

ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS

Draft

Technical Progress Report No. 17

For the Period 1 October - 31 December 1998

Contractor

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Alternative Fuels and Chemicals from Synthesis Gas

Technical Progress Report

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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 - no activity this quarter

TASK 3: RESEARCH AND DEVELOPMENT

3.1 Improved Processes for DME

3.1.1 Improving DME Catalyst Activity

- Our experiments showed that the correlation between catalyst stability and reactor gas composition established for the dual catalyst system containing AlPO_4 also applies to the dual catalyst system containing a commercial dehydration catalyst (referred to hereafter as *commercial catalyst system*).
- Stable LPDMETM operation can be obtained with the commercial catalyst system by operating under stable conditions. However, there is a 10-20% trade-off in productivity with a shift from optimal conditions to stable conditions.
- Five conditions in our preliminary plan for the LaPorte LPDMETM trial have been tested in 300-cc laboratory autoclaves using the commercial catalyst system. Four showed acceptable productivity and stability, and one exhibited unacceptable stability.
- More rapid catalyst deactivation was observed with the commercial catalyst system when the catalyst loading in the slurry was tripled. The cause is being investigated.

3.1.2 Understanding Liquid Phase Processes

- The viscosity of the slurry samples collected before and after the sudden decrease in gas holdup in the Kingsport LPMEOHTM reactor on 28 June was analyzed. The results showed

that the decrease in gas holdup was not accompanied by an increase in slurry viscosity. Therefore, the gas holdup change cannot be explained by the slurry viscosity.

- Analysis of catalyst samples from the Kingsport LPMEOH™ reactor implicates arsenic as the primary cause of catalyst activity loss in the current run. From 40 days into the run, there has been a fairly steady accumulation of arsenic and sulfur on the catalyst. The rate of arsenic accumulation has been 3-4 times greater than that of sulfur. Figures 3.1.1 and 3.1.2 show a strong correlation between the amount of arsenic present on the catalyst and the amount of activity lost. Figure 3.1.1 presents both the catalyst activity (η) and the amount of arsenic present on the catalyst as a function of time. Figure 3.1.2 correlates the activity with arsenic loading. It is especially striking that not only is there a general trend, but that even the smaller fluctuations in arsenic level on the catalyst correlate with changes in η . Although the sulfur and iron levels have also increased fairly steadily over the course of the run, the fluctuations in concentration of these compounds have not been reflected in changes in catalyst activity.
- The average copper crystallite size in the catalyst samples from the Kingsport LPMEOH™ plant had grown as large as 400Å until recent additions of fresh catalyst brought this value down to 330Å. These crystallite sizes are significantly greater than the maximum of 290Å measured during the first Kingsport run, yet the total activity loss in the present run is smaller. It is probable that this average dimension does not truly represent the condition of the catalyst. There is certainly a distribution of crystallite sizes in the reactor due to the addition of many batches of fresh catalyst over the past six months. We are obtaining STEM images of the catalyst to assess the true condition of the copper crystallites.
- Our physical characterization of potential methanol catalysts for LPMEOH™ and LPDME™ processes is almost complete. Although commercial, pelletized methanol catalysts have similar physical properties, the precursor powders we are testing vary widely. As shown in Table 3.1.1, the viscosity of 30 wt % slurries in Drakeol-10 at 25°C varied over two orders of magnitude. Based on this initial screening, we plan activity and stability tests of Catalyst B this coming quarter.

Table 3.1.1 Physical Properties of Potential Methanol Catalysts

Catalyst	Bulk Density (g/cc)	BET Surface Area (m ² /g)	Pore Volume (cc/g)	Slurry Density (g/cc)	Slurry Viscosity (cP)
Standard	1.09	66	0.23	1.117	87
Catalyst A	0.69			1.098	171
Catalyst B	0.77	56	0.29	1.134	47
Catalyst C	0.51	102	0.43	1.091	4526
Catalyst D	0.65	110	0.44	Pending	Pending

3.1.3 Scaleup of Aluminum Phosphates for an LPDME™ Trial at LaPorte

- Work was suspended on aluminum phosphate scaleup because we identified a commercially available, less expensive catalyst with equivalent performance. At the time of this decision,

we had qualified two of the original eight batches from our scaleup partner as acceptable for use in the LaPorte LPDME™ trial. We had also demonstrated that our partner's calcination equipment produced acceptable catalyst. Of the remaining six batches, only one was tested in an LPDME™ experiment. Its performance was unacceptable; the methanol catalyst deactivated more rapidly when this batch of aluminum phosphate was present. The problem with these 500-gallon batches is associated with poor control of Al:P ratio in the precipitate. No such composition problem was encountered either in the laboratory preps or in our partner's 30-gallon preps. Our scaleup partner prepared two additional batches with which they tried to improve the reproducibility of the precipitation by using more dilute solutions and limiting the total amount of base addition. However, this did not improve the control of the Al:P ratio, and the sample we tested performed poorly in the lab.

Figure 3.1.1 Catalyst Activity (Eta) and Arsenic Loading During the Present Kingsport LPMEOH™ Run

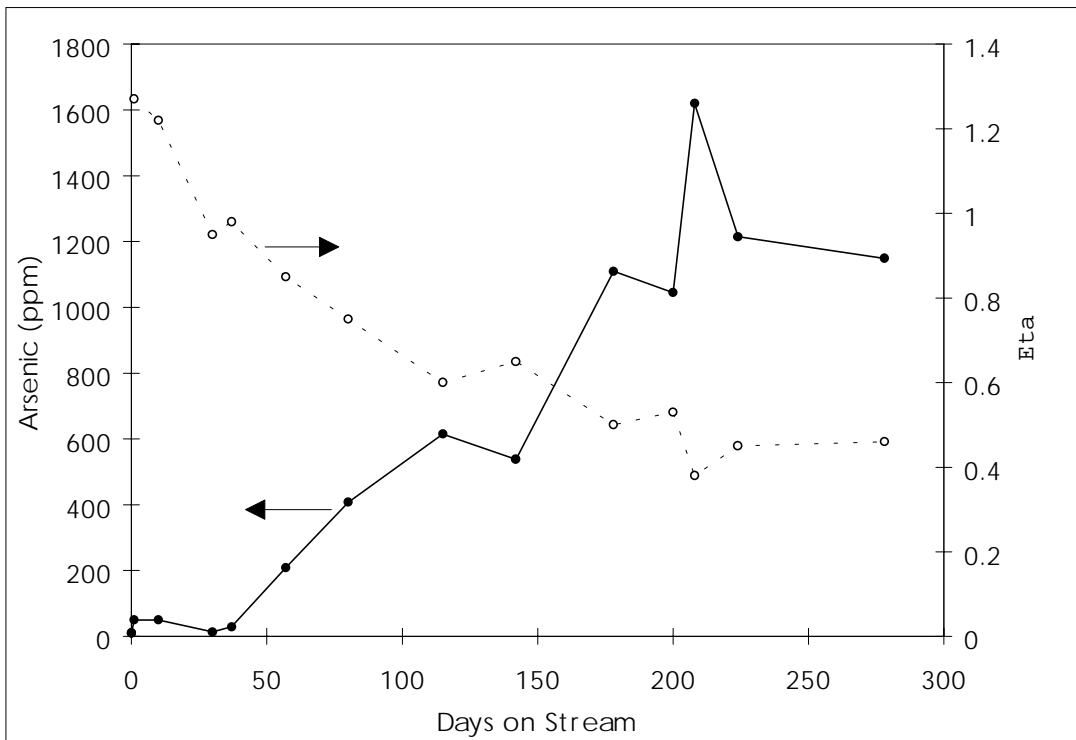
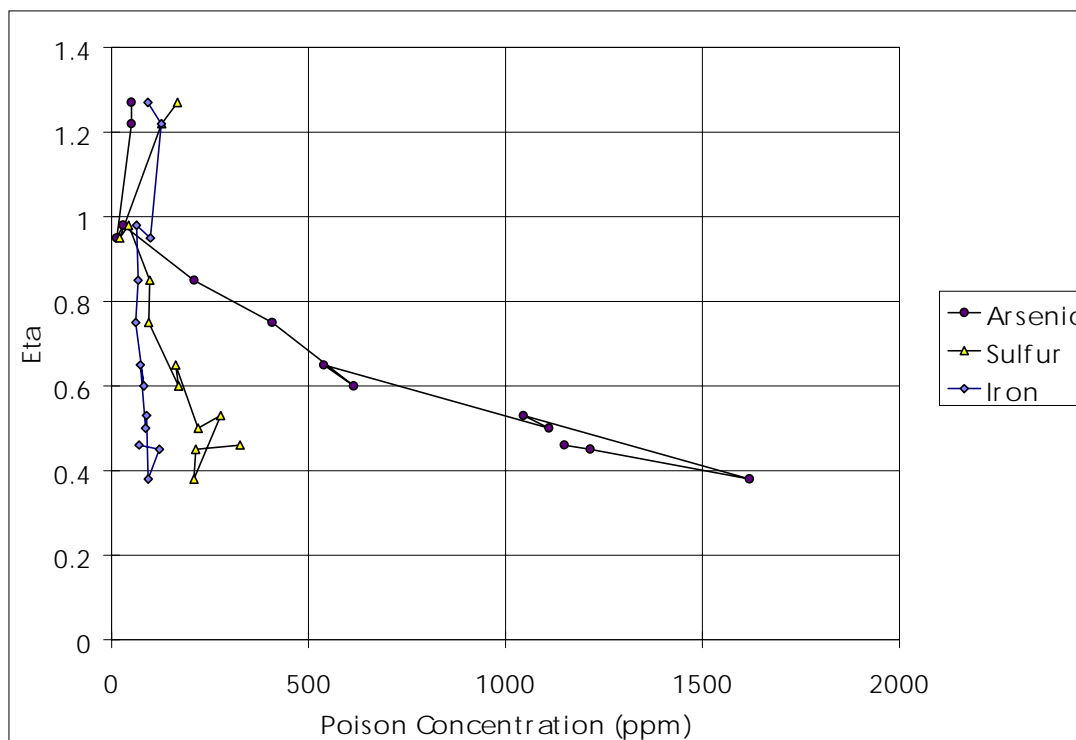


Figure 3.1.2 Correlation of Catalyst Activity (Eta) with Loading of Various Poisons



3.1.4 Miscellaneous Activities

- A patent application, entitled “Single Step Synthesis Gas-to-Dimethyl Ether Process with Methanol Introduction,” was filed in December 1998. The authors are X. D. Peng, A. W. Wang and B. A. Toseland.

TASK 3.2 New Fuels from Dimethyl Ether (DME)

3.2.1 Overall 1QF99 Objectives

The following objective appeared in Section III of the previous Quarterly Technical Progress Report No. 16:

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

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 evaluation - high-pressure test apparatus (BTRS). Results obtained for the SnO₂/MgO catalyst as a function of reactor temperature and pressure are listed in Table 3.2.1. The same catalyst sample was used for all runs. By GC analysis, the feed gas consisted of 72.6 mol % DME and 4.7 mol % O₂; the balance was N₂. The feed was generated using a liquid DME pumping rate of 10.0 mL/hr and an air flow of 20 sccm. Assignments of products are based on GC retention times and require confirmation via GCMS. In addition to the identified species list below, numerous unidentified peaks of relatively low area were observed for each run. For most runs, CO₂ balances were 50-60%. The sum of the unknown species is probably not sufficient to account for the missing C; rather, the discrepancy can be attributed to material not yet identified. When all temperature/pressure combinations were completed, data were recollected at 275°C and 750 psig (labeled “1st” and “2nd” in table). Note that product selectivities and DME conversions were quite similar for the two runs at 275°C and 750 psig, suggesting that no major change in the catalyst occurred over the course of the study. The selectivities for monoglyme are different from the literature results. The large selectivity for methyl formate is surprising. Experiments are continuing at higher feed O₂ concentrations.

**Table 3.2.1 Results for High-Pressure Runs Involving SnO₂/MgO Catalyst
Feed: 72.6 mol % DME, 4.7 mol % O₂, 22.7 mol % N₂.**

T, °C P (psig)	250 300	250 500	250 750	275 300	275 500	1st	2nd	300 300	300 500	300 750
						275 750	275 750			
DME conv. (%)	6.76	5.37	19.47	8.06	9.97	9.70	10.31	11.14	12.75	12.59
C balance (%)	69.0	82.6	30.0	60.2	54.1	59.5	57.3	52.3	48.0	51.8
O ₂ conv. (%)	100.0	100.0	99.4	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Product selectivity (%C)*										
CO	0.000	0.000	0.82	17.95	15.38	12.03	12.04	18.05	16.06	13.65
CO ₂	13.66	9.497	10.273	12.82	10.97	10.66	9.550	12.70	12.89	13.50
CH ₄	4.802	2.250	0.439	1.256	1.461	1.187	1.390	3.512	3.280	2.791
ethylene	0.111	0.000	0.000	0.063	0.057	0.000	0.000	0.128	0.095	0.068
ethane	00.256	0.000	0.000	0.000	0.000	0.000	0.000	0.056	0.000	0.000
propane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
methanol	11.34	8.704	8.615	8.532	9.095	9.685	10.10	9.881	10.61	11.77
methyl formate	60.46	72.58	65.571	54.91	57.10	60.60	60.21	47.61	48.73	50.79
methyl ethyl ether	4.671	2.029	0.000	0.804	0.627	0.362	0.466	1.692	1.036	0.637
ethanol (to be verified)	0.875	0.977	0.546	0.845	1.454	1.421	1.677	1.876	2.449	2.361
diethyl ether	0.000	0.000	0.306	0.122	0.238	0.372	0.479	0.246	0.402	0.574
dimethoxymethane	0.596	0.332	0.592	0.430	0.524	0.705	0.652	0.371	0.487	0.651
2-methoxyethanol	0.276	0.358	0.371	0.267	0.514	0.688	0.884	0.506	0.764	0.937
monoglyme	2.837	2.881	0.945	1.665	2.125	1.764	2.157	3.112	2.933	2.316
ethylene glycol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
DEGME**	0.123	0.389	0.245	0.336	0.453	0.532	0.398	0.000	0.000	0.000
diglyme	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.254	0.270	0.000
triglyme	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00	0.000	0.000

*Product selectivities based on quantities of identified products.

**DEGME = diethylene glycol methyl ether, CH₃OCH₂CH₂OCH₂CH₂OH

With the same sample of catalyst, evaluation of SnO₂/MgO using the BTRS was continued. Data were collected at a higher feed O₂ concentration (8.75 mol % vs. 4.7 mol % previously) and a feed pressure of 500 psig. Results at 250, 275, and 300°C are listed in Table 3.2.2, along with data at lower feed O₂ concentrations for comparison. Data at 275°C for the “high” O₂ feed are suspect. As stated above, product assignments are based on GC retention times and require confirmation via GCMS. In addition to the identified species list below, numerous unidentified peaks of relatively low area were observed for each run.

Some general conclusions about higher feed O₂ concentration are: (1) higher DME conversions (2) higher conversion to CO and CO₂ and (3) lower conversion to monoglyme and methyl formate; higher conversion to dimethoxymethane. The use of higher feed O₂ concentrations would appear to offer no advantage.

**Table 3.3.2 Current Results for High-Pressure Runs Involving SnO₂/MgO Catalyst
DME/O₂ =6.5 Compared with Previous Run Using DME/O₂ = 15.4
“High” O₂ feed: 57.0 mol % DME, 8.75 mol % O₂, 34.2 mol % N₂; DME/O₂ = 6.5
“Low” O₂ feed: 72.6 mol % DME, 4.7 mol % O₂, 22.7 mol % N₂; DME/O₂ = 15.4**

	High O ₂ feed			Low O ₂ feed			
	T, °C P (psig)	250 500	275 500	300 500	250 500	275 500	300 500
DME conv. (%)		16.22	32.55	50.61	5.37	9.97	12.75
C balance (%)		63.8	47.7	28.70	82.6	54.1	48.0
O ₂ conv. (%)		100.0	100.0	100.0	100.0	100.0	100.0
Product selectivity (%C)*							
CO		0.000	43.22	24.36	0.000	15.38	16.06
CO ₂		15.48	11.03	19.18	9.497	10.97	12.89
CH ₄		4.047	21.17	3.438	2.250	1.461	3.280
ethylene		0.086	0.885	0.082	0.000	0.057	0.095
ethane		0.165	0.000	0.162	0.000	0.000	0.000
propane		0.000	0.000	0.000	0.000	0.000	0.000
methanol		10.44	5.003	8.334	8.704	9.095	10.61
methyl formate		61.68	15.78	39.13	72.58	57.10	48.73
methyl ethyl ether		3.094	1.218	1.097	2.029	0.627	1.036
ethanol (to be verified)		0.688	0.488	0.749	0.977	1.454	2.449
diethyl ether		0.701	0.156	0.878	0.000	0.238	0.402
dimethoxymethane		1.118	0.421	0.792	0.332	0.524	0.487
2-methoxyethanol		0.366	0.138	0.485	0.358	0.514	0.764
monoglyme		1.933	0.350	1.326	2.881	2.125	2.933
ethylene glycol		0.000	0.000	0.000	0.000	0.000	0.000
DEGME**		0.195	0.143	0.000	0.389	0.453	0.000
diglyme		0.000	0.000	0.000	0.000	0.000	0.270
triglyme		0.000	0.000	0.000	0.000	0.000	0.000

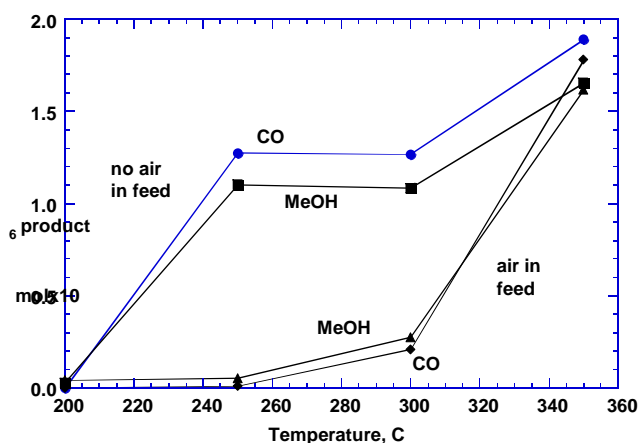
*Product selectivities based on quantities of identified products

**DEGME = diethylene glycol methyl ether, CH₃OCH₂CH₂OCH₂CH₂OH

Methyl formate stability. The large quantities of methyl formate produced in our high-pressure DME/O₂ runs led us to evaluate the stability of methyl formate under reaction conditions. A feed

consisting of methyl formate in N₂ or in N₂ and air was passed over SnO₂/MgO at 20 psig. Gaseous methyl formate was obtained by pumping liquid methyl formate, 4.2 mL/hr, into a heated coil of tubing where it was vaporized. In the *absence* of air, most of the methyl formate decomposed at 250°C or higher. The major products were near equimolar quantities of CO and methanol (HCO₂CH₃ = CH₃OH + CO). Much smaller quantities of CO₂, DME, 2-methoxyethanol, monoglyme, and one unknown were observed. In the *presence* of O₂, much less methyl formate reacted at temperatures below 350°C, but essentially the same products were observed. Figure 3.2.1 shows that in the *absence* of O₂, much larger quantities of MeOH and CO were generated at 300°C or below. Evidently, O₂ blocks catalyst sites that are active for methyl formate decomposition.

Figure 3.2.1
Methy Formate Decomposition Products



Reagent methyl formate actually contains about 0.9 mol % MeOH and 0.1 mol % 2-methoxyethanol and a trace of the unknown species at 13.1 min (Table 3.2.3.). A mass spectrum indicates a molecular weight of 121 or 104 for the unknown. Based on retention times of known substances, it is not methyl methoxyacetate (MW 104).

Table 3.2.3 Stability of Methyl Formate over SnO₂/MgO in the Presence and Absence of O₂.

Feed with no O₂: 49.1 sccm N₂, 25.2 sccm methyl formate (33.9 mol %)
Feed with O₂: 25.0 sccm N₂; 23.9 sccm air, 25.2 sccm methyl formate (34.0 mol %)
20 psig feed; 0.698 g (1 cc) catalyst

Products	mmol of product							
	Feed without O ₂				Feed with O ₂			
	200°C	250°C	300°C	350°C	200°C	250°C	300°C	350°C
CO	-	1.275	1.268	1.890	-	0.0102	0.2082	1.780
CH ₄	--	-	-	0.0009	-	-	-	-
CO ₂	-	0.0070	0.0086	0.0116	0.0036	0.0072	0.0348	0.1169
DME	-	0	0.0009	0.0028	-	-	0.0004	0.0011
MeOH	0.0270	1.102	1.083	1.655	0.0420	0.0523	0.2744	1.616
EtOH	-	-	-	0.0001	-	-	-	0.0001
dimethoxymethane	-	-	-	0.0003	-	-	-	-
2-methoxy-ethanol	0.0013	0.0084	0.0092	0.0093	0.0014	0.0013	0.0045	0.0119
monoglyme	0.0003	-	0.0004	0.0004	0.0003	0.0004	0.0005	0.0004
unknown 13.1 min ^a	0.0134	0.0007	0.0013	0.0004	0.0146	0.0137	0.0132	0.0017
unknown 16.1 min ^b	-	-	-	0.0004	-	-	-	-
% conv. Mefor..	19.0	76.4	70.1	83.3	low ^c	low ^c	low ^c	64.7
% conv. O ₂	-	-	-	-	4.6	17.8	32.3	51.2

a. response factor taken to be 3×10^{-7} mmol/area

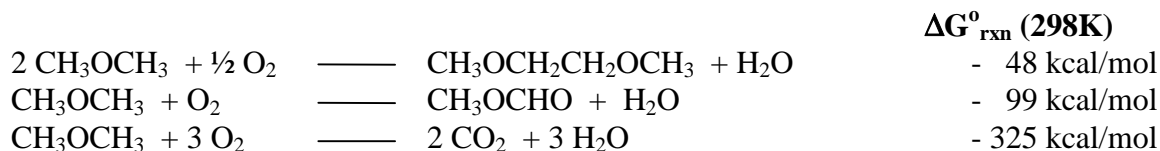
b. response factor taken to be 2×10^{-7} mmol/area

c. % conversion based on difference in calculated initial concentration and GC concentration after reaction.

Low means that a negative conversion was obtained.

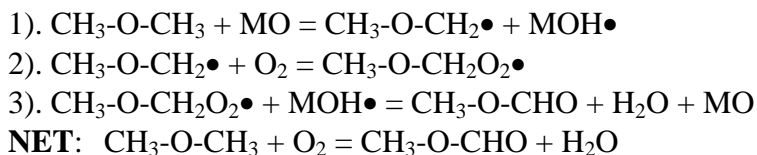
Thermodynamics and mechanism. In addition to a few catalysts that produce small quantities of coupled products such as monoglyme and dimethoxymethane, several of the catalysts over the past months have produced CO₂, CO, MeOH, Mefor (methyl formate) and CH₄ in varying selectivity. More recently a high-pressure study using SnO₂/MgO catalyst in the BTRS at 300°C and 275 psig gave Mefor selectivity as high as 58%.

A comparison of the thermodynamics ($\Delta G^{\circ}_{\text{rxn}}$ (298K)) for the reactions to monoglyme, Mefor and CO₂ is shown below:



Like the reactions to form deep oxidation products, i.e., CO₂, this reaction to MeFor, with a large equilibrium constant, is a highly favorable one. It was shown earlier that the MeOH + CO reaction to Mefor is very unfavorable at the low CO pressures measured and at the elevated temperatures of interest. However, this direct reaction of the two starting materials is the likely source of Mefor. Thus, in addition to deep oxidation products, the reaction to Mefor must also be eliminated or minimized if high selectivity to coupled products is to be achieved. It is an interesting fallout of this work, however, affording an alternate route to Mefor.

Most of the materials studied are oxidation catalysts. In the presence of an activated O₂ molecule and certain oxide surfaces, the following 3-step radical chemistry -- modified from atmospheric chemistry -- can be used to describe the formation of Mefor:



While this may not be in perfect sync with the atmospheric chemistry, i.e., photo-initiation, it recognizes the possible role of a catalyst.

The abstraction of “H” is obviously desirable for this mechanism, but it is the subsequent reaction of the CH₃-O-CH₂• radical with O₂ molecule, a radical scavenger, which must be avoided. It is not known at this time whether the O₂ molecule is surface activated or gaseous. However, assuming formation of a DME radical that, upon collision with a DME molecule or O₂ molecule, gives either coupling products or oxidation products, respectively, selectivity estimates from kinetic theory can be made for the formation of monoglyme vs Mefor. Thus, the following can be shown:

Product	Selectivity Estimates, %	
	Gas Phase	Surface
monoglyme	74.6	80.7
Mefor	25.4	19.3

These estimates are based solely on the collision frequency of the various molecules at 300°C and their respective concentrations. If one admits that O₂ is a more efficient radical scavenger than DME, then the Mefor selectivity above is a lower kinetic limit since radical chemistry can be inherently non-selective. This study indicates that a high selectivity to monoglyme will be favored if:

1. the DME radical on the surface is scavenged by another DME radical, a process that becomes more feasible at elevated pressure by increasing its surface concentration relative to O₂. This assumes that the O₂ efficiency does not change or changes very little.
2. a DME/ O₂ ratio of 10/1 vs 5/1 is used.
3. the conversion of an adsorbed O₂ molecule to an oxide anion of the lattice is rapid (instantaneous) relative to its reaction with a DME radical.

2. *CETANER™ Properties*

Reagent purity. To avoid unexpected results and to strive for completeness, the purity of reagents used for cetane number testing and aging studies was examined by GC. Results are summarized in Table 3.2.4. Triglyme and triethylene glycol methyl ether (TEGME) also contained numerous unidentified contaminants.

Table 3.2.4 Purity of Glymes and Their Alcohols by GC

Substance	Aldrich purity	Est. purity by GC*	Identified contaminants (highest to lowest conc.)
Monoglyme	99.9	98.7/98.0	MeOH, DEGME, triglyme, 2MEtOH
Diglyme	99	99.3/-	2MEtOH, DEGME, MeOH, TEGME, triglyme
Triglyme	99	98.4/-	2MEtOH, MeOH, DEGME, TEGME, EG, monoglyme
2-methoxy ethanol	99.9+	>99.9/-	DEGME, monoglyme, TEGME, triglyme
DEGME	99	99.8/99.7	MeOH, TEGME
TEGME	95	97.3	diglyme, DEGME, 2MEtOH, MeOH

* purity by GC: 1st value - total GC counts. 2nd value - based on amount of identified contaminants.

Fuel miscibility. The diesel fuel miscibility of the alcohols that are expected by-products of DME oxidative coupling, methanol, 2-methoxyethanol, and DEGME (diethylene glycol methyl ether, or $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$) were examined. At 9.8 wt % MeOH, 11.9 wt % 2-methoxyethanol, or 10.0 wt % DEGME, all alcohol/diesel fuel mixtures were two phases. Some components of the diesel fuel were apparently extracted into the alcohol layer, since each alcohol layer acquired a yellow color.

Aging study. A series of samples (Table 3.2.5) was prepared to evaluate the stability of monoglyme and diglyme in diesel fuel, particularly with regard to hydrolysis. Hexadecane ($\text{C}_{16}\text{H}_{34}$, also called cetane) was used in place of diesel fuel to permit GC analysis of potential products. Diesel fuel itself is a mixture of >200 species by GC, making detection of additional species formed almost impossible. To each glyme/hexadecane solution was added a trace of water, which caused no phase separation, or a larger volume of water, which yielded two phases. Each sample was analyzed by GC (Table 3.2.6). For samples consisting of two phases, both the organic and aqueous phases were analyzed. Only two unknowns were detected, one at 4.85 min that resulted from an impurity in hexadecane and another at 25.9 min, resulting from an impurity in diglyme. Notice that much of the monoglyme and diglyme was extracted into the aqueous phase for samples containing two phases. Each sample was transferred to stainless steel cylinders and sealed. Analysis at three-week intervals is planned.

Table 3.2.5 Compositions of Samples for Aging Study

Sample	Vol %/mole fraction			% added water*	# phases
	hexadecane	monoglyme	diglyme		
1	85/0.668	15/0.332	-	0.017	1
2	85/0.668	15/0.332	-	10	2
3	85/0.735	-	15/0.265	0.017	1
4	85/0.735	-	15/0.265	10	2
5	70/0.453	30/0.547	-	0.017	1
6	70/0.453	30/0.547	-	10	2
7	70/0.533	-	30/0.467	0.017	1
8	70/0.533	-	30/0.467	10	2
9	100	-	-	0.017	1
10	100	-	-	10	2

* volume % added water based on organic volume

Table 3.2.6 GC Analysis of Aging Samples Immediately after Preparation

Sample	phase	Mole fraction by GC*					
		hexa-decane	mono-glyme	diglyme	MeOH	unknown 4.8 m	unknown 25.9 m
1	organic	0.634	0.359	-	0.0035	0.0036	-
2	organic	0.741	0.254	-	-	0.0051	-
2a	aqueous	8.1x10 ⁻⁵	0.996	-	-	0.0043	-
3	organic	0.699	-	0.296	-	0.0049	-
4	organic	0.876	-	0.113	-	0.0110	-
4a	aqueous	6.9x10 ⁻⁵	-	0.994	-	0.00057	-
5	organic	0.415	0.578	-	0.0028	0.0035	-
6	organic	0.533	0.463	-	-	0.0034	-
6a	aqueous	1.4x10 ⁻⁴	0.996	-	-	0.0037	-
7	organic	0.491	-	0.505	-	0.0042	1.4x10 ⁻⁴
8	organic	0.760	-	0.233	-	0.0065	2.2x10 ⁻⁴
8a	aqueous	1.1x10 ⁻⁴	-	0.995	-	0.0050	1.9x10 ⁻⁴
9	organic	0.979	-	-	0.0053	0.0149	-
10	organic	0.975	-	-	-	0.0250	-
10a	aqueous	0.0348	-	-	-	0.965	-

*based on total organics only; response factors for unknowns were estimated

Peroxide testing. Testing of a series of diesel fuel-CETANER™ blends for peroxide formation was continued. Testing with peroxide test strips continued to show no detectable peroxide concentrations after 8.8 months of storage in D1-size steel cylinders. Testing using the Ti⁴⁺ method described previously seemed to yield peroxide concentrations of 3-5 ppm (Table 3.2.7). However, no discernible peaks were found in the UV/vis corresponding to the Ti⁴⁺ peroxy species. Testing is continuing.

Table 3.2.7 Results for Peroxide Testing of Fuel Blends Stored in Steel Cylinders (MG = monoglyme; DMM = dimethoxymethane; d = days)

Blend	Concentrations, volume %				H ₂ O ₂ conc. in weight ppm after:							
	diesel	MG	DMM	MeOH	0 d	28 d	59 d	89 d	125 d	167 d	202 d	265 d
1	60.0	29.2	9.68	1.16	1.4	1.6	1.5	2.0	1.5	1.9	0	3.7
2	70.0	21.9	7.26	0.87	1.8	3.4	1.2	0	1.5	2.4	3.4	5.3
3	60.0	36.8	1.68	1.56	2.9	1.4	2.3	2.8	1.6	1.9	0	5.2
4	70.0	27.6	1.26	1.17	1.4	0	0	1.8	0	0.9	5.9 ^a	0
5	100	0	0	0	1.1	0	0	2.2	1.3	0.9	0.6	0.9

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

Other blends stored in glass containers also showed no significant concentration of peroxides, as indicated in Table 3.2.8. Testing of each sample with peroxide test strips showed zero levels of peroxide.

The first catalyst examined was La_2O_3 , which is considered a weaker acid catalyst than Al_2O_3 and may not be as aggressive in decomposing the oxygenates. The 2-methoxyethanol liquid was vaporized into a N_2 stream to give an 18.7 mol % concentration of the alcohol. At 250°C and a contact time of 0.9 secs, the conversion was less than 1% and the carbon selectivity of the products was 60% MeOH, 12% CO_2 and 12% unknowns. At 300°C the conversion was 1.2%. CO_2 increased to 50% and small amounts of methylformate and EtOH were observed, all at the expense of MeOH, with unknowns increasing to 15%. At a longer residence time of 1.9 secs, coupling products became evident, with diglyme, DEGME and monoglyme at 9.9%, 7.2% and 1%, respectively, but the unknowns also increased substantially to 30%. The presence of monoglyme implied reaction of MeOH with the feed. No DME was observed. Carbon balances ranged from 1.002 to 1.036.

In view of this result and the earlier results reported, we decided to try a phosphate salt, a catalyst has weak Bronsted acidity, to determine how it would perform.. The results are summarized in Table 3.2.9. At 300°C and a contact time of 4.7 sec, we measured low conversion, and the primary products were CO, methylformate and MeOH, with only a trace of diglyme.

The conversion increased to 3% at 350°C , and methylformate became the primary product at 63%, but coupling products also became evident, along with traces of DME. It was apparent from the presence of ethylene glycol that hydrolysis of 2-methoxyethanol was occurring. Doubling the residence time at 350°C resulted in no apparent change in conversion, implying that some deactivation was occurring, but the total of diglyme, DEGME and monoglyme products was then 15.7%, an encouraging result.

We then decided to add 25 mol % MeOH to the feed to ascertain its impact on product distribution. The conversion of 2-methoxyethanol increased substantially to 19%, and the carbon selectivity of monoglyme based on 2-methoxyethanol increased from 3 to 9.7%. (If it is assumed that one of the four carbons in monoglyme originates from MeOH feed only, the selectivity is 7.2% instead of 9.7%.) The selectivity to diglyme and DEGME decreased, but so did the ethylene glycol and unknowns. The observation of 1,4-dioxane implies that DEG is present on the catalyst surface and readily internally cyclizes.

Returning to a pure 2-methoxyethanol feed at 350°C and the longer contact time of 9.5 secs gave a more reasonable 7% conversion, with selectivities similar to those measured before addition of MeOH. We will explore these observations further and also attempt to examine this catalyst at elevated pressure.

An initial hazards assessment is being conducted to screen acidic resin catalysts in a slurry reactor system. In addition, a GC microreactor is being assembled for rapid screening of catalysts.

3.2.3 2QFY99 Objectives

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

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

Table 3.2.9 Product Distribution for Reaction of 2-Methoxyethanol over Phosphate Catalyst

Temperature	300°C	350°C	350°C	350°C	350°C
Contact Time (secs)	4.7	4.7	9.5	9.0	9.5
Mol. Fraction in Feed					
2MetOH	0.187	0.187	0.187	0.171	0.187
MeOH	0.0	0.0	0.0	0.057	0.0
O ₂	0.0	0.0	0.0	0.0	0.0
N ₂	0.813	0.813	0.813	0.772	0.813
% Conversion					
2MetOH	0.44	3.03	2.42	19.1	7.10
% Carbon Selectivity					
CO	77.33	7.32	0.63	4.41	1.19
CH ₄	0.00	0.00	0.00	0.00	0.00
CO ₂	0.00	5.08	3.14	2.42	2.92
DME	0.00	0.17	0.15	2.67	0.18
MeOH	4.10	6.49	10.40	---	13.51
Methyl formate	16.65	63.25	51.46	59.76	47.93
EtOH	0.00	0.00	0.20	0.05	0.16
DMM	0.00	0.00	0.00	0.00	0.00
DMET	0.00	0.93	2.97	9.72	2.74
HOCH ₂ CH ₂ OH	0.00	1.98	1.24	0.70	0.34
1,4-dioxane	0.0	0.0	0.30	0.33	1.70
DEGME	0.00	4.45	6.06	4.98	4.42
diglyme	1.92	2.29	6.67	3.48	6.33
triglyme	0.00	0.00	0.00	0.00	0.00
Unknowns	0.00	8.04	16.77	11.48	18.57
Carbon Balance	1.004	1.018	0.999	0.919	0.976

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 previous experiments, 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 different components of these catalysts, several copper-containing catalysts were synthesized by precipitation of the nitrates with potassium hydroxide solution (Tables 3.3.1 and 3.3.2). Copper content was varied from 0 up to 73 mol %.

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

Catalyst description	Composition Zr/Zn/Mn/Cu	Copper content mol %
LG 30	1:1:1:0	0
LG 33	1:1:1:0.25	8
LG 31	1:1:1:0.5	14
LG 26	1:1:1:1	25
LG 32	1:1:1:2	40
LG 35	1:1:1:4	57
LG 38	1:1:1:6	67
LG 39	1:1:1:8	73

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

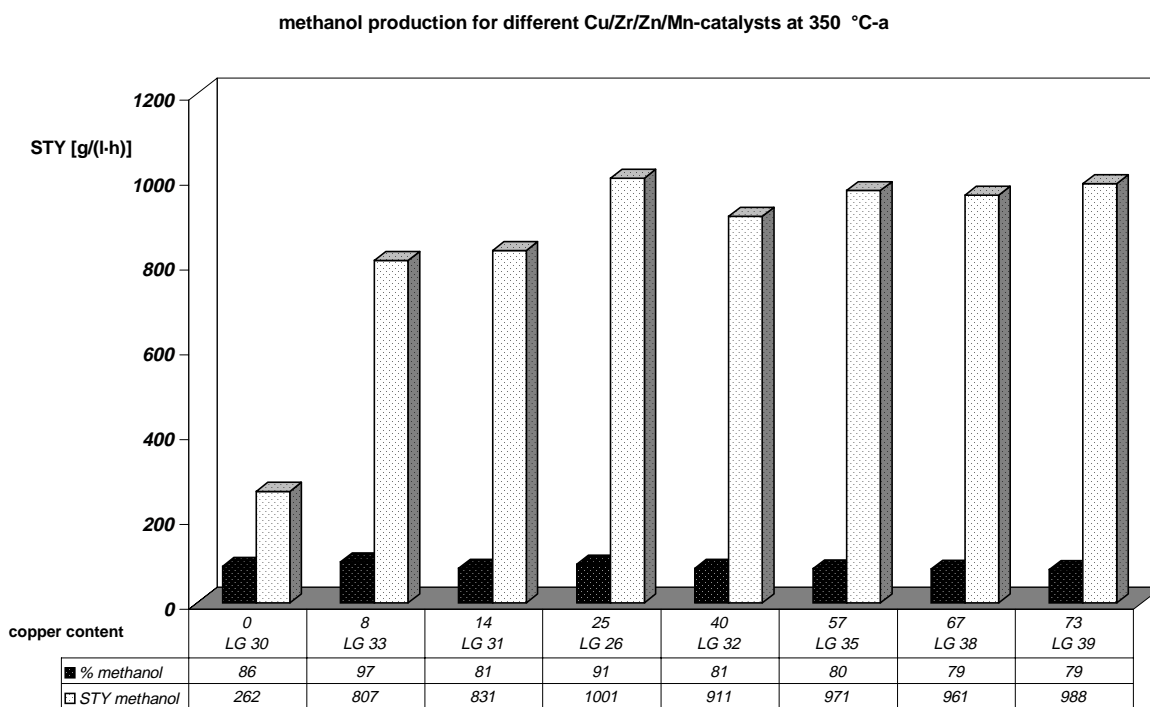
Catalysts	Zr/Zn/Mn/Cu (Co)
Synthesis method	Precipitation (at 333K, until pH = 12) of the nitrates with KOH
Calcination	6 hr at 723K (4K/min)
Reduction	4 hr at 513K (1K/min) with 5% H ₂ in N ₂

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

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 alcohol catalysts are described in the literature.

Figure 3.3.1 Influence of Copper Content on Methanol Production at 350°C



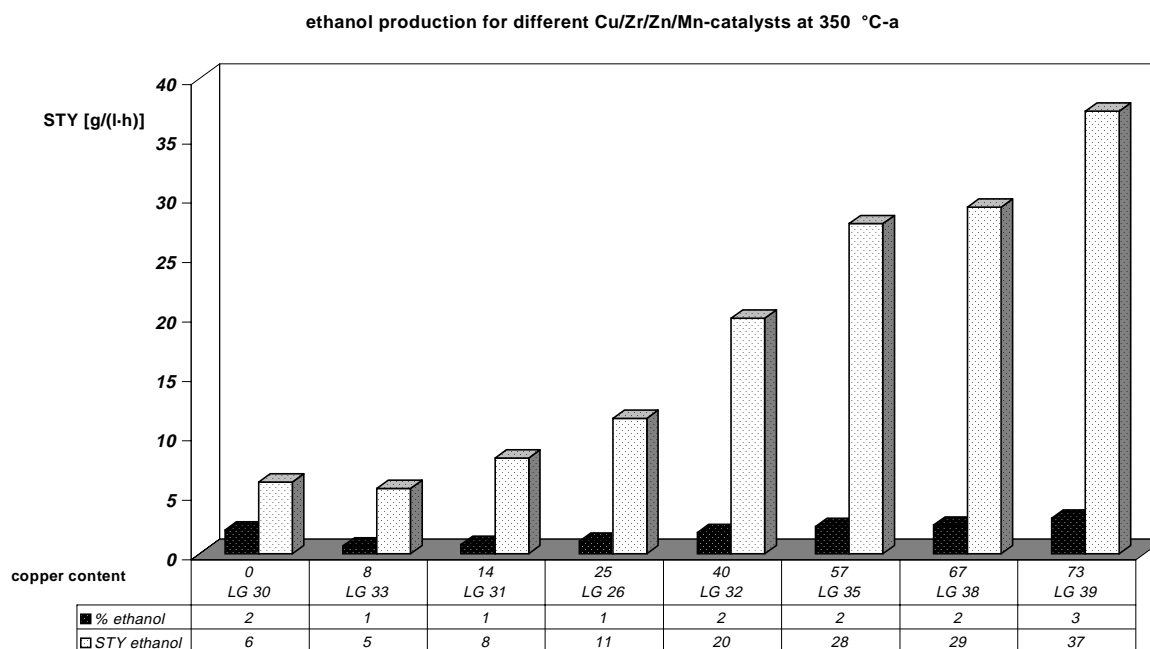
Unit II, $V_{\text{cat}}=3$ ml, $D_{\text{cat}}=0.25-0.71$ mm, $\text{GHSV}=9,000$ h⁻¹, $p=125$ bar

In our studies, the effect of copper on methanol production over the Zr/Zn/Mn/K-oxide catalyst was as expected (Figure 3.3.1). Without copper, the Zr/Zn/Mn/K-oxide catalyst showed only minor activity. With an additional copper component, methanol production approached the thermodynamically limited level and was almost independent of the copper concentration, displaying only a slight increase with increasing copper concentration.

The alcohols ethanol and n-propanol, which, contrary to methanol, are not thermodynamically controlled products, showed a different behavior (Figure 3.3.2). With increasing copper content, ethanol production constantly increased. For isobutanol, a maximum production of 72 g/(l·hr) was obtained at a copper content of 57 mol % (Figure 3.3.3). A higher copper content led to a slight decrease in isobutanol production.

At the higher temperature, methanol again followed thermodynamics and showed a fairly constant value for all copper-containing catalysts (Figure 3.3.4). The negative effect of temperature increase on copper catalysts can be clearly seen by comparing production of the higher alcohols at both temperatures (Figures 3.3.5 and 3.3.6).

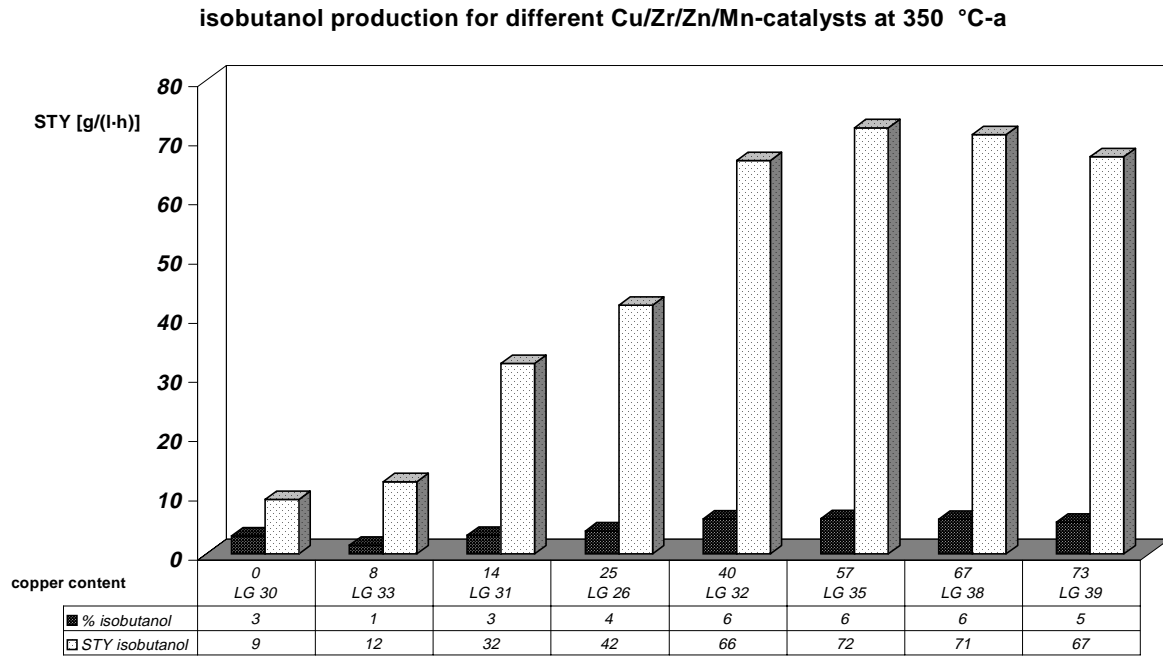
Figure 3.3.2 Influence of Copper Content on Ethanol Production at 350°C



Unit II, $V_{\text{cat}}=3$ ml, $D_{\text{cat}}=0.25\text{-}0.71$ mm, $\text{GHSV}=9,000$ h⁻¹, $p=125$ bar

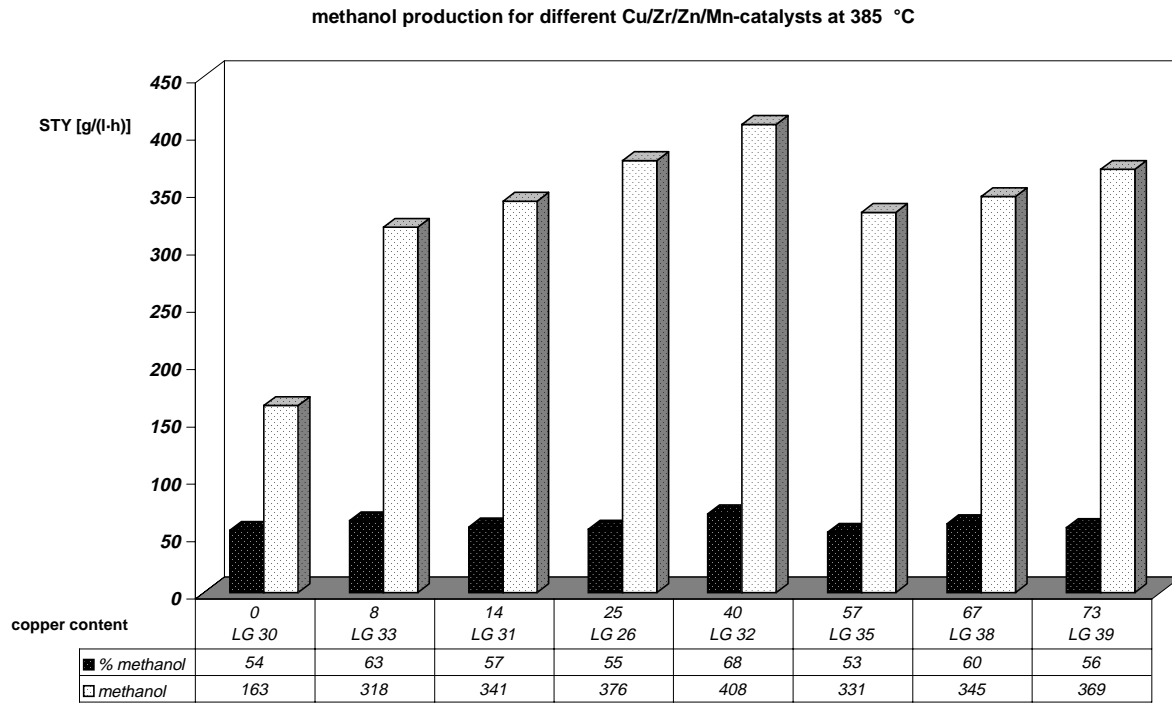
At 385°C, the increase in ethanol with increasing copper content was significantly lower than at 350°C. At the highest copper levels, the temperature increase even led to a deterioration in ethanol STY. Isobutanol yield showed a clear maximum at a copper content of 25 mol %. Higher copper concentrations showed a falling isobutanol yield, even below the values obtained at the lower temperature.

Figure 3.3.3 Influence of Copper Content on Isobutanol Production at 350°C



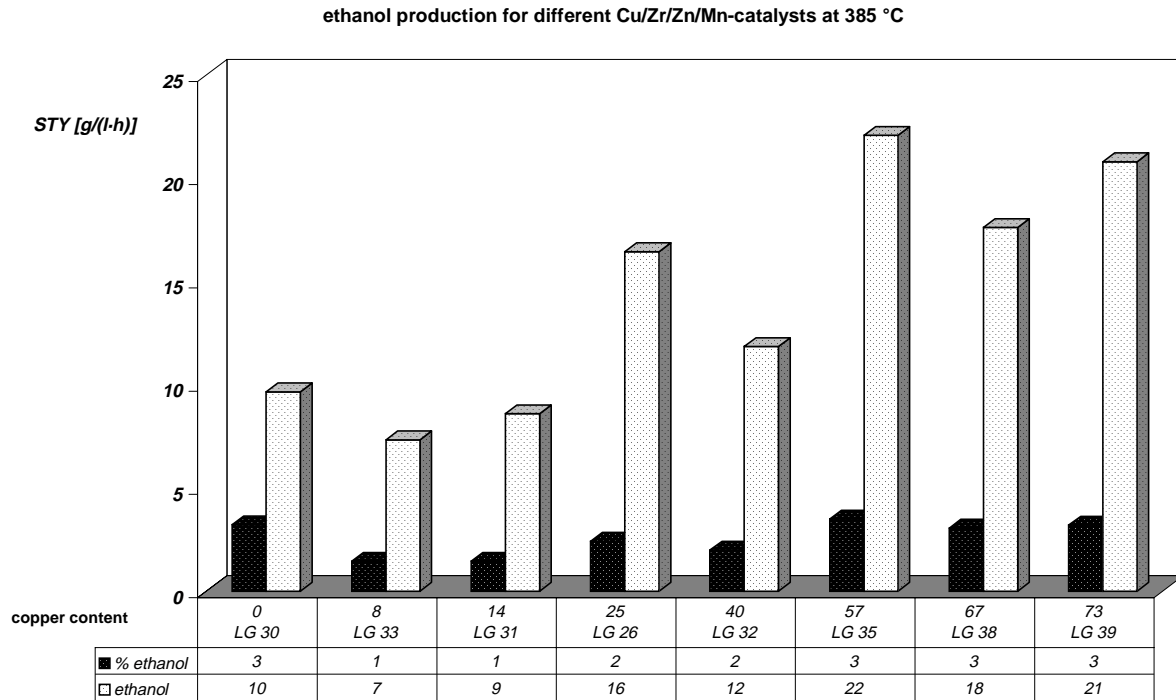
Unit II, $V_{\text{cat}}=3$ ml, $D_{\text{cat}}=0.25\text{-}0.71$ mm, $\text{GHSV}=9,000$ h⁻¹, $p=125$ bar

Figure 3.3.4 Influence of Copper Content on Methanol Production at 385°C



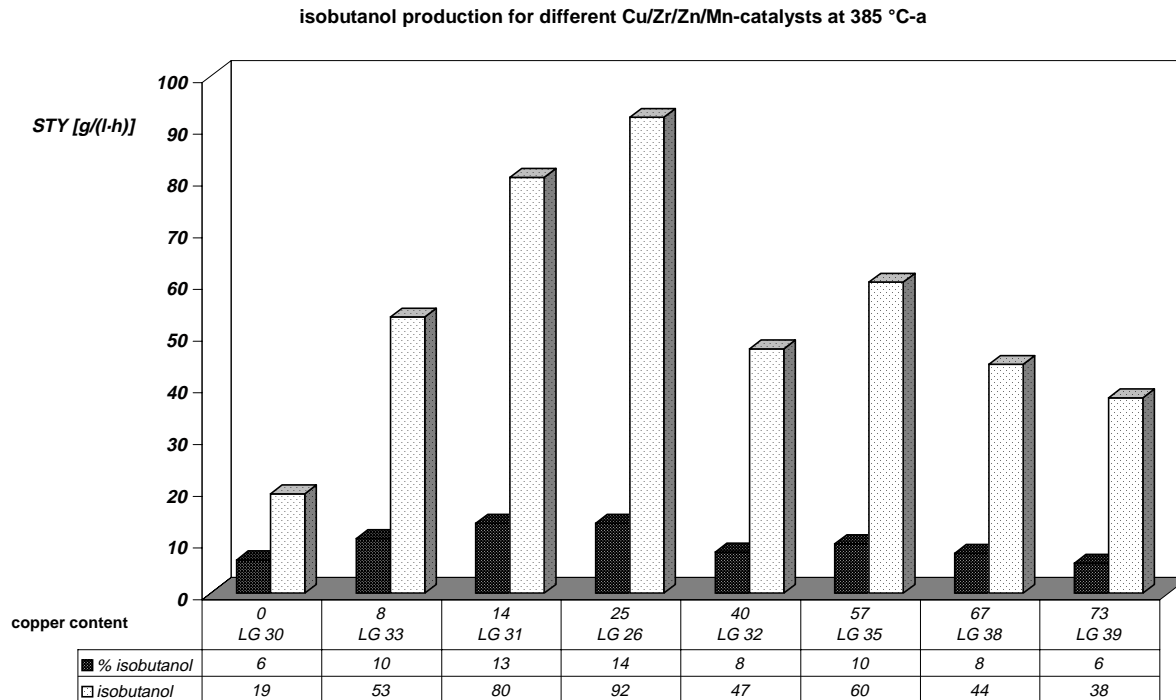
Unit II, $V_{\text{cat}}=3$ ml, $D_{\text{cat}}=0.25\text{-}0.71$ mm, $\text{GHSV}=9,000$ h⁻¹, $p=125$ bar

Figure 3.3.5 Influence of Copper Content on Ethanol Production at 385°C



Unit II, $V_{\text{cat}}=3$ ml, $D_{\text{cat}}=0.25\text{-}0.71$ mm, $\text{GHSV}=9,000$ h⁻¹, $p=125$ bar

Figure 3.3.6 Influence of Copper Content on Isobutanol Production at 385°C



Unit II, $V_{\text{cat}}=3$ ml, $D_{\text{cat}}=0.25\text{-}0.71$ mm, $\text{GHSV}=9,000$ h⁻¹, $p=125$ bar

Thermal Deactivation

The second measurement at 350°C showed improved results towards isobutanol, but only for the lower copper concentrations (Table 3.3.3). Catalysts with a high copper content displayed a clear deactivation effect. Methanol, as well as isobutanol, showed a sharp decrease in activity at this repeated 350°C measurement.

Table 3.3.3 Thermal Deactivation

Catalyst	LG 33	LG 33	LG 39	LG 39
Copper content [mol %]	8	8	73	73
Temperature [°C]	350°C-a	350°C-b	350°C-a	350°C-b
LIQUID PRODUCT				
% Methanol	97	79	79	74
% Isobutanol	1	6	5	3
STY [g/(l*h)]				
Methanol	807	450	988	668
Isobutanol	12	35	67	29

2. Summary and Outlook

The Zr/Zn/Mn/K-oxide catalyst could be activated by copper addition, reaching an isobutanol yield of 72 g/(l·h) at 350°C, compared to 9 g/(l·h) for the copper-free catalyst. At 385°C, a yield of 92 g/(l·h) was obtained, in contrast with 19 g/(l·h) for the copper-free catalyst.

An increasing copper content displayed only a minor influence on methanol yield, which was limited by thermodynamics. However, higher alcohols showed a constant increase in yield with increasing copper content.

At higher temperatures (385°C in this study), the thermal instability of the catalyst systems investigated increased with increasing copper content. At the highest copper concentrations, even a decrease in higher alcohol yield could be found, compared to the values obtained at 350°C.

Investigation of the copper-promoted Zr/Zn/Mn/K-oxide catalyst system will be continued. The influence of the precipitation method will be studied, as will the addition of other metals. We will also attempt to find an optimized HAS catalyst using the information gleaned from our previous investigations. Furthermore, the exact role of copper in the reaction scheme will be studied.

TASK 5: PROJECT MANAGEMENT

5.1 Liquid Phase Fischer-Tropsch Demonstration

Detailed analysis of the data from the Fischer-Tropsch IV demonstration continued. The analysis included heat and mass balances at different process conditions, heat loss calculations, catalyst activation results, gas holdup and catalyst inventory estimation, as well as reactor heat transfer calculations. A topical report documenting both the Fischer-Tropsch III and IV runs was begun.

On November 9-10, a technical meeting was held between Air Products and SSFI (Shell Synthetic Fuels, Inc.) personnel to exchange and discuss the Fischer-Tropsch data analysis and results. Preliminary data and results were given to SSFI for both their technical and confidentiality review. The meeting was very productive, with substantial progress made on data analysis. However, a significant amount of work still needed to be completed. As per the action plan developed at that meeting, SSFI conducted further analytical work for light hydrocarbons and catalyst slurry samples. F-T III analytical data and results were also provided by SSFI. In addition, SSFI evaluated the data for catalyst stability. The catalyst appeared fairly stable during F-T IV. Air Products incorporated the wax, the light hydrocarbon and the aqueous phase composition data into the mass balances and performed an elemental balance. A correlation for wax density based on analytical data from F-T IV was used for calculations, and all the affected F-T IV data were re-worked.

Data analysis for both Fischer-Tropsch III and IV runs was completed with input from SSFI. A draft data package was prepared and sent to SSFI for their final technical, as well as confidentiality review. A meeting was set up with DOE for early January 1999 to present the data package. The data show excellent heat/mass/elemental balance and fully support the preliminary conclusion of a highly successful demonstration during F-T IV.