.0971	0.0924	0.0617
dimethoxymethane (3.85)	0.0000	0.0000	0.0010	0.0023
2-methoxyethanol (6.28)	0.0002	0.0006	0.0048	0.0075
monoglyme (7.21)	1.4884	2.2891	1.3480	0.9646
ethylene glycol (9.13)	0.0000	0.0069	0.0058	0.0109
diglyme (19.69)	0.0000	0.0002	0.0001	0.0001
% conv. Monoglyme	<1	7	45	61
% conv. O_2	-	76	99	98

a. feed consists of 48.9 sccm N_2, 25.2 sccm monoglyme
rt - GC retention time in min

Monoglyme reactivity in the presence of O_2 was evaluated at 250, 300, and 350°C, as
summarized above. At 250°C, in addition to CO and CO_2, the three major <u>identified</u> products
were methanol, methyl formate, and ethylene glycol (based on retention times). Trace amounts
of 2-methoxyethanol and diglyme were also observed. Since the concentration of DME was near
zero, diglyme probably does not result from coupling of monoglyme and DME; rather, diglyme
may result from condensation of 2-methoxyethanol. Four major unidentified products at
retention times of 4.65, 9.84, 12.96, and 13.13 min were also observed. (Retention times of
known organics are listed in Table 3.2.1 for reference). Numerous unidentified minor products
were also detected. Increasing the reactor temperature to 300°C gave increased conversion of
monoglyme, 7 to 45%, but only the concentrations of CO and CO_2 increased significantly. A
higher conversion was observed at 350°C, 61%, with significant increases in CO_2, methanol, and
ethylene glycol concentrations. One of the unknowns observed at 250°C (13.13 min) was not
detected at 350°C. These results confirm the notion that, as expected, it is best to work at low
temperature.

Catalyst evaluation - high pressure test apparatus (BTRS). Initial testing of the SnO_2/MgO
catalyst in the BTRS has started at elevated pressure. In the first run (Run 1, Table 3.2.2), a feed
consisting of 25 sccm N_2, 25 sccm air and 4.17 ml/hr liquid DME (25 sccm gas) was used with a
total feed pressure of 275 psig. The DME/O_2 ratio was 5 and the DME feed partial pressure was
96.7 psia. In a second run (Run 2), the partial pressure of DME was increased by eliminating N_2
from the feed. The feed consisted of 25.0 sccm air and 9.3 ml/hr liquid DME (50 sccm gas) at a
total pressure of 275 psig. The DME/O_2 ratio was 10 and the DME partial pressure was 193
psia. Data were collected over 15.5 hours, and average %C selectivities over the last 4 hours are
listed below. Assignments of products are based on GC retention times and require confirmation
via GCMS. Most surprising is the large concentration of methyl formate, which was not

reported as a product in the literature. Several minor unidentified peaks were present, along with one peak of significant area (5.42 min) near the retention time of ethanol (5.60 min).

Table 3.2.2 Results for SnO$_2$/MgO in BTRS
DME conversions based on sum of identified products: Run 1, 14.5%; Run 2, 5.9%

Run	Average C atom selectivity, %												
	CO	CO$_2$	CH$_4$	C$_2$H$_4$	C$_2$H$_6$	C$_3$H$_8$	MeOH	Mefor	MEE	DMM	MeEtOH	MG	DG
1	31.19	9.04	10.18	0.25	0.56	0.00	6.90	35.85	2.00	0.49	0.32	3.20	0.00
2	19.94	7.76	nq	0.07	0.00	0.04	9.62	58.17	0.51	0.43	0.20	2.99	0.26

Mefor = methyl formate; MEE = methyl ethyl ether; DMM = dimethoxymethane; MeEtOH = 2-methoxyethanol;
MG = monoglyme; DG = diglyme; TG = triglyme; nq = not quantitated, but CH$_4$ present

2. CETANER™ Properties

CETANER^{TM} stability. An action item from a recent meeting with a potential partner involved evaluation of CETANER^{TM}-diesel fuel reactivity, especially with regard to the possible formation of 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH). A possible pathway to 2-methoxyethanol is hydrolysis of monoglyme. Since 2-methoxyethanol has a cetane number of only 13.2, substantial concentrations of the alcohol would likely reduce the cetane number of a fuel blend. The most straightforward way to look for 2-methoxyethanol (or other reaction products) is GC analysis of an aged CETANER^{TM}-diesel fuel blend. Such samples are available from our ongoing peroxide testing, and those examined were as follows: one sample prepared 8 April 1998 comprised 60 vol % diesel, 29.1 vol % monoglyme, 9.7 vol % dimethoxymethane, and 1.2 vol % methanol. A second sample, prepared 13 March 1998, comprised 60 vol % diesel and 40 vol % monoglyme. Also examined was a newly prepared sample with the same composition as the 8 April material and a sample spiked with 2-methoxyethanol.

Diesel fuel is a mixture of many components, about 200 by GC analysis. However, CETANER^{TM} components or potential degradation products are expected during the 17 min of the GC where diesel fuel shows 31 peaks. A GC of diesel fuel alone showed no peaks due to 2-methoxyethanol or CETANER^{TM} components, except for a trace of methanol. The newly prepared sample showed only peaks due to diesel fuel, monoglyme, dimethoxymethane, and a larger methanol peak. When this sample was spiked with 2-methoxyethanol, an additional peak at 6.28 min was observed. The aged samples showed only peaks corresponding to diesel fuel or CETANER^{TM} components with the exception of a trace peak at 6.28 min due to 2-methoxyethanol. The observed 2-methoxyethanol concentration was very low, with only about 1 mole of 2-methoxyethanol for each 10,000 moles of monoglyme. Thus, a near-insignificant amount of monoglyme may have decomposed to trace 2-methoxyethanol, but certainly not enough to affect the fuel blend cetane number.

During another meeting, a second potential partner expressed a preference for a methanol-free CETANER™ and urged us to evaluate water miscibility properties of such CETANER^{TM}-fuel blends. We reported previously on the miscibility of methanol-containing CETANER^{TM} blends. The CETANER^{TM} sample examined consisted of 90 vol % monoglyme and 10 vol % dimethoxymethane. The water miscibility of CETANER^{TM}-diesel fuel blends was evaluated by

adding 10-µl increments of water until phase separation occurred in each 10 ml of blends containing 10, 20, 30 and 40 vol % CETANER^{TM}. Table 3.2.3 lists the maximum water concentration for which one phase was observed. These values are lower (that is, less water miscible) than those in earlier testing for a methanol-containing sample. The total water volume added to each sample was increased to 250 µl, and the aqueous layer was analyzed by GC. Quantities of organics extracted into the aqueous phase are lower than for the methanol-containing CETANER^{TM} (Table 3.2.3).

Table 3.2.3 Water Miscibility of CETANER^{TM}-Diesel Fuel Blends
(CETANER^{TM} = 90 vol % monoglyme, 10 vol % dimethoxymethane)

vol % diesel	vol % CETANER^{TM}	added water (vol %) before phase separation	% extracted from organic phase	
			dimethoxymethane	monoglyme
90	10	<0.10	0.83	2.72
80	20	<0.10	not done	not done
70	30	0.10	0.28	0.66
60	40	0.20	0.25	0.54

Peroxide testing. Testing of a series of diesel fuel-CETANER^{TM} blends for peroxide formation is continuing, and a description of the test procedure used and details of the blend compositions can be found in previous reports. Current testing continues to show no significant peroxide concentrations after more than six months of storage in D1 size steel cylinders (Table 3.2.4). Testing with peroxide test strips also showed no detectable peroxide concentrations.

Table 3.2.4 Results for Peroxide Testing of Fuel Blends Stored in Steel Cylinders
(DMET = 1,2-dimethoxyethane, DMM = dimethoxymethane; d = days)

	Concentrations, volume %				H_2O_2 conc. in weight ppm after:						
Blend	diesel	DMET	DMM	MeOH	0 d	28 d	59 d	89 d	125 d	167 d	202 d
1	60.0	29.2	9.68	1.16	1.4	1.6	1.5	2.0	1.5	1.9	0
2	70.0	21.9	7.26	0.87	1.8	3.4	1.2	0	1.5	2.4	3.4
3	60.0	36.8	1.68	1.56	2.9	1.4	2.3	2.8	1.6	1.9	0
4	70.0	27.6	1.26	1.17	1.4	0	0	1.8	0	0.9	5.9[a]
5	100	0	0	0	1.1	0	0	2.2	1.3	0.9	0.6

a. Believed to be inaccurate; no band at 406 nm observed in UV/vis.

Flash point calculations. The low flash point of certain CETANER^{TM} compositions relative to the minimum flash point for European diesel fuel of 55°C may be a concern. U.S. diesel fuel has a minimum flash point of 38°C. Flash points of potential CETANER^{TM} components are listed in Table 3.2.5. Meeting the European and U.S. targets would require minimizing the concentration of low flash point compounds, particularly monoglyme, in CETANER^{TM}. The only component with a flash point greater than European diesel is diglyme, and it is therefore the only component that will not decrease the flash point upon blending. 2-methoxyethanol has a relatively high flash point, but its cetane number of 13 is low. The flash point of dimethoxymethane is very low, and its presence in CETANER^{TM} needs to be avoided.

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Table 3.2.5 Flash Points of Possible CETANER^{TM} Components

Compound	Flash point, °C
methanol	11
dimethoxymethane	-17
monoglyme	0
2-methoxyethanol	46
diglyme	70

To estimate the concentration of monoglyme that could be tolerated in European and U.S. diesel, a literature method (Ind. Eng. Chem. Res. 37, 2029, 1998) was used to calculate flash points. The method assumes that the flash point of a blend depends only on the vapor pressure of the most volatile component, in this case, monoglyme, and uses the equation

$$T_1/T_2 = 1 + (T_1 R \ln x / DH)$$

where T_1 is the flash point of monoglyme (273 K), T_2 is the calculated flash point of the blend, x is the mole fraction of monoglyme in the blend, and DH is the heat of vaporization of monoglyme (39.1 kJ/mol). To calculate a mole fraction, the average molecular weight of diesel fuel was assumed to be 225 (MW of cetane), and a density of 0.825 g/ml was used. A blend containing 10 vol % monoglyme has a calculated flash point of 26°C. This value is in good agreement with the Penn State experimental value of 25.6°C for a 10.9 wt % (about 11 vol %) monoglyme in diesel fuel. The calculated maximum concentrations of monoglyme that can be present and still meet the flash point specs are about 2 vol % for European diesel and about 6 vol % for U.S. diesel fuel. These values hold for any CETANER^{TM} composition in which monoglyme is the lowest flash point component. For example, CETANER^{TM} containing 20 vol % monoglyme and 80 vol % diglyme blended at 10 vol % (2 vol % monoglyme in the blend) would have a calculated flash point of about 55°C, the minimum for European diesel. If flash point requirements must be met, the concentrations of monoglyme in CETANER^{TM} must be minimized.

3. CETANER™ Health Hazards

Potential health hazards. The sole U.S. producer of glymes, Ferro Corp., was contacted to inquire about available toxicological information. Ferro is willing to share its information, but it apparently has nothing beyond that which is publicly available.

Air Products' toxicologist contacted toxicologists at Shell regarding potential toxicological concerns for CETANER^{TM}. According to the Shell toxicologists, the toxicological properties of the glymes are not a major problem. More important are the environmental effects of these materials. Areas of concern are the biodegradability, bioaccumulation, and toxicity for aquatic life. Also important is the nature of airborne decomposition products. No immediate show-stoppers were identified. In-house personnel from Chem Environmental Tech were contacted regarding possible environmental testing. The company suggested that a "microtox" test can be done in-house. Chem Environmental will obtain quotes for biodegradation testing done with an ASTM method. Current literature based on limited testing suggests that monoglyme "may be

resistant to biodegradation" (Hazardous Substance Data Bank). This would seem to contradict the established metabolism of glymes to alkoxyacids and eventually to CO_2.

An examination of the MTBE literature is currently in progress. The focus is on using the MTBE case as a model for CETANER^{TM}. Information relating to MTBE properties, its appearance in the environment, and court cases during the past year has been collected and is being summarized.

4. External CETANER™ Testing

Testing for AET. Earlier attempts to determine the miscibility of CETANER^{TM}- No. 2 diesel fuel at -40°C were frustrated by the high cloud point of the fuel. Advance Engine Technology (AET) sent Air Products a fuel sample with a very low cloud point, -61°C. The fuel is designated Straight Run Light Gas Oil (SRLGO) and is obtained from tar sands. Blends of SRLGO with 10 to 40 vol % CETANER^{TM} (90 vol % monoglyme, 5 vol % dimethoxymethane, 5 vol % methanol) were prepared. The compositions were completely miscible at room temperature. Cooling to -42°C in an acetonitrile/dry ice bath resulted in no phase separation.

AET study. The preliminary testing of reference and commercial fuel in the Small Compression Engine Emissions/Fuel Testing Rig was begun in order to determine the repeatability of the test rig and the emission measuring equipment. An additional 8-liter sample of CETANER^{TM} was prepared and shipped to AET. The sample had the same composition as the previous one. To insure accuracy of composition, the reagents were blended by weight, and volume percentages were calculated. The density of the sample was 0.8629 g/ml.

5. Partnerships

ENI. A two-day meeting was held with representatives of ENI to discuss possible collaboration on the CETANER^{TM} program. ENI shared some of its results involving oxidative coupling of DME. They also examined the Japanese catalyst SnO_2/MgO at near-ambient pressure and found no coupling products.

A short pre-feasibility study plan for September to December 1998 was prepared, approved internally, and forwarded to ENI.

Non-Oxidative Coupling Chemistry

Dehydration of 2-methoxyethanol. From the above discussion under **flash point calculations**, it is clear that a preferred CETANER^{TM} composition will have diglyme (or higher glyme) as its most abundant component. The cost-effective production of diglyme will obviously be difficult. Several routes to diglyme can be envisioned. One possibility is the intermolecular dehydration of 2-methoxyethanol, a species that has been observed in our DME oxidative coupling runs:

$$2\ CH_3OCH_2CH_2OH\ \rightarrow\ CH_3OCH_2CH_2OCH_2CH_2OCH_3\ +\ H_2O$$

2-methoxyethanol   diglyme

Another potential reaction product, vinyl methyl ether, $CH_2=CHOCH_3$, results from intramolecular dehydration. Intermolecular dehydration of alcohols is generally carried out over acid catalysts such as g-Al_2O_3 at modest temperatures. At higher temperatures (>250°C), olefins are the more favorable product. With regard to dehydration of 2-methoxyethanol specifically, little was found in the literature. A Japanese patent (JP 10017514; abstract only) describes the dehydration over Na and Cs-exchanged Y zeolite at 230°C for 8 hr to give diglyme in 24% selectivity and 15% conversion. In a second patent, SU 1735264 (abstract only), vinyl methyl ether was produced in 85-94% yield by reaction in aqueous KOH and $KHSO_4$ at 80-110°C.

We are attempting to evaluate 2-methoxyethanol dehydration in our ambient pressure reactor system. A gaseous alcohol feed was generated by flashing the liquid. At 200°C with a dehydration catalyst, four products were identified as follows (most to least abundant): ethylene glycol, monoglyme, diglyme, and methanol. Ethylene glycol and methanol presumably arise from hydrolysis of the reactant, while monoglyme results from the dehydration reaction of 2-methoxyethanol with methanol. One fairly large peak was unidentified. The retention time of this species is slightly less than that of diglyme and has been observed in some oxidative coupling runs. These experiments were not without difficulties. The quantity of reactant 2-methoxyethanol detected in the GC was far too large to be realistic. At temperatures of 225 and 250°C, the 2-methoxyethanol peak became so large that the runs were ended. The room temperature trap downstream of the reactor contained 10-15 ml of liquid product. GC analysis showed that the liquid contained 2-methoxyethanol, monoglyme, diglyme, methanol, and numerous unidentified species.

3.2.3 1QFY99 Objectives

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

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

3.3 New Processes for Alcohols and Oxygenates

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

Catalyst Performance
In former investigations, promising results in activating the Zr/Zn/Mn/K-oxide catalyst at lower reaction conditions were shown by catalysts promoted with copper. To study the influence of copper, several copper-containing catalysts were synthesized by precipitation of the nitrates with potassium hydroxide solution (Tables 3.3.1 and 3.3.2).

Table 3.3.1 Investigated Zr/Zn/Mn/K-Oxide Catalysts

Catalyst Description	Composition Zr/Zn/Mn/Cu	K [mol %]	Promoter Co [wt %]	Pd [wt %]
LG 2	4:1:1:2		0.2[1]	
LG 15	4:1:1:2			
LG 23	4:1:1:2	4		
LG 24-1	4:1:1:2	4	0.1[2]	
LG 24-2	4:1:1:2	4	0.2[2]	
LG 26	1:1:1:1	4		
LG 27	4:1:1:2	4		0.25
LG 29	4:1:1:2	4	0.2[1]	
LG 30	1:1:1:0	4		
LG 31	1:1:1:0.5	4		
LG 32	1:1:1:2	4		

[1] Co coprecipitated with the other metals, [2] Co impregnated.

Table 3.3.2 Preparation Method of the Zr/Zn/Mn/Cu-K Catalysts

Catalysts	Zr/Zn/Mn/Cu (Co)
Synthesis method	precipitation (at 333 K, until pH 12) of the nitrates with KOH
Calcination	6 hr at 723 K (4 K/min)
Reduction	4 hr at 513 K (1 K/min) with 5% H_2 in N_2
Impregnation with Co/Pd	Incipient wetness method

Product samples were taken after 18 hr of stabilization at 350 (350°C-a) and 385°C. Then, after 1.5 hr of stabilization at 350°C, another sample was taken at this temperature to check for deactivation of the catalyst (350°C-b).

Influence of Potassium on Higher Alcohol Synthesis
Two Zr/Zn/Mn/Cu/K-oxide catalysts free of potassium were also tested (Figure 3.3.1). It can be clearly seen that the basic functions provided by alkali content are needed, especially for higher alcohol synthesis. Methanol STY (space time yield) increases about 30% upon potassium promotion, ethanol STY is doubled and isobutanol production is even quadrupled. Based on these results, all other synthesized catalysts have been impregnated with 4 mol % potassium from K_2CO_3.

STY to different products at 385 °C

STY [g/(l·h)]

	LG 15 Cu/Zr/Zn/Mn	LG 23 Cu/Zr/Zn/Mn-K	LG 2 Co/Cu/Zr/Zn/Mn	LG 29 Co/Cu/Zr/Zn/Mn-K
☐ STY methanol	293	393	253	332
■ STY isobutanol	15	71	18	77
☐ STY ethanol	3	6	4	9

Unit II, V_{cat}=3 ml, D_{cat}=0.25-0.71 mm, GHSV=11,600 h^{-1}, p=125 bar
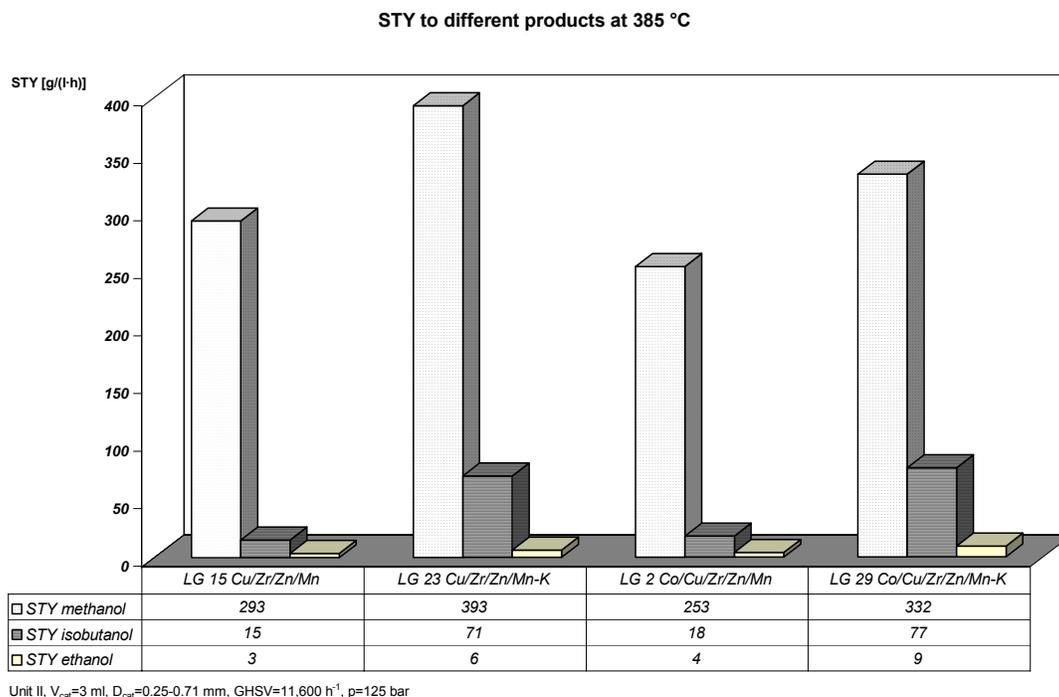
Figure 3.3.1 Influence of Potassium Promotion for Two Zr/Zn/Mn/K-Oxide Catalysts

Influence of Copper on Higher Alcohol Synthesis

The activating influence of copper on carbon monoxide hydrogenation is well known. Various copper-containing methanol and higher alcohols catalysts are described in the literature. In our search for ways of activating the Zr/Zn/Mn/K-oxide system, this catalyst was synthesized with varying amounts of copper (Table 3.3.1).

The effect copper exhibits on methanol production over the Zr/Zn/Mn/K-oxide catalyst is as shown in Figure 3.3.2. Without copper, the Zr/Zn/Mn/K-oxide catalyst shows only minor activity. With an additional copper component, methanol production is almost independent of copper concentration, showing only a slight increase with increasing copper concentration.

Influence of copper on methanol production

STY [g/(l·h)]	0 LG 30 Zr/Zn/Mn-K	14 LG 31 Zr/Zn/Mn/Cu-K	25 LG 26 Zr/Zn/Mn/Cu-K	40 LG 32 Zr/Zn/Mn/Cu-K
▣ 350°C-a	262	831	1001	911
▪ 385°C	163	341	376	408
▢ 350°C-b	87	749	767	817

copper [mol%]

Unit II, V_{cat}=3 ml, D_{cat}=0.25-0.71 mm, GHSV=11,600 h^{-1}, p=125 bar
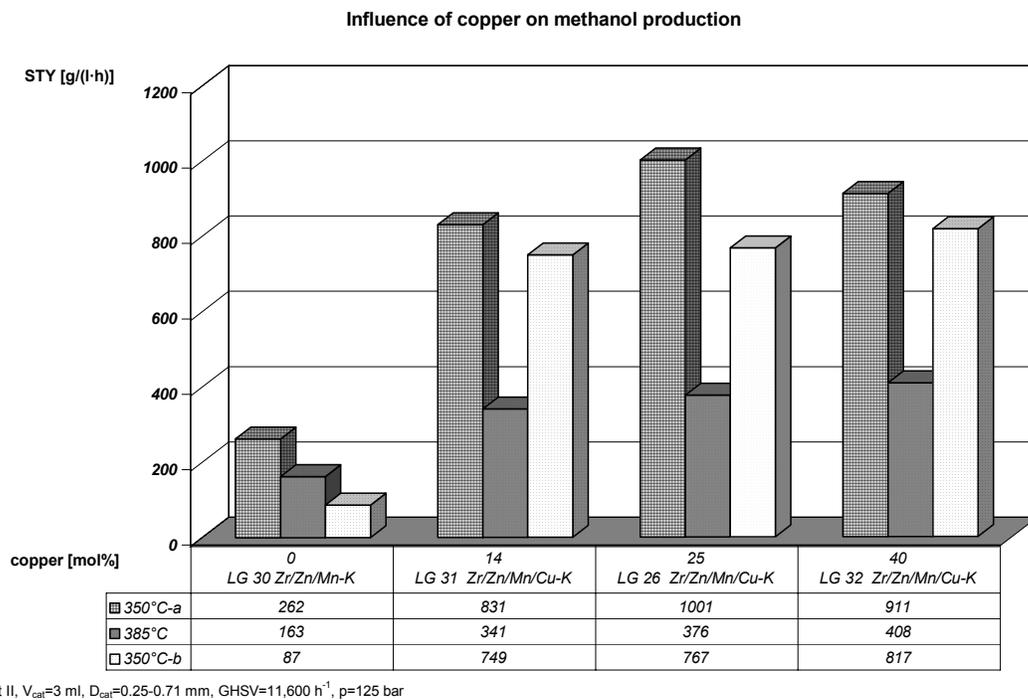
Figure 3.3.2 Influence of Copper on Methanol Production

Copper addition to the Zr/Zn/Mn/K-oxide catalyst has a different effect on higher alcohol synthesis than on methanol synthesis (Figures 3.3.3 and 3.3.4). The rate of methanol production is thermodynamically controlled, whereas the rate of production of linear alcohols, ethanol and propanol is kinetically controlled. Copper addition leads to a sharp increase in methanol and all branched products, whereas ethanol concentration does not increase as sharply because as an intermediate, it is further reacted.

With very high copper content (40 mol % in LG 32), less ethanol is produced at higher temperatures. With this catalyst, at 385°C, less isobutanol is produced compared to the measurement at 350°C. At the lower temperature, an increasing copper concentration leads to an increased yield of all higher alcohols.

The second measurement at 350°C shows improved results towards isobutanol, but again only for the lower copper concentrations. With the equimolar Zr/Zn/Mn/Cu/K-oxide catalyst, an isobutanol STY of 77 g/(l_{cat}·h) is reached at this temperature. The changes that Zr/Zn/Mn/K-oxide catalysts undergo when exposed to syngas under our reaction conditions have also been reported by Vanderspurt et al. (U.S. Patent 5.707.920 **1998**) and were confirmed by our experiment with a coprecipitated Zr/Zn/Mn/K-oxide catalyst (Figure 3.3.5). Methanol production remains nearly constant over the observed reaction time, whereas activity as well as productivity toward the higher alcohols, especially isobutanol, increases with time on stream.

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Influence of copper on ethanol production

copper [mol%]	0 LG 30 Zr/Zn/Mn-K	14 LG 31 Zr/Zn/Mn/Cu-K	25 LG 26 Zr/Zn/Mn/Cu-K	40 LG 32 Zr/Zn/Mn/Cu-K
350°C-a	6	8	11	20
385°C	10	9	16	12
350°C-b	6	10	15	14
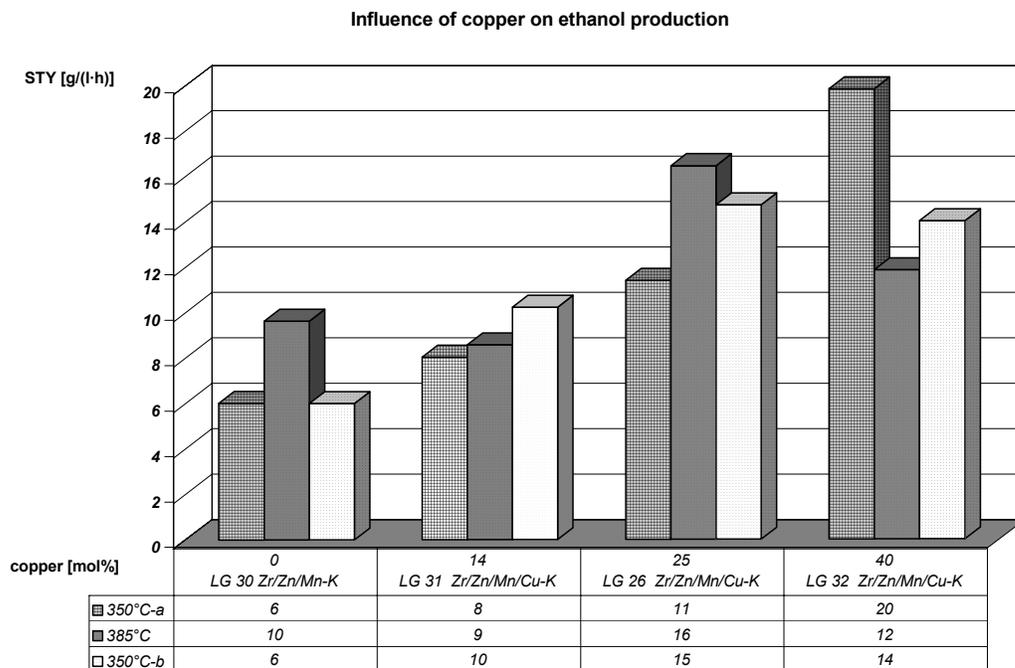
Unit II, V_{cat}=3 ml, D_{cat}=0.25-0.71 mm, GHSV=11,600 h^{-1}, p=125 bar

Figure 3.3.3 Influence of Copper on Ethanol Production

Influence of copper on isobutanol production

copper [mol%]	0 LG 30 Zr/Zn/Mn-K	14 LG 31 Zr/Zn/Mn/Cu-K	25 LG 26 Zr/Zn/Mn/Cu-K	40 LG 32 Zr/Zn/Mn/Cu-K
350°C-a	9	32	42	66
385°C	19	80	92	47
350°C-b	8	69	77	48
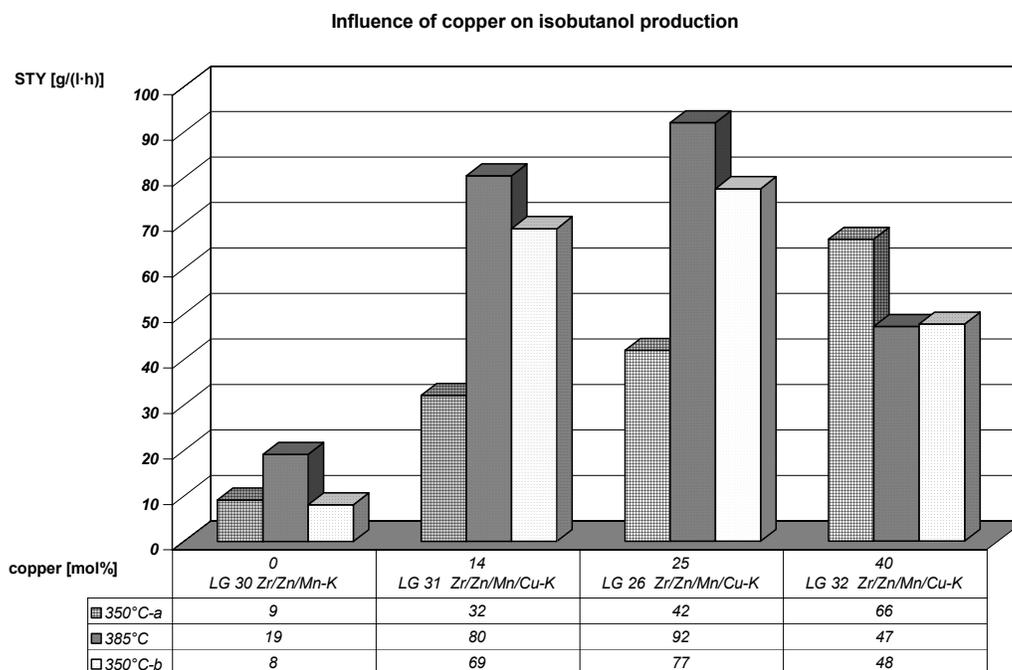
Unit II, V_{cat}=3 ml, D_{cat}=0.25-0.71 mm, GHSV=11,600 h^{-1}, p=125 bar

Figure 3.3.4 Influence of Copper on Isobutanol Production

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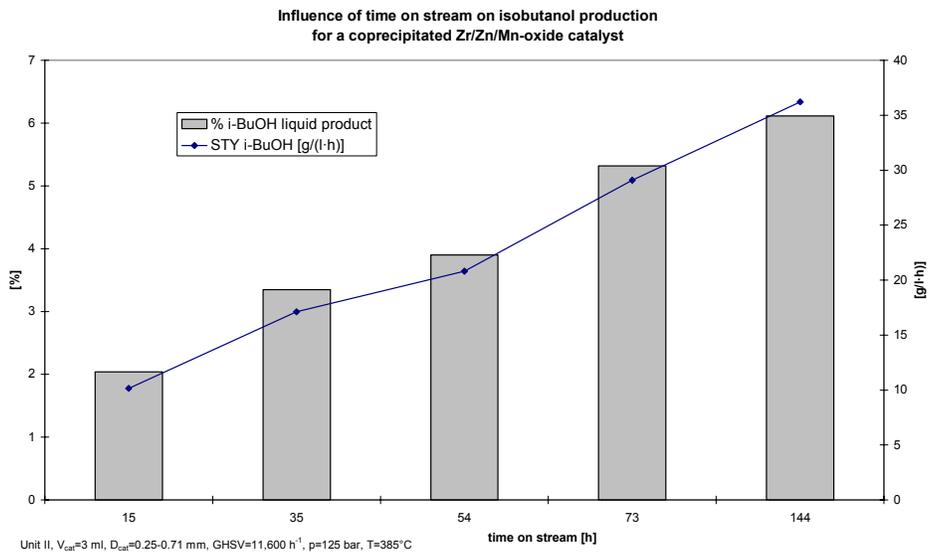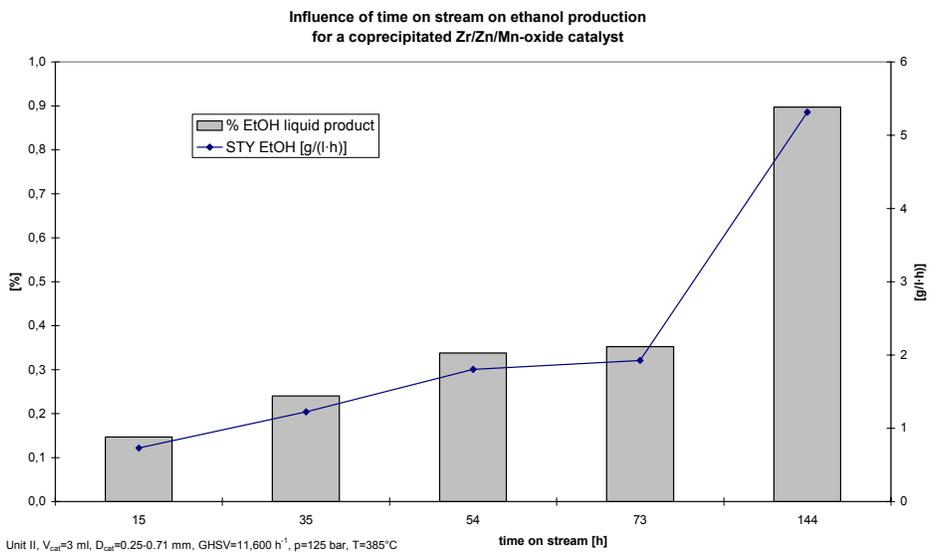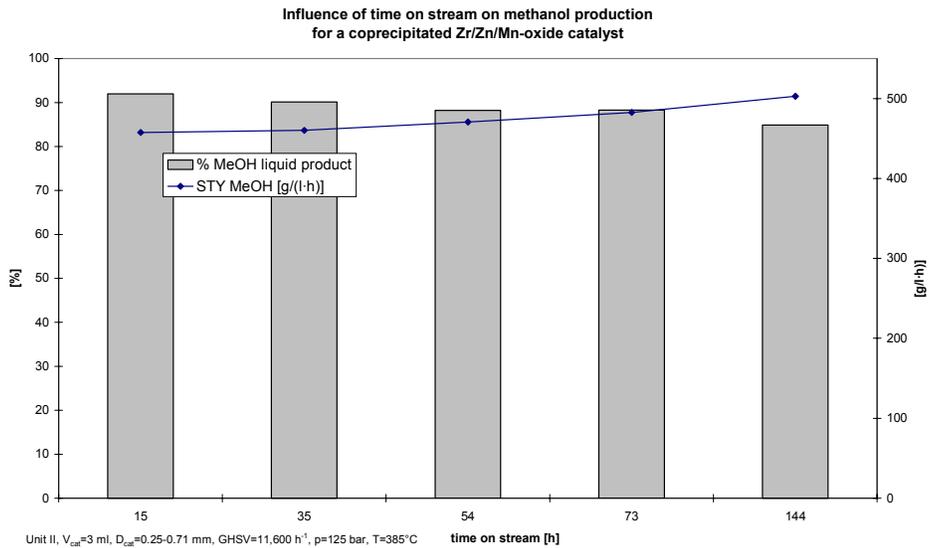
Figure 3.3.5 Influence of Time on Stream for a Coprecipitated Zr/Zn/Mn/K-Oxide Catalyst for Different Products

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Influence of Cobalt on Higher Alcohol Synthesis

Cobalt has little effect on higher alcohol production with the Zr/Zn/Mn/K-oxide catalyst (Table 3.3.3). However, cobalt does increase the selectivity to isobutanol.

Table 3.3.3 Influence of Cobalt on STY to Different Products

STY [g/($l_{cat} \cdot$h)]	LG 23 Zr/Zn/Mn/Cu-K	LG 24-1 Zr/Zn/Mn/Cu-Co-K	LG 24-2 Zr/Zn/Mn/Cu-Co-K	LG 29 Co/Zr/Zn/Mn/Cu-K
350°C				
Methanol	855	911	685	483
Ethanol	4	6	5	6
Isobutanol	30	39	22	24
385°C				
Methanol	393	329	243	332
Ethanol	6	8	7	9
Isobutanol	71	72	65	77

Unit II, V_{cat}=3 ml, D_{cat}=0.25-0.71 mm, GHSV=11,600 h^{-1}, p=125 bar

Influence of Palladium on Higher Alcohol Synthesis

The influence of an additional palladium component on higher alcohol synthesis over a copper-containing Zr/Zn/Mn/K-oxide catalyst has also been investigated. It was found that activity towards isobutanol at the lower temperature is significantly enhanced by promotion of the catalyst with 0.25 wt % of palladium. At both reaction conditions, selectivity towards isobutanol is improved, paralleling the decrease in methanol activity (Table 3.3.4). The different influence exhibited by copper and palladium on higher alcohol synthesis will be further investigated.

Table 3.3.4 Influence of Palladium on STY to Different Products

STY [g/($l_{cat} \cdot$h)]	LG 23 Zr/Zn/Mn/Cu-K	LG 27 Zr/Zn/Mn/Cu-Pd-K
350 C-a		
methanol	855	742
ethanol	4	8
isobutanol	30	48
385°C		
methanol	393	319
ethanol	6	9
isobutanol	71	72

Unit II, V_{cat}=3 ml, D_{cat}=0.25-0.71 mm, GHSV=11,600 h^{-1}, p=125 bar

TASK 5: PROJECT MANAGEMENT

5.1 Liquid Phase Fischer-Tropsch Demonstration

B. L. Bhatt co-chaired a session on C1-Chemistry and presented a paper entitled "Slurry Phase Fischer-Tropsch Synthesis Process Development" at the 15th Annual International Pittsburgh Coal Conference on 14-18 September 1998. The paper discussed the evolution of the F-T technology through the four LaPorte runs, with a focus on details from F-T I and II. Key issues such as catalyst-wax separation, reactor productivity improvements, reactor temperature control, and in-situ catalyst activation were addressed. The paper was well received and generated significant interest.