

ALTERNATIVE FUELS AND CHEMICALS FROM SYNTHESIS GAS

Draft

Technical Progress Report No. 37

For the Period 1 January - 31 March 1999

Contractor

AIR PRODUCTS AND CHEMICALS, INC.

7201 Hamilton Boulevard
Allentown, PA 18195-1501

Prepared for the United States Department of Energy
Under Contract No. DE-FC22-95PC93052
Contract Period 29 December 1994 - 28 December 1997

DISCLAIMER

This work was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Alternative Fuels and Chemicals from Synthesis Gas

Technical Progress Report

1 January - 31 March 1999

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

LPDMETM

Study of the effect of reduction method. In the LPDMETM process, with a dual catalyst system, the methanol catalyst can be reduced either in the presence of the dehydration catalyst (*co-reduction*) or by itself, followed by addition of the dehydration catalyst to the system (*separate reduction*). The lab experiments demonstrated that the reduction method had little effect on the activity and stability of our current dual catalyst system containing commercial methanol synthesis and methanol dehydration catalysts.

Investigation of the effect of catalyst loading. Higher catalyst loading (e.g., 30 grams) in 300-cc lab autoclave reactors resulted in more-than-baseline catalyst deactivation. Efforts were made to identify the cause of this solid loading effect (i.e., the "30-gram problem"):

- The 30-gram problem is real; it has been observed repeatedly. One experiment using the recovered slurry from a 30-gram experiment showed that the greater activity loss observed in the 30-gram run could not be fully accounted for by catalysts clumping to the walls of the reactor interiors.
- A LPMEOHTM experiment using 30-gram loading showed baseline stability. This indicates that the 30-gram problem is specific to the dual catalyst system. More rapid loss of the slurry oil under high catalyst loading conditions, per se, is not the problem.

- The “entrance effect,” i.e., localized, deactivating atmosphere around the gas inlet to the slurry, was ruled out as a possible cause. We reached this conclusion by using an axial impeller that enhanced mixing in the gas inlet and by using a process method that made the feed gas zone less deactivating; neither improved stability.
- We previously developed a process method to stabilize LPDME™ dual-catalyst systems by mitigating the detrimental interaction between the two catalysts. While this method (“process modification”) has stabilized catalyst systems in many cases using 10-gram catalyst loading, it showed little stabilization effect under high catalyst loading conditions. This suggests that either the “30-gram problem” is not related to the detrimental interaction between the two catalysts or the process modification cannot *completely* eliminate the interaction.

Speculation on the cause of the 30-gram problem. All results we have compiled from 30-gram runs using the current dual-catalyst system of commercial materials suggest two possibilities:

- 1) The detrimental interaction in this catalyst system cannot be completely eliminated by modifying the reaction conditions. It is small and negligible at 10-gram catalyst loading, but is amplified with increasing catalyst loading due to the increased opportunity of interaction. The way to verify this hypothesis and solve the problem is to try alternative dual-catalyst systems, and to hope the problem is specific to the current catalyst system.
- 2) However, the so-called “30-gram problem” may have a another cause. The strong evidence for this hypothesis is that the problem cannot be mitigated by the process modification. It is also suggested by some randomness observed in 30-gram runs (e.g., periods of stable operation and sharp drops). It may well be related to the properties of the slurry (e.g., agglomeration). Again, this hypothesis can be tested by using alternative methanol synthesis and dehydration catalysts. Other experiments will also be tried to diagnose the problem and develop solutions.

Additives in LPMEOH™

Efforts were continued to establish the experimental methodology for investigating the effect of additives on LPMEOH™ performance. Some preliminary results suggest that the additive may improve mass transfer.

LPDME™ Process Schemes

A paper entitled “Single Step Syngas-to-DME Processes for Optimal Productivity, Minimal Emissions and Natural Gas-Derived Syngas” was prepared for publication in *Industrial Engineering & Chemistry*. It shows how integration of LPDME™ with syngas generation allows the LPDME™ reactor to operate at the optimal kinetic regime, produces minimal waste and uses natural gas as the starting material.

Task 3.2 New Fuels from Dimethyl Ether (DME)

3.2.1 Overall 2QF99 Objectives

The following set of objectives appeared in Section III of the previous Quarterly Technical Progress Report No. 17:

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

3.2.2 Results and Discussion

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 through the oxidative coupling of DME.

Oxidative Coupling Chemistry

1. Catalysis

Catalyst evaluation - high-pressure test apparatus (BTRS). Changes in calculational procedures resulted in improved carbon balances for earlier runs involving SnO₂/MgO. As shown in Table 3.2.1, the highest monoglyme selectivity achieved was 5.9% at 300°C and 300 psig feed. Table 3.2.2 shows that increased O₂ feed concentrations have a detrimental effect on monoglyme selectivity.

Results for the catalyst XO₂ at high pressure are listed in Table 3.2.3. Although the catalyst was active even at 200°C, low monoglyme selectivities were obtained, 1.5-2.6%, over the temperature range of 200 to 300°C. Monoglyme selectivities were lower than those for SnO₂/MgO, which led to an interesting observation. XO₂ showed trace coupling activity at low pressure, while SnO₂/MgO showed none, implying that reasonable catalysts may be “missed” based on our selection criteria using low-pressure screening data.

Table 3.2.1 Evaluation of SnO₂/MgO (Recalculation of Earlier Data)
Feed: 72.6 mol % DME, 4.7 mol % O₂, 22.7 mol % N₂; DME/O₂ = 16.3; contact time, 1.6 sec

order run	1	2	3	5	6	4	10	7	8	9
T, °C	250	250	250	275	275	275	275	300	300	300
P (psig)	300	500	750	300	500	750	750	300	500	750
DME conv. (%)	1.3	3.1	33.0	9.0	12.2	13.2	14.0	15.4	16.6	19.6
C balance	1.04	1.02	0.72	0.96	0.93	0.93	0.92	0.90	0.90	0.87
O ₂ conv. (%)	100	100	99.5	100	100	100	100	100	100	100
Product selectivity (% C)										
CO			11.7	17.4	14.7	11.4	11.3	17.2	15.2	12.9
CO ₂	13.1	9.00	9.96	12.4	10.5	10.1	8.98	12.1	12.2	12.7
CH ₄	4.66		0.43	1.23	1.41	1.21	1.32	3.39	3.14	2.67
ethylene	0.11			0.61	0.55			0.12	0.090	0.064
ethane	0.25							0.053		
methanol	10.9	8.30	8.35	8.25	8.68	9.22	9.49	9.41	10.0	11.1
methyl formate	58.0	69.3	63.6	53.1	54.5	57.7	56.6	45.4	46.1	47.9
methyl ethyl ether	4.48	1.94		0.78	0.60	0.35	0.44	1.61	0.98	0.60
ethanol	0.84	0.93	0.53	0.82	1.39	1.35	1.58	1.79	2.32	2.23
diethyl ether			0.30	0.12	0.23	0.35	0.45		0.38	0.54
dimethoxymethane	0.57	0.32	0.57	0.42	0.50	0.67	0.61		0.46	0.61
methyl acetate	0.20									
2-methoxyethanol	0.27	0.34	0.36	0.26	0.49	0.66	0.83	0.48	0.72	0.88
monoglyme	5.45	5.50	1.83	3.22	4.06	3.36	4.06	5.93	5.55	4.37
trioxane			0.33		0.37	0.69	1.39	0.31	0.62	1.06
1,4-dioxane	0.20	0.15		0.17	0.17	0.13	0.18	0.29	0.28	
methyl methoxyacetate		0.28	0.45			0.26				
dimethyl oxalate		0.15	0.22					0.15		0.26
DEGME	0.15	0.46	0.30	0.41	0.54	0.63				
unknowns	0.82	1.22	1.09	1.39	2.00	1.83	3.55	2.04	1.88	3.06

Table 3.2.2 Evaluation of SnO₂/MgO at Higher O₂ Concentration (Recalculation of Earlier Data)
Feed: 57.0 mol % DME, 8.75 mol % O₂, 34.2 mol % N₂; DME/O₂ = 8.9; contact time, 1.6 sec

order run	3	2	1
T, °C	250	275	300
P (psig)	500	500	500
DME conv. (%)	*	15.7	57.5
C balance	1.13	1.04	0.55
O ₂ conv. (%)	100	100	100
Product selectivity (% C)			
CO	0.000	42.7	23.6
CO ₂	14.2	10.9	18.6
CH ₄	4.14	21.1	3.37
ethylene	0.088	0.88	0.079
ethane	0.17		
propene			0.16
methanol	9.67	4.94	8.08
methyl formate	60.3	15.6	37.1
methyl ethyl ether	3.10	1.20	1.06
ethanol	0.73	0.48	0.73
diethyl ether	0.64	0.15	0.85
dimethoxymethane	0.98	0.42	0.77
2-methoxyethanol	0.35	0.14	0.47
monoglyme	3.87	0.69	2.57
DEGME	0.24		
unknowns	1.38	0.70	1.52

Table 3.2.3 Evaluation of XO₂
Feed: 71.6 mol % DME, 5.52 mol % O₂, 22.8 mol % N₂; DME/O₂ = 13.3; contact time, 1.1 sec

Order run	2	3	1
T, °C	200	250	300
P (psig)	520	520	415
DME conv. (%)	6.6	24.6	26.5
C balance	0.99	0.80	0.78
O ₂ conv. (%)	49.7	59.7	44.2
Product selectivity (% C)			
CO	4.81	19.7	20.9
CO ₂	7.44	17.1	37.9
CH ₄	-	2.30	4.21
ethylene	-	0.12	0.39
ethane	-	0.07	0.31
propene	-	0.44	0.22
methanol	10.1	14.1	28.3
methyl vinyl ether	-	-	0.39
methyl formate	70.4	37.0	0.66
methyl ethyl ether	0.24	1.80	-
ethanol	0.33	0.53	0.87
dimethoxymethane	0.48	1.55	0.94
2-methoxyethanol	0.55	0.26	0.35
monoglyme	1.86	1.53	2.57
unknowns	3.80	3.52	1.33

Table 3.2.4 Evaluation of AXB Oxide
Feed: 71.6 mol % DME, 5.52 mol % O₂, 22.8 mol % N₂; DME/O₂ = 13.3; contact time, 0.55 sec

run number	Quartz chips used									
	none			upstream					both	up
	1	2	3	4	5	6	7	8	9	10
T, °C	200	250	300	200	250	300	325	350	300	300
P (psig)	520	520	520	520	520	520	520	520	476	476
DME conv. (%)	9.2	*	*	5.2	8.4	4.9	4.0	4.1	21.6	4.4**
C balance	0.98	1.21	1.22	1.02	0.99	1.03	1.05	1.05	0.82	1.01**
O ₂ conv. (%)	95.7	99.3	99.5	78.3	78.1	82.0	88.4	87.2	58.6	82.0**
Product selectivity (% C)										
CO	7.67	14.0	19.7	6.23	14.8	16.5	18.2	19.8	15.0	11.6
CO ₂	5.07	21.3	30.9	6.05	18.2	31.7	28.9	29.7	55.6	33.0
CH ₄	0.51	7.55	2.83	0.38	5.58	6.41	8.05	10.7	2.11	7.02
ethylene		0.18	0.37		0.11	0.14	0.25	0.36		0.16
ethane		0.47	0.07		0.50	0.62	0.63	0.69		0.62
propene			0.11			0.16	0.29	0.32	0.07	0.06
methanol	8.43	15.7	29.1	8.12	12.3	33.0	32.8	27.7	25.0	16.7
methyl formate	73.8	27.1	10.5	76.1	39.5	2.15	0.10		0.83	24.4
methyl ethyl ether	0.25	6.39	0.77	0.30	4.40	4.82	4.80	4.66	1.01	4.22
ethanol	0.26	0.70	1.00	0.30	0.56	0.63	0.65	0.39		0.40
diethyl ether	0.10	0.26	0.15	0.09	0.24					0.20
dimethoxymethane	0.17	0.18	0.16	0.19	0.17	0.18	0.23	0.26		0.28
2-methoxyethanol	0.28	0.25	0.34	0.33	0.18	0.32	0.67	0.64		
monoglyme	1.18	4.88	3.37	1.47	2.48	2.47	2.91	2.58	0.40	1.32
trioxane	0.80									
methyl methoxyacetate							0.38	0.37		
unknowns	1.20	1.08	0.49	0.43	0.88	0.83	1.04	1.26	0.00	0.00

* unrealistic value

** unrealistically large O₂, N₂ concentrations but others OK

Results for AXB oxide at high pressure are listed in Table 3.2.4. This catalyst had shown trace coupling activity at low pressure. However, like XO₂, monoglyme selectivities were lower than those for SnO₂/MgO under comparable conditions. The catalyst was run using three different reactor configurations. In Runs 1-3 (Table 3.2.4), only the catalyst was present in the reactor tube. The major organic products were CO₂, CO, methanol, and methyl formate. Monoglyme selectivity was 3.4% at 300°C. Packing quartz chips upstream of the catalyst (Runs 4-8) resulted in more or less modest changes in product selectivities. At 300°C, the major organic products were CO₂, CO, methanol, and CH₄. The selectivity of monoglyme was greater than that for methyl formate. A comparison of Run 6 and/or Run 3 data indicated an increase in CO₂ production at the expense of methyl formate and monoglyme when quartz chips were placed both upstream and downstream of the catalyst. Subsequent removal of the downstream quartz chips (Run 10) resulted in decreased CO₂ production, while those of methyl formate and monoglyme increased. In any case, running the catalyst with no quartz chips upstream or downstream appeared to give the highest monoglyme selectivity.

Passing a DME/O₂ feed over Y_nO_m at high pressure gave the results listed in Table 3.2.5. Unrealistic GC concentrations of N₂ and O₂ prevented calculation of DME and O₂ conversions

and carbon balances. A monoglyme selectivity of 3.4 % was obtained at 300°C for a feed DME/O₂ ratio of 13.3. Decreasing the feed O₂ concentration at 300°C resulted in a decrease in monoglyme selectivity. Table 3.2.6 lists results for exposing Z_pO_q to DME/O₂ at high pressure. Due to time constraints, only one reaction temperature was evaluated, and a low monoglyme selectivity, 2.6%, was obtained.

Table 3.2.5 Evaluation of Y_nO_m
Feed A: 71.6 mol % DME, 5.52 mol % O₂, 22.8 mol % N₂; DME/O₂ = 13.3
Feed B: 72.6 mol % DME, 2.74 mol % O₂, 24.6 mol % N₂; DME/O₂ = 26.5

Feed order run	A	B	B
T, °C	300	300	350
P (psig)	467	467	485
DME conv. (%)	**	**	**
C balance	**	**	**
O ₂ conv. (%)	**	**	**
Product selectivity (% C)			
CO	10.4	7.93	8.99
CO ₂	26.2	30.1	33.1
CH ₄	3.59	3.85	6.91
ethylene	0.13	0.16	0.21
propene			0.28
propane	0.68		
methanol	38.2	38.1	43.1
methyl formate	13.3	12.0	0.19
methyl ethyl ether	0.96	0.75	0.91
EtOH	2.07	2.04	1.79
diethyl ether	0.30	0.25	0
dimethoxymethane	0.14	0.30	0
2-methoxyethanol	0.58	0.69	0.70
monoglyme	3.43	2.69	3.16
DEGME	0	0.76	0
unknowns	0.57	0	0.67

** unrealistic values due to incorrect GC concentrations of O₂, N₂; other concentrations believed to be accurate.

Table 3.2.6 Z_pO_q Catalyst**Feed: 71.6 mol % DME, 5.5 mol % O₂, 22.8 mol % N₂; DME/O₂ = 13.0; contact time, 0.91 sec**

order run	1
T, °C	300
P (psig)	435
DME conv. (%)	4.0
C balance	1.03
O ₂ conv. (%)	98.9
Product selectivity (% C)**	
CO	36.2
CO ₂	25.4
CH ₄	4.08
ethylene	0.20
ethane	0.19
propene	0.46
methanol	26.0
methyl formate	0.20
methyl ethyl ether	0.97
EtOH	1.44
methyl acetate	0.45
2-methoxyethanol	0.50
monoglyme	2.56
methyl methoxyacetate	0.31
unknowns	1.04

The lack of oxidative coupling activity for the various oxides examined has been troubling, especially with regard to the literature catalyst SnO₂/MgO. Other researchers have also failed to observe DME coupling using this catalyst. We have assumed this might be due to differences in experimental conditions. The literature experiments were performed in the DME explosive range using a feed containing only DME and O₂ (5:1 molar ratio) at about 200°C (a temperature at which we see no activity). Without a major hazards review, blending only DME and O₂ was not feasible here. As an approximation, a feed containing the literature partial pressures of DME and O₂ (195.0 and 40.0 psia, respectively) was generated by blending air and DME. Specifically, this was accomplished by blending 109 sccm air and 106 sccm DME gas (20 mL/h liquid) at a total pressure of 395 psia. Since setting flows and total pressure does not always give the precise conditions desired, the actual experimental feed pressure was 425 psia - 238 psia DME and 39 psia O₂; DME/O₂ = 6.1. Table 3.2.7 compares the results of our evaluation of SnO₂/MgO with those of the literature. Several striking points are apparent for the data at 200°C:

1. We see almost no reaction of DME, while the literature reports 11% DME conversion along with 78.1% O₂ conversion versus our 4.8%.
2. The literature reports no methyl formate product, while we observe 53.8% methyl formate.
3. The literature reports 13.5% dimethoxymethane and 34.5% monoglyme, while we see none.

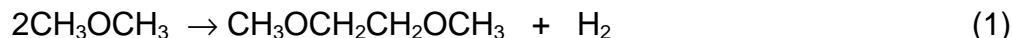
Table 3.2.7 Evaluation of SnO₂/MgO Catalyst at High O₂ Concentration
Feed: 54.0 mol % DME, 8.86 mol % O₂, 37.1 mol % N₂; DME/O₂ = 6.10; contact time, 0.6 sec
Literature feed: 73 mol % DME, 17 mol % O₂

order run	<i>literature</i>	1	2	3	4	5
T, °C	200	200	225	250	275	300
P (psig)	250	425	425	425	425	425
DME conv. (%)	11.0	0*	2.3	6.5	38.2	39.0
C balance	?	1.02	0.99	0.96	0.90	0.88
O ₂ conv. (%)	78.1	4.8	1.4	21.4	95.9	95.5
Product selectivity (% C)**						
CO	23.2	15.9	14.2	13.8	37.0	38.8
CO ₂	14.8	23.5	28.6	36.3	14.3	13.2
CH ₄	9.6				29.0	28.6
ethylene	0.8*				0.14	0.14
ethane	0.8*				2.27	2.25
propane	0.8*				0.14	0.13
methanol	3.5	6.74	7.56	7.63	10.3	9.22
methyl formate	0	53.8	49.7	42.3	2.51	3.72
methyl ethyl ether	0				1.72	1.63
EtOH	0				0.31	0.39
diethyl ether	0					0.048
dimethoxymethane	13.5				1.14	0.76
monoglyme	34.5				0.25	0.38
unknowns	?	0	0	0	0.97	0.63

* literature reports sum of C₂ and C₃ species.

For reference, the reactivity of DME and O₂ were evaluated using an empty reactor tube, and the results are summarized in Table 3.2.8. Only at 300°C was a significant amount of monoglyme produced (2.4%). For comparative purposes, results for SnO₂/MgO under conditions as close as possible to those of the empty reactor are also listed in Table 3.2.8.

Alternative approaches to DME coupling. Catalytic oxidative coupling of DME (or any other hydrocarbon) will invariably result in some CO₂ because DME radicals are very reactive with O₂. An alternative is DME coupling under anaerobic conditions, as represented by Reaction 1.



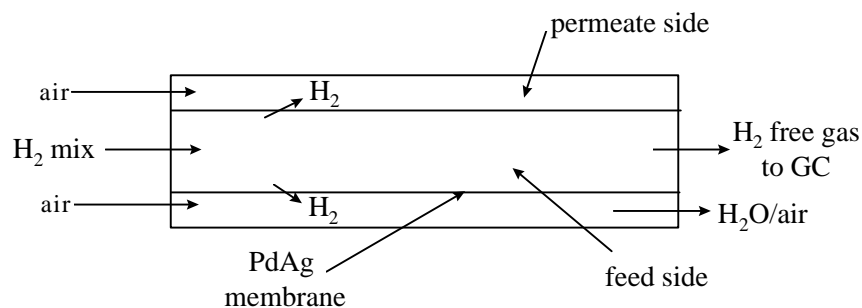
Reaction 1 is not thermodynamically favorable, but it can be driven by removal of H₂ as it is formed. Removal of H₂ can be accomplished by using a H₂-selective palladium membrane reactor. Pd-based membranes are commercially available and are marketed as devices to remove H₂ from gas mixtures prior to GC analysis. The function of the membrane is to quantitatively remove H₂ from a gas stream passed through the separator (see illustration below). The permeate side of the membrane is swept with air, which converts H₂ to water, thus driving permeation of H₂.

Table 3.2.8 Evaluation of an Empty Reactor

Feed: 72.6 mol % DME, 5.47 mol % O₂, 21.9 mol % N₂; DME/O₂ = 13.3; 106 sccm DME, 40.0 sccm air
Feed for SnO₂/MgO: 72.6 mol % DME, 4.7 mol % O₂, 22.7 mol % N₂; DME/O₂ = 16.3; contact time, 1.6 sec

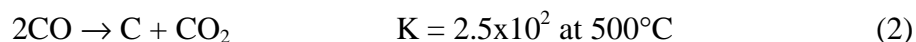
	Empty reactor			SnO ₂ /MgO
	T, °C	200	250	300
	P (psig)	445	415	500
DME conv. (%)		3.3	5.7	6.5
C balance		1.04	0.99	0.99
O ₂ conv. (%)		94.4	94.7	97.8
Product selectivity (% C)**				
CO		8.11	14.9	19.2
CO ₂		6.60	36.9	30.5
CH ₄		0.38	0.13	3.74
ethylene				0.16
ethane				0.07
propane			0.14	0.19
methanol		7.21	12.8	16.7
methyl formate		72.1	32.4	23.1
methyl ethyl ether		0.28		0.76
EtOH		0.29	0.21	1.71
diethyl ether		0.43		0.42
dimethoxymethane		0.73	1.21	0.55
2-methoxyethanol		0.18		0.72
monoglyme		0.82	0.25	2.39
trioxane		0.58		0.62
1,4-dioxane			0.53	0.28
methyl methoxyacetate		0.26		
DEGME		0.52		
unknowns		1.48	0.51	0.55
				1.88

Figure 3.2.1 Hydrogen-Selective Palladium Membrane Reactor



The hydrogen separator used was a GOW-MAC device containing a Pd-Ag alloy membrane. A DME/N₂ feed was passed down the feed side of the membrane, while air was passed on the sweep side. Various flow rates of feed and sweep gas were used at temperatures of 100 to 500°C. GC analysis of the feed gas exiting the membrane is reported in Table 3.2.9. Only at 400°C or higher was any significant reactivity observed. At these temperatures, the major products were CO₂, CO, and CH₄. Trace amounts of ethane and an unknown (C₂ or lower) were found. Coupling

products were not observed. These results are consistent with pyrolysis of DME as reported in the literature [J. Chem. Phys. 31, 1008-1017 (1959)], for which the primary products were CO, CH₄, and H₂ in approximately equimolar quantities. For example, DME (6.8 psia) passed through a quartz tube at 507°C gave the following products: 1.9 mol % H₂CO, 32.5 mol % H₂, 32.6 mol % CO, 34.6 mol % CH₄, and 0.3 mol % C₂H₆. In our experiments, H₂ permeates through the membrane and is not detected. CO₂ can arise from reaction with contaminant O₂ or via disproportionation of CO as in Reaction 2, perhaps catalyzed on the Pd membrane surface.



As in oxidative coupling using O₂, near-ambient pressure may be too low to generate the radical concentrations required for the bimolecular coupling reaction.

The results using the membrane reactor are similar to those for earlier low-pressure experiments in which a DME/N₂ feed was passed through Pd/Al₂O₃. The products were relatively large; about equimolar quantities of CO and CH₄ and low CO₂ concentrations at 250°C or higher were observed. However, traces of the coupling product 2-methoxyethanol, CH₃OCH₂CH₂OH, were detected.

Table 3.2.9 Conditions and Product Selectivities for DME Passed Through a Pd/Ag Membrane

feed flows		air sweep		feed		DME conv. %	C balance	C selectivity, %					
DME	N ₂	sccm	T, °C	P(psia)	CO			CO ₂	CH ₄	C ₂ H ₆	MeFor?	MeOEt	unkn**
12.2	11.9	250	100	14	12.1	0.88					81.9	18.3	
12.2	11.9	250	200	14	12.2	0.88					74.1	26.0	
12.2	11.9	250	250	14	11.8	0.88					50.8	23.7	
12.2	11.9	250	300	14	11.7	0.88					29.3	9.90	
12.2	11.9	250	400	14	13.9	0.87	51.0	41.2	6.39	0.16	0.37	0.67	0.22
12.2	11.9	250	450	14	12.1	0.88		31.6		1.95		3.56	2.59
5.8	6.0	250	100	14	5.9	0.94						79.4	20.7
5.8	6.0	250	400	14	5.2	0.95		37.9	54.3			5.43	2.61
5.8	6.0	550	400	12	11.8	0.88			25.5			50.8	23.7
5.8	0	550	400	4	27.6	0.73	31.7	61.0	6.52	0.06		0.51	0.18
5.8	0	550	500	4	24.5	0.76	21.4	76.2	62.2	0.09		0.25	0.96

* methyl ethyl ether (MeOEt) is a contaminant in the DME feed and not a reaction product.

** unknown, retention time 2.56 min.

2. CETANERÔ Properties

Flash points of diesel fuel blends. As reported earlier, the concentrations of monoglyme present in diesel fuel blends may need to be limited because of flash point requirements. The literature flash point (FP) of pure monoglyme is either 0 or -6°C (Ferro product literature). Our earlier calculations pointed to a maximum monoglyme concentration of 2 and 6 vol % in European and U.S. diesel fuel, respectively. Listed in Table 3.2.10 is a series of blends of monoglyme and/or diglyme with diesel fuel. Flash points were determined by the closed-cup method. The diesel fuel had a FP of 61°C, while that of pure diglyme was 55°C, compared with the literature value of 57°C. Addition of diglyme between 1 to 40 vol % resulted in a slight decrease in the blend FP,

while monoglyme, as expected, had a more pronounced effect. Monoglyme concentrations of 2 and 4 vol % resulted in flash points of 43 and 34°C, respectively. Thus, the maximum allowable monoglyme concentration based on the FP of U.S. diesel fuel (38°C) is less than 4 vol %. Note that the blend flash points are approximately the same for equal concentrations of added monoglyme, whether diglyme is present or not. For example, the FP of Sample 2, which contains 1 vol % monoglyme, 51, is very close to that of Sample 12, which contains 1 vol % monoglyme and 9 vol % diglyme.

Table 3.2.10. Experimental Flash Points of Diesel Fuel/Monoglyme/Diglyme Blends

	sample number	concentration, volume %		experimental flash point, °C
		monoglyme	diglyme	
diesel fuel:	1	0	0	61
	2	1	0	51
	3	5	0	27
	4	10	0	25
	5	15	0	22
	6	0	1	61
	7	0	5	58
	8	0	10	56
	9	0	15	55
	10	0	40	53
pure diglyme:	11	0	100	55
	12	1	9	49
	13	2	8	42
	14	4	6	33
	15	5	5	26
	16	2	18	43
	17	4	16	34
	18	8	12	24
	19	10	10	24

Aging study. GC analysis of samples from an aging study are listed in Table 3.2.11. The samples contained monoglyme and/or diglyme and the diesel fuel substitute hexadecane. Each sample also contained a trace of added water, which caused no phase separation, or a larger volume of water, which yielded two phases. For samples consisting of two phases, both the organic and aqueous phases were analyzed. All samples showed virtually no change in composition, and no decomposition products were observed over a 98 day period. Two unknowns arose from impurities in hexadecane (4.85 min) and diglyme (25.9 min). One additional unknown at 24.3 min, observed in very low concentrations, may have arisen from diglyme contamination. Notice that much of the monoglyme and diglyme were extracted into the aqueous phase for samples containing two phases.

Table 3.2.11 GC Analysis of Aging Samples

sample	phase	time, weeks	Mole fraction by GC**						
			hexa-decane	mono-glyme	diglyme	MeO H	unknown 4.8 min	unknown 25.9 min	unknown 24.3 min
1	organic	0	0.634	0.359	-	0.0035	0.0036	-	-
		22	0.636	0.364	-	-	-	-	-
		42	0.627	0.373	-	-	-	-	-
		63	0.625	0.375	-	-	-	-	-
		98	0.618	0.382	-	-	-	-	-
2	organic	0	0.741	0.254	-	-	0.0051	-	-
		22	0.749	0.251	-	-	-	-	-
		42	0.746	0.254	-	-	-	-	-
		63	0.748	0.252	-	-	-	-	-
		98	0.744	0.256	-	-	-	-	-
2a	aqueous	0	8.10E-05	0.996	-	-	0.0043	-	-
		22	7.99E-04	0.999	-	-	-	-	9.03E-05
		42	5.11E-04	0.999	-	-	-	-	-
		63	2.70E-04	0.9997	-	-	-	-	-
		98	2.00E-04	0.9998	-	-	-	-	-
3	organic	0	0.699	-	0.296	-	0.0049	-	-
		22	0.701	-	0.299	-	-	-	-
		42	0.702	-	0.298	-	-	-	-
		63	0.702	-	0.298	-	-	1.30E-04	-
		98	0.699	-	0.301	-	-	-	0.0002
4	organic	0	0.876	-	0.113	-	0.011	-	-
		22	0.887	-	0.113	-	-	-	-
		42	0.886	-	0.114	-	-	-	-
		63	0.887	-	0.114	-	-	-	-
		98	0.886	-	0.114	-	-	-	-
4a	aqueous	0	6.90E-05	-	0.994	-	0.00057	-	-
		22	5.97E-04	-	0.999	-	-	-	-
		42	2.00E-04	-	0.9997	-	-	-	-
		63	3.60E-04	-	0.9995	-	-	-	1.10E-04
		98	1.00E-04	-	0.9995	-	-	3.60E-04	-
5	organic	0	0.415	0.578	-	0.0028	0.0035	-	-
		22	0.413	0.587	-	-	-	-	-
		42	0.414	0.586	-	-	-	-	-
		63	0.412	0.588	-	-	-	-	-
		98	0.416	0.584	-	-	-	-	-

Table 3.2.11 (continued) GC Analysis of Aging Samples

Sample	phase	time, days	Mole fraction by GC**						
			hexa-decane	mono-glyme	diglyme	MeOH	unknown 4.8 min	unknown 25.9 min	unknown 24.3 min
6	organic	0	0.533	0.463	-	-	0.0034	-	-
		22	0.534	0.466	-	-	-	-	-
		42	0.537	0.463	-	-	-	-	-
		63	0.537	0.463	-	-	-	-	-
		98	0.538	0.462	-	-	-	-	-
6a	aqueous	0	1.40E-04	0.996	-	-	0.0037	-	-
		22	8.25E-05	0.9997	-	-	-	-	1.87E-04
		42	1.51E-04	0.9996	2.00E-04	-	-	-	-
		63	1.10E-04	0.9987	1.07E-03	-	-	-	1.60E-04
		98	5.00E-05	0.9993	-	-	4.0E-4*	-	2.40E-04
7	organic	0	0.491	-	0.505	-	0.0042	1.40E-04	-
		22	0.493	-	0.507	-	-	2.38E-04	-
		42	0.492	-	0.507	-	-	-	-
		63	0.493	-	0.507	-	-	2.40E-04	-
		98	0.492	-	0.508	-	-	-	-
8	organic	0	0.760	-	0.233	-	0.0065	2.20E-04	-
		22	0.768	-	0.232	-	-	2.54E-04	-
		42	0.768	-	0.232	-	-	2.57E-04	-
		63	0.768	-	0.232	-	-	2.60E-04	-
		98	0.768	-	0.232	-	-	-	-
8a	aqueous	0	1.10E-04	-	0.995	-	0.005	1.90E-04	-
		22	1.17E-04	-	0.9996	-	-	2.05E-04	-
		42	2.08E-04	-	0.9996	-	-	2.02E-04	-
		63	5.90E-04	-	0.9992	-	-	2.10E-04	-
		98	1.40E-04	-	0.9997	-	-	2.10E-04	-
9	organic	0	0.979	-	-	0.0053	0.0149	-	-
		22	1.000	-	-	-	-	-	-
		42	1.000	-	-	-	-	-	-
		63	0.9998	-	-	-	-	-	1.90E-04
		98	0.9997	-	-	-	-	-	2.90E-04
10	organic	0	0.975	-	-	-	0.025	-	-
		22	1.000	-	-	-	-	-	-
		42	1.000	-	-	-	-	-	-
		63	1.000	-	-	-	-	-	-
		98	1.000	-	-	-	-	-	-

Table 3.2.11 (continued) GC Analysis of Aging Samples

Sample	phase	time, days	Mole fraction by GC**							
			hexa-decane	mono-glyme	diglyme	MeOH	unknown 4.8 min	unknown 25.9 min	unknown 24.3 min	
10a	aqueous	0	0.0348	-	-	-	-	0.965	-	-
		22	0.403	-	-	-	-	-	-	0.597
		42	0.308	-	-	-	-	-	-	0.692
		63	0.019	-	-	-	-	-	-	0.981
		98	0.192	-	-	-	-	-	-	0.808

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

* unknown at 4.09 min in GC

Peroxide testing. Final testing for peroxide formation of a series of diesel fuel-CETANER™ blends stored in D1 size steel cylinders was completed (Table 3.2.12). After 1 year of storage, testing with peroxide test strips showed no detectable peroxide concentrations. Testing using the Ti⁴⁺ method described previously showed no discernible UV/vis peaks corresponding to the Ti⁴⁺ peroxy species, that is, no detectable peroxides. The study has been terminated.

Table 3.2.12 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	365 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	2.8
2	70.0	21.9	7.26	0.87	1.8	3.4	1.2	0	1.5	2.4	3.4	5.3 ^a	2.8
3	60.0	36.8	1.68	1.56	2.9	1.4	2.3	2.8	1.6	1.9	0	5.2 ^a	5.8 ^a
4	70.0	27.6	1.26	1.17	1.4	0	0	1.8	0	0.9	5.9 ^a	0	1.0
5	100	0	0	0	1.1	0	0	2.2	1.3	0.9	0.6	0.9	1.5

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

Final testing for peroxide formation of a series of diesel fuel-CETANER™ blends stored in glass containers was completed (Table 3.2.13). After approximately 1 year, testing using the Ti⁴⁺ method described previously showed no discernible UV/vis peaks corresponding to the Ti⁴⁺ peroxy species, that is, no detectable peroxides. Testing using peroxide test strips also showed no evidence of peroxides. The study has been terminated.

Table 3.2.13 Results for Peroxide Testing of Fuel Blends Stored in Glass Containers
(MG = monoglyme; DMM = dimethoxymethane)

blend	concentrations, volume %				time, days	H ₂ O ₂ conc., weight ppm
	diesel	MG	DMM	MeOH		
6	60.0	40.0	0	0	0	0.3
					31	2.4
					66	5.4 ^b
					103	4.2 ^b
					143	2.6
					233	5.1 ^b
					367	5.7 ^b
7	60.0	29.1	9.67	1.20	0	3.6
					30	1.2
					61	1.2
					98	2.1
					138	2.4
					228	2.8
					345	2.9
8	60.0	40.0	0	0	0	4.0 ^a
					28	2.4
					56	3.8
					96	2.3
					186	4.2
					334	4.7

a. Believed to be accurate; observed band at 406 nm in UV/vis.

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

Biodegradability, toxicity of glymes. A second round of biodegradability and microtox testing involving potential CETANER™ components was completed. Carbonaceous Biological Oxygen Demand (CBOD) testing showed low biodegradation for both monoglyme and diglyme. The half alcohols of the glymes, 2-methoxyethanol and diethylene glycol methyl ether, showed more significant biodegradability at 28 days. Some caution in interpreting the results in Table 3.2.14 is required, since the control showed >100% biodegradation at 28 days. However, the relative biodegradation of the four substances is accurate.

Table 3.2.14 Results of CBOD Screening Testing of Potential CETANER™ Components

substance	% Biodegradation	
	5 days	28 days
Monoglyme	<1	<2
Diglyme	<1	3
2-Methoxyethanol	4	95
Diethylene glycol methyl ether (DEGME)	3	45
Glucose/Glutamic Acid (control)	68	140

Results of “microtox” testing, which is a measure of aquatic toxicity, are listed in Table 3.2.15. The larger the EC50 value, the less toxic is the substance. Thus, 2-methoxyethanol and DEGME are less toxic than the glymes, and all four are much less toxic than phenol, which is generally considered to be “toxic.”

hours, the selectivity varied from 53.8 to 52.0%.) The ethylene glycol selectivity of 31% was also the highest of the resins and was evidence that the product H₂O was acting to hydrolyze the feed. For instance, with a different catalyst, a 1996 Chinese patent teaches the use of toluene as an azeotropic agent to remove the product H₂O.

Table 3.2.16 Product Distribution for Condensation of 2-Methoxyethanol

<i>Catalyst</i>	A-15 Resin	A-15 Resin	Dowex 50X2-400	Nafion	Phosphate	γ-Al₂O₃	LA-30	ZSM-5
Temperature	95°C	120°C	120°C	120°C	150°C	150°C	150°C	145°C
Rxn Time (hrs)	5	5	5	5	5	5	5	5
Wt % in Feed								
2-methoxyethanol	49.93	52.38	50.05	49.99	50.06	50.05	50.01	50.02
% Conversion								
2-methoxyethanol	0.5	9.6	0.3	6.0	trace	trace	0.6	12.0
Wt % Selectivity								
DME(?)	1.3	0.8	0.0	0.4	N/A	N/A	0.0	0.3
MeOH	7.9	2.2	16.5	1.7	N/A	N/A	3.6	0.5
Methyl formate	0.0	0.0	0.0	0.0	N/A	N/A	0.0	0.0
EtOH	0.0	0.0	0.0	0.0	N/A	N/A	0.0	0.0
DMM	0.0	0.0	0.0	0.0	N/A	N/A	0.0	0.0
HOCH ₂ CH ₂ OH	30.5	31.3	16.1	17.0	N/A	N/A	7.3	33.1
1,4Dioxane	0.0	0.22	0.0	0.0	N/A	N/A	0.0	0.0
DEGME	1.6	4.8	1.4	2.5	N/A	N/A	1.5	3.0
diglyme	44.1	52.0	52.9	76.6	N/A	N/A	76.9	59.8
DEG	0.0	8.7	0.0	0.0	N/A	N/A	0.0	2.7
TEGME	0.0	0.0	0.0	0.0	N/A	N/A	0.0	0.0
triglyme	0.0	0.0	0.0	0.0	N/A	N/A	0.0	0.0
Unknowns (difference)	14.6	0.24	13.1	1.8	N/A	N/A	10.7	0.6

Calibrated response factors were used for all components except DME and unknowns. The light unknown was assumed to be DME.

The Dowex gel resin catalyst was much less reactive at 120°C. The acid-washed Nafion resin had 6% conversion at 120°C and the highest diglyme selectivity of 77%. Its diglyme selectivity was constant, from 76.4 to 76.8% over the 5 hours at 120°C. The Nafion catalyst apparently causes less hydrolysis of the feed, since the EG selectivity is only 17%. This observation is consistent with the fact that only 2.5% DEGME and no DEG is formed: DEGME can be formed from either the hydrolysis of diglyme or the reaction of the OH-group on 2-methoxyethanol molecule with the MeO-group of another. Thus, in either case, the Nafion is less aggressive towards the ether linkage.

Of the three amorphous/microcrystalline oxide catalysts -- a phosphate, γ-Al₂O₃ and LA-30 (SiO₂/Al₂O₃) -- only the SiO₂/Al₂O₃ showed any activity at 150°C. The materials probably require

higher temperatures. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ is silica-rich and tends to be a strong Bronsted acid, whereas the phosphate is a weak Bronsted acid and the $\gamma\text{-Al}_2\text{O}_3$ has Lewis acidity. The conversion is low, $\sim 1\%$, and the diglyme selectivity is comparable to the Nafion. At such low conversions, most of the H_2O product can be in the reactor head-space so that the similar selectivity compared to Nafion may be fortuitous - at higher conversions in this batch process, it may degrade rapidly as product H_2O remains in the condensed phase.

Finally the ZSM-5 catalyst was the most active, with 12% conversion at 145°C . Its selectivity of 60% was modest compared to the others and was in the range of 59.8 to 63.2% over the 5 hours. Like the A-15 resin, it causes hydrolysis, giving a constant EG selectivity of 33-36%. Other zeolites, untreated or modified, would be of interest to study. For instance, at these low conversions, 1,4-dioxane is produced in only small amounts over A-15 resin. At higher conversions, dioxane production could be retarded with smaller or partially blocked pores/cavities. Over active catalysts, addition of DME at low temperatures is one way that the literature teaches to increase glyme selectivity.

III. 3QFY99 Objectives

The objective for the next quarter is to complete a topical report.

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)

Performance of Mixtures of the Zn/Cr/K-Oxide and a Cu/Co-Oxide System

Catalysts such as the "Falter"-system (Zr/Zn/Mn/K-oxide) or the BASF-"Isobutylöl" catalyst (Zn/Cr/K-oxide) are active as well as selective in CO hydrogenation towards isobutanol. However, severe reaction conditions are needed to obtain good results. Therefore, we attempted to combine these catalysts with the IFP-catalyst system (i.e., Cu/Co-system). At moderate reaction conditions this system produces linear alcohols with high activity and selectivity, especially ethanol and n-propanol, which are believed to be intermediates in isobutanol synthesis.

The BASF-"Isobutylöl" catalyst LG47 was combined with the Cu/Co/Al/Zn/Na-oxide catalyst LG20 (Table 3.3.1). The catalysts were thoroughly mixed in a ball mill for 5 hours.

Table 3.3.1 Preparation of the Cr/Zn-Cu/Co-Mixtures

Catalyst	LG 47	LG 44	LG 46	LG 48	LG 49
Composition					
Zn/Cr/K:	1:0	10:1	5:1	2:1	1:1
Cu/Co/Al/Zn/Na (LG 47 : LG20)					
Synthesis method	Physical mixture (ball mill, 5 hr)				
Reduction	4 hrs at 513 K (1 K/min) with 5% H ₂ in N ₂				

Product samples were taken after 18 hr of stabilization at 350 (350°C-a) and 385°C. Then, after 3 hr of stabilization at 350°C, another sample was taken at this temperature to check for deactivation of the catalyst (350°C-b).

Results of the Cu/Co-catalyst (LG20) are provided in Table 3.3.2.

Table 3.3.2 STY [g/(l·h)] to Different Products for the Cu/Co/Al/Zn/Na-Catalyst (LG20)
Unit II, p = 125 bar, GHSV = 9400 h⁻¹. V_{cat} = 3.0 ml, D_{cat} = 0.25-0.71 mm, syngas 1:1

	350°C	385°C
methanol	338	15
ethanol	229	59
n-propanol	95	74
isobutanol	36	13

At the lower temperature of 350°C, an increasing Cu/Co-content led to improved space-time-yields of the linear alcohols ethanol and n-propanol, as well as the branched isobutanol (Figure 3.3.1).

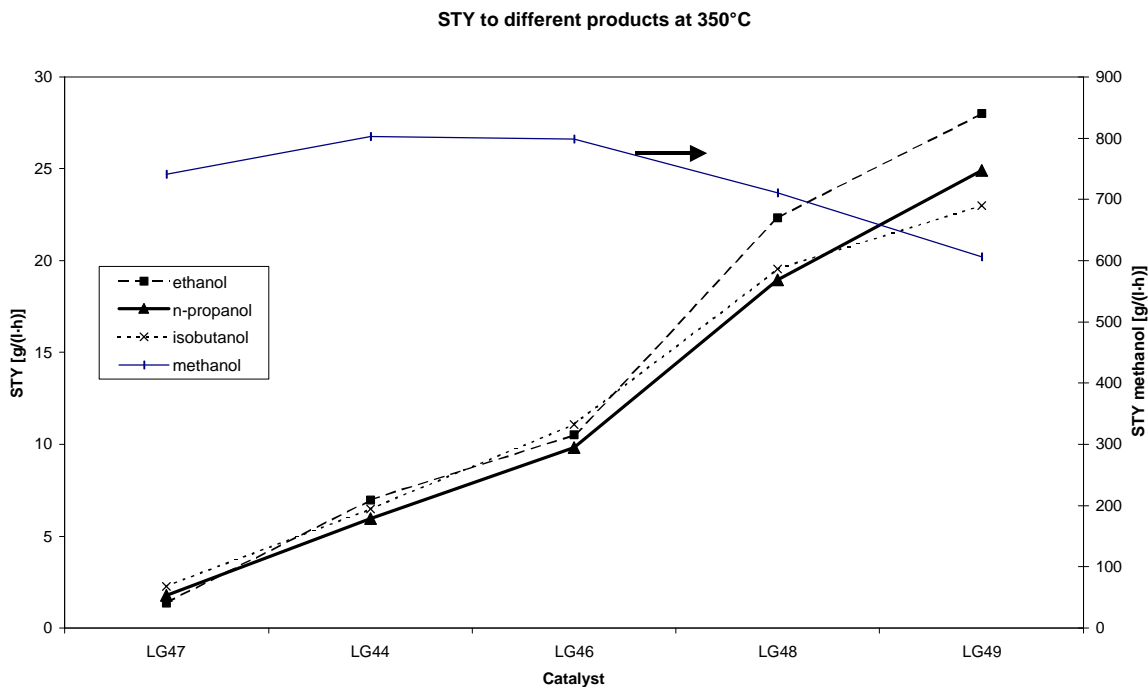
At the higher temperature, the conversion of the linear alcohols towards isobutanol by the Zn/Cr/K-oxide catalyst seemed to be significantly enhanced (Figure 3.3.2). Furthermore the ratio of isobutanol to its linear intermediates increased more strongly. Selectivity towards isobutanol increased at both temperatures because of a decrease in methanol productivity at the higher Cu/Co contents.

Table 3.3.3 Methane STY [g/(l·h)] for Different Zn/Cr-Cu/Co-Mixtures)
Unit II, p = 125 bar, GHSV = 10,000 h⁻¹. V_{cat} = 4.0 ml, D_{cat} = 0.25-0.71 mm, syngas 1:1

catalyst	LG47	LG44	LG46	LG48	LG49
350°C	<10	18	24	40	55
385°C	26	41	58	125	177
350°C-b	<10	16	17	18	28

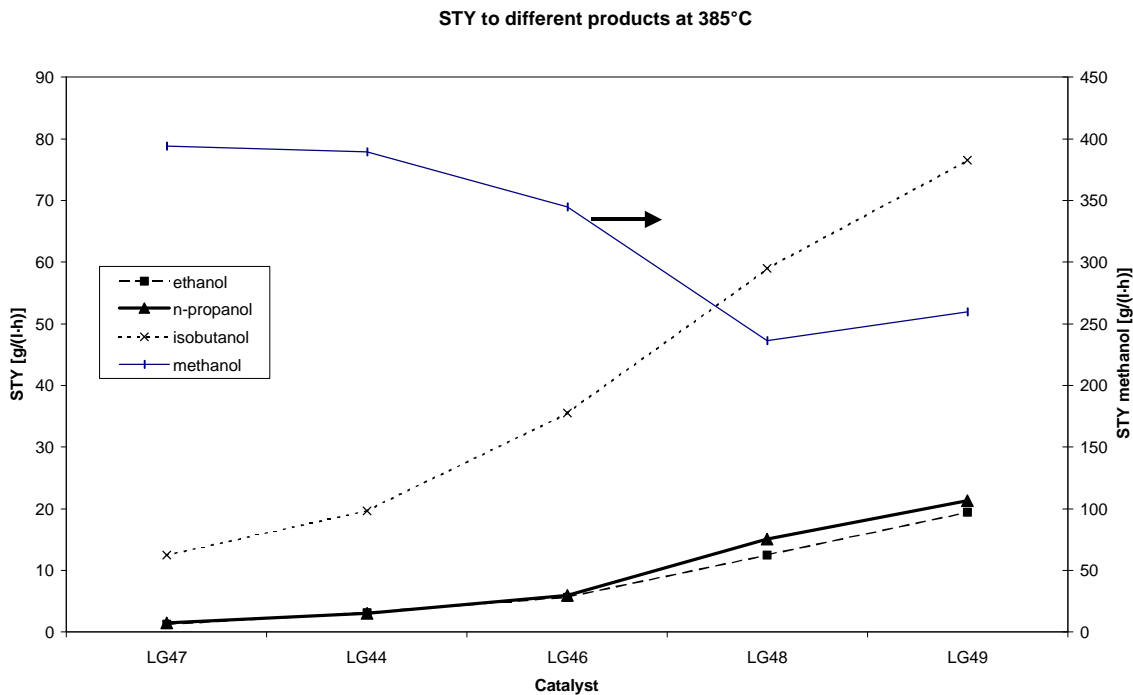
However, at the higher temperature, a considerable amount of the by-products methane and higher alkanes was produced (Table 3.3.3). The second measurement at 350°C showed an improved result towards methane. A change in catalytic behavior after the reaction time at 385°C could also be observed for the other reaction products (Figure 3.3.3). The development of productivities with increasing Cu/Co-content showed a pattern similar to that observed at 385°C (Figure 3.3.2). Isobutanol displayed a sharper increase in activity with increasing Cu/Co-content compared to the increase in linear alcohol activity.

We will try to use the Cu/Co-system at temperatures of 385°C by modifying the manufacturing procedure. The Zn/Cr/K-oxide catalyst will be pretreated at reaction conditions, after which it will be ground with the Cu/Co-system. In this way, the deactivation of the Cu/Co-system at higher temperatures may be prevented. If the alterations caused by the exposure of the Zn/Cr-system to syngas at 385°C are not reversed during the mixing procedure, the so obtained mixed catalyst should show an enhanced performance.



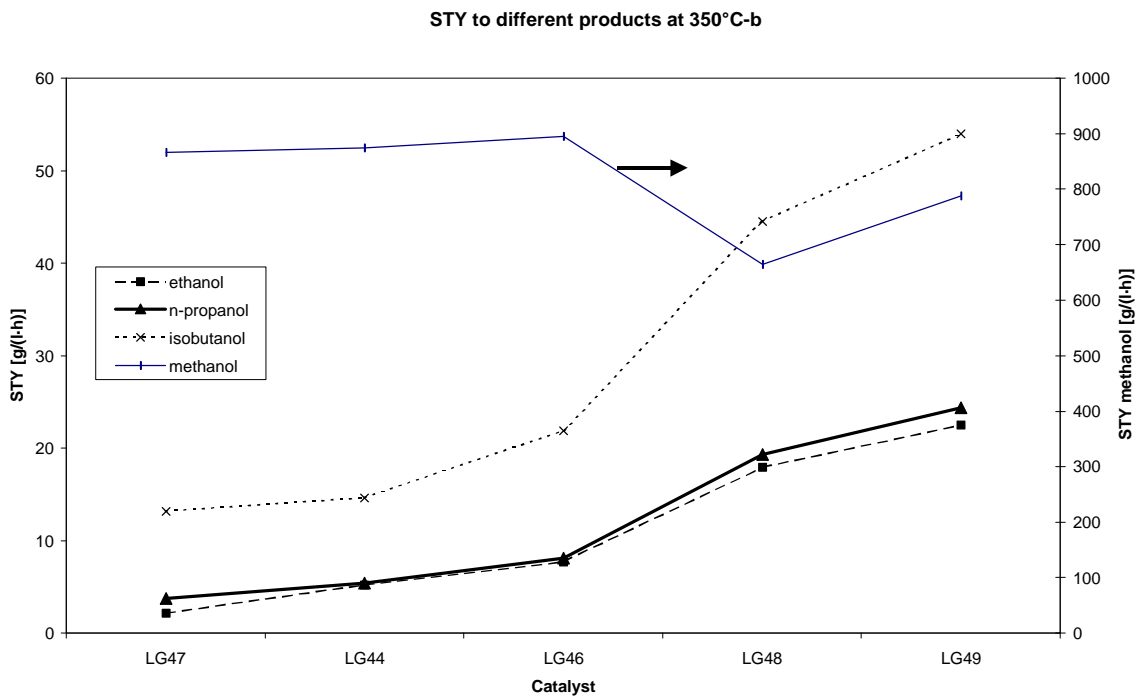
Unit II, $V_{\text{cat}}=3$ ml, $D_{\text{cat}}=0.25-0.71$ mm, $\text{GHSV}=10,000$ h⁻¹, $p=125$ bar, syngas 1:1.

Figure 3.3.1 STY to Different Products for Different Zn/Cr-Cu/Co-Mixtures at 350°C



Unit II, $V_{\text{cat}}=3$ ml, $D_{\text{cat}}=0.25\text{-}0.71$ mm, $\text{GHSV}=10,000$ h⁻¹, $p=125$ bar, syngas 1:1.

Figure 3.3.2 STY to Different Products for Different Zn/Cr-Cu/Co-Mixtures at 385°C



Unit II, $V_{\text{cat}}=3$ ml, $D_{\text{cat}}=0.25\text{-}0.71$ mm, $\text{GHSV}=10,000$ h⁻¹, $p=125$ bar, syngas 1:1.

Figure 3.3.3 STY to Different Products for Different Zn/Cr-Cu/Co-Mixtures at 350°C-b

Performance of the Cu/Zr/Zn/K-Oxide System

The 25 mol % coprecipitated copper catalyst LG37 was further investigated to increase its selectivity towards isobutanol. For this reason it was modified in several ways (Table 3.3.4). First, the catalyst was promoted with 0.25 wt % iron, which was previously used in combination with copper in the synthesis of higher, linear alcohols¹ (LG43). Furthermore, the influence of the manganese on catalytic activity towards isobutanol was investigated by synthesizing a manganese-free Cu/Zr/Zn-K-oxide catalyst (LG42).

Table 3.3.4 Preparation of the Zr/Zn/Cu-Oxide Catalysts

Catalyst	LG 37	LG 43	LG 42
Composition			
Cu:Zr:Zn:Mn	1:1:1:1	1:1:1:1	1:1:1:0
Cu content [mol%]	25	25	33
Promoter	4 mol% K	0,25 wt% Fe 4 mol% K	4 mol% K
Synthesis method		Coprecipitation (353 K, pH 9,0)	
Calcination		6 h at 723 K (4 K/min)	
Reduction		4 h at 513 K (1 K/min) with 5 % H ₂ in N ₂	
Promotor		4 mol % K	

Product samples were taken after 18 hours of stabilization at 350 (350°C-a) and 385°C. Then, after 3 hr of stabilization at 350°C, another sample was taken at this temperature to check for catalyst deactivation (350°C-b).

¹ A. Kiennemann et al., Appl. Cat. A **1993**, 99, 175-194.

**Table 3.3.5 Product distribution and STY [g/(l_{cat}·h), Cu/Zr/Zn/K-Oxide Catalyst
Unit II, p = 125 bar, GHSV = 9500 h⁻¹. V_{cat} = 4.0 ml, D_{cat} = 0.25-0.71 mm, syngas 1:1**

Catalyst	LG 37	LG 43	LG 42
		Fe-impregnated	Mn-free
Temperature [°C]	350	350	350
Liquid product distribution			
% methanol	88	78	74
% ethanol	1	4	2
% n-propanol	1	3	1
% i-butanol	3	2	2
% 2-methylbutanol-1	<1	<1	<1
STY [g/(l_{cat}·h)]			
Methane	22	<10	26
Methanol	973	283	880
Ethanol	13	14	20
n-propanol	15	10	14
i-butanol	51	8	27
2-methylbutanol-1	5	2	5

**Table 3.3.6 Product Distribution and STY [g/(l_{cat}·h), Cu/Zr/Zn/K-Oxide Catalyst
Unit II, p = 125 bar, GHSV = 9500 h⁻¹. V_{cat} = 4.0 ml, D_{cat} = 0.25-0.71 mm, syngas 1:1**

Catalyst	LG 37	LG 43 Fe-impregnated	LG 42 Mn-free
Temperature [°C]	385	385	385
Liquid product distribution			
% methanol	59	46	63
% ethanol	3	4	2
% n-propanol	3	5	2
% i-butanol	11	8	6
% 2-methylbutanol-1	2	2	1
STY [g/(l_{cat}·h)]			
methane	69	53	49
methanol	297	165	279
ethanol	18	15	9
n-propanol	23	17	7
i-butanol	77	28	29
2-methylbutanol-1	14	6	5

At 350°C, impregnation of the Cu/Zr/Zn/Mn/K-oxide catalyst with iron led to a strongly diminished overall activity (Table 3.3.5). Selectivity towards linear alcohols was increased, which did not lead to increased isobutanol selectivity.

Exclusion of the manganese component showed a negative influence on HAS. Isobutanol activity as well as selectivity was lessened over the Mn-free catalyst at this temperature (Table 3.3.5).

At 385°C, the iron-promoted catalyst again showed an overall reduced activity compared to the iron-free Cu/Zr/Zn/Mn/K-oxide catalyst (Table 3.3.6). The changes in selectivity towards the various products were the same as those observed at the lower reaction temperature. The selectivity towards ethanol and n-propanol were enhanced, whereas isobutanol selectivity was diminished. At 385°C the exclusion of manganese in the Cu/Zr/Zn/K-oxide catalyst led to a comparable overall activity. However, selectivity shifted towards methanol.

Summary and Outlook

The alteration of the Cu/Zr/Zn/Mn-system with 0.25 wt % iron did not improve isobutanol synthesis. The exclusion of manganese from the Cu/Zr/Zn/Mn-system caused a deterioration of HAS.

The physical mixing of a Zn/Cr-catalyst with a Cu/Co-system led to an improved isobutanol activity, as well as selectivity. With the 1:1-mixture, an isobutanol yield of 76 g/(l·h) was reached at 385°C. As expected for a catalyst with this high Cu/Co-content, methanization was rather high at this temperature. The reaction time at 385°C led to changes in the catalyst, yielding improved results at 350°C. The repetition measurement at 350°C yielded 54 g/(l·h) isobutanol, with much lower methanization. In the future, the Zn/Cr-catalyst will be pretreated with syngas under reaction conditions prior to the mixing, to prevent the exposure of the Cu/Co-sites to higher temperatures.

TASK 5: PROJECT MANAGEMENT

5.1 Liquid Phase Fischer-Tropsch Demonstration

A meeting was held with DOE personnel on 7 January to discuss the F-T III/F-T IV data analysis and present a data package to DOE. The data show excellent heat/mass/elemental balance and fully support the preliminary conclusion of a highly successful demonstration during F-T IV. The presentation was well received, and DOE was impressed at the depth of the data analysis.

An initial draft of a topical report on F-T III/F-T IV was completed mid-February and sent to SSFI (Shell Synthetic Fuels, Inc.) for their technical and confidentiality review. We received their comments in early March and incorporated them into the report. SSFI reviewed the revised draft and a final approval was given to release the report. The draft was submitted to DOE at the end of March, meeting the schedule agreed upon with DOE. SSFI provided significant input and full cooperation in completing the report in a detailed and timely fashion.