Appendix D. TECHNICAL AND EXPERIMENTAL DATA

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I. TASK 2: Catalyst Research

A. Methanol Homologation

1. Introduction

Investigations on the novel low pressure methanol homologation system have continued. This quarter we completed studies on catalyst lifetime and characterization. The lifetime studies confirm our suspicion that the catalyst is stable and the apparent loss of activity is due to the buildup of methane in the reactor. The characterization studies have led to the unambiguous identification of the materials isolated from the reactor at the end of the homologation reactions. The characterization of these components has provided us with a unique opportunity to explore the detailed chemistry of this system.

2. Catalyst Recycle/Lifetime Studies

In the first quarter of this contract we addressed the question of catalyst lifetime and stability. We showed that the decline and eventual halt in gas uptake during a homologation reaction were not due to catalyst instability. Rather, we obtained evidence suggesting that the decline and halt in gas uptake were due to the buildup of inert gases in the reactor and eventual "suffocation" of the catalyst (this was shown by the observation that activity could be restored by simply venting the reactor and repressurizing with fresh syngas). This problem is therefore an artifact of carrying out these reactions in a batch reactor.

During the second quarter of this contract we have analyzed the offgas from the homologation reaction in order to determine the identity of the inert gases. Some typical gas analyses are shown in Table 1. These results show that methane formation is substantial and often accounts for 50% of the vented gas. Methane is almost certainly formed via catalytic hydrogenation of methanol:

$$CH_3OH + H_2 \longrightarrow CH_4 + H_2O$$

On a molar basis, the amount of methane observed represents a 5-10 % conversion of methanol. The H_2/CO ratio is unchanged from the 2:1 feed ratio. Apparently, H_2 depletion via methane formation is offset by CO depletion from the formation of acetic acid. As a result the feed and consumption ratios are nearly equal and match that required stoichiometrically for the homologation of methanol. The small amount of CO_2 shows that little water-gas shift occurs.

In addition to methane, several volatile organic products are formed during the reaction. These include dimethyl ether, methyl ethyl ether, acetaldehyde, and diethyl ether. The partial pressures of these components will be significant at the operating temperature (140°C) and also contribute to catalyst suffocation. Based on our observations, we estimate that the syngas partial pressure drops from an initial 900 psi to 300-400 psi during the course of a homologation run.

Key to Table 1

ID-#	
1 Catalyst	Compound added as catalyst precursor.
2 mmol	Amount of catalyst precursor, mmoles.
3 Cocatalyst	Compound added as cocatalyst.
4 mmol	Amount of cocatalyst added, mmoles.
5 Additive	Catalyst additives employed.
6 mmol	Amount of catalyst additive, mmoles.
7 Promoter	Other promoter employed.
8 mmol	Amount of promoter, mmoles.
9 MeOH(mL)	Amount of methanol used.
10 Pressure,psi	Reaction pressure in psig.
11 H_2/CO	Syngas molar (volume) ratio.
12 Temp.,°C	Reaction temperature.
13 Time,hr	Reaction time in hours.
14 Gas analysis, mole%:	
15 H_2	Hydrogen
16 CO	Carbon monoxide
17 CH_4	Methane
18 CO_2	Carbon dioxide

Table 1. Representative Reactor Offgas Analyses

KGM-#	5-87	5-101
1 Catalyst	$RuCl_3$	$RuCl_3$
2 mmole	4	4
3 Cocatalyst	C4	C4
4 mmole	2	2
5 Additive	A109	A110
6 mmole	2	2
7 Promoter	A28	A28
8 mmole	40	40
9 MeOH, mL	40	40
10 Pressure, psig	1000	1000
11 H_2/CO	2:1	2:1
12 Temp., °C	140	140
13 Time, h	2	2
14 Gas Analysis, mole %		
15 H_2	31	57
16 CO	14	32
17 CH_4	53	9
18 CO_2	2	2

Experimental procedure: B(a); Analytical procedure C(c); Key on page 21.

3. Catalyst Characterization Studies

The crystalline product isolated from the homologation reaction has been unequivocally identified. This complex results from the reaction of C4, A25, and A28 in the presence of carbon monoxide. Similar complexes have been described in the literature and characterized by X-ray crystallography. This type of complex has also been isolated from reaction runs with other A25-type additives. We have found that these complexes can be easily synthesized in high yield and on a large scale by the reaction of these components in methanol. All of these new complexes have been characterized by multinuclear NMR, IR, and, in some cases, elemental analysis.

Ruthenium is present at the end of these reaction as a well known complex (C16) formed from ruthenium, A28, and carbon monoxide. This species is readily identified by infrared spectroscopy.

4. Mechanistic Studies

The crystalline complex (C23) isolated at the end of these reactions accounts for >95 % of the C4 and A25 charged to the reactor. This suggests that C23 may be an active catalytic component for methanol homologation. We now have evidence supporting this possibility.

We find that C23 can be charged to the reactor in place of C4 and A25 and used to homologate methanol with no change in activity or selectivity. This is demonstrated in Table 2 which shows a comparison of results obtained with C23 versus a charge made up of an equal amount of C4 and A25. At the end of the reaction C23 was again isolated in high yield.

Structurally, C23 is uniquely postured to form either acetaldehyde or acetic acid (C16 is known to catalyze the hydrogenation of aldehydes and we have evidence that this occurs in the homologation system; see below). This possibility has been explored by investigating the chemistry of this complex.

At 140°C in methanol solution (N_2 atmosphere), C23 produces acetic acid very slowly; after 45 min only 0.12 equiv acetic acid (based on C23) are formed. This rate is much too slow to account for the formation of acetic acid during the catalytic reaction. However, the addition of CO significantly accelerates this reaction. Thus, heating C23 under 90 psi CO results in the formation of 0.5 equiv acetic acid in 15 min (140°C, methanol). Presumably, the CO pressures used for the catalytic reaction would result in an even higher reaction rate. Alternatively, if C23 is treated with H_2 (400 psi, 140°C, MeOH), acetaldehyde is formed quantitatively. No ethanol and only a trace of acetic acid are observed during this hydrogenolysis. Finally, treatment of C23 under catalysis conditions (2:1 H_2/CO, 140°C, MeOH, 1000 psig) but with no ruthenium or additives results in the formation of a mixture of acetaldehyde and acetic acid. The acetaldehyde selectivity is 80 % (Table 3). Again, no ethanol is observed in the absence of ruthenium.

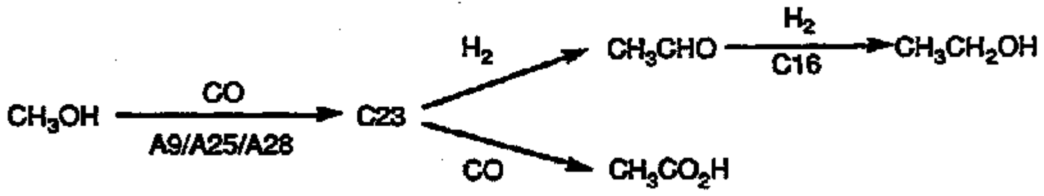
These results show that C23 can be converted to both acetaldehyde and acetic acid, depending on the reaction conditions. In addition, under homologation reaction conditions, this complex forms acetaldehyde with the same selectivity as that observed for ethanol. This is compelling evidence that this complex is not only an intermediate in the catalytic cycle but also serves as the branch point for acetaldehyde/ethanol or acetic acid. In order to provide further evidence for this possibility it is necessary to determine the rate of acetaldehyde and acetic acid formation by C23 to see if it matches that observed for homologation. This will be the topic of future studies.

During the course of these studies, it became apparent that C23 is not completely soluble under our standard reaction conditions (140°C, 0.05 M C23, methanol). If this is true and C23 is a key catalytic component, then the homologation rate should be zero-order in C23 if the amount of C23 charged is greater than that which will dissolve under reaction conditions. To test this possibility we determined initial gas uptake rate at various C23 concentrations. These data are shown graphically in Figures 1 and 2. Figure 2 clearly shows that the increase in rate levels off at higher C23 charges. At lower C23 (0.2-1.0 mmole) concentrations the rate approximates first order in C23. More data need to be collected in this region to further define this result. In addition, the solubility of C23 in methanol at 140°C needs to be accurately determined to see if it matches the point where the curve in Figure 2 begins to level off. Finally, Figure 3 shows that the selectivities to both ethanol and methane do not change with C23 concentration.

We have also carried out a brief study of the dependence of homologation rate on A28 concentration. We find that over a concentration range of 1.0-0.1 M the rate is zero-order in [A28]. These date are depicted graphically in Figures 4 and 5. Figure 6 shows that the ethanol and methane selectivities are independent of [A28] as well. A future experiment will examine the homologation rate with no A28. It may be possible that A28 is only required to generate C23 and C16; no A28 beyond this amount is required for catalysis.

As we have described previously, acetaldehyde is a detectable intermediate during the homologation of methanol. Obviously, the rate of acetaldehyde hydrogenation is rather slow. There is much precedent in the literature for the decarbonylation of acetaldehyde to methane. This reaction would not be unexpected in our system given the catalyst components we employ. If true, this undesired side reaction would lower the ethanol selectivity. In order to test this possibility we carried out a homologation run in the presence of a small amount of $^{13}CH_3{}^{13}CHO$. The products were then analyzed by gas chromatography/mass spectrometry. These results show that no back reaction occurs; the label is incorporated entirely in ethanol and no labeled methane is observed. Moreover, no label is found in acetic acid. These results were further confirmed by a homologation reaction in the presence of propionaldehyde. This aldehyde is only hydrogenated to propanol and no ethane or propionic acid are observed. These results show that acetaldehyde is an irreversibly-formed intermediate on the pathway to ethanol only.

Our current model for this reaction is shown in the reaction scheme below. First, methanol, CO, and several of the catalyst components react to form C23. This species is very stable and appears to be a thermodynamic sink for most of these catalyst additives. The reaction then branches to form either acetaldehyde (hydrogenation) or acetic acid (carbonylation). Acetaldehyde is then hydrogenated by the ruthenium component, C16, to ethanol. Consistent with this, we find that a homologation system with no ruthenium yields acetaldehyde in nearly the same selectivity as would be expected for ethanol (Table 4). The ethanol selectivity is therefore a function of the relative rates of hydrogenolysis and carbonylation of C23. Further experiments designed to confirm and exploit this possibility are in progress. At the present time we do not know how methane is formed; this will also be the subject of future experimentation.



Key to Tables 2-5

ID-#	
Catalyst	Catalyst precursor.
mmole	Amount of catalyst precursor, mmoles.
Catalyst	Catalyst precursor.
mmole	Amount of catalyst precursor, mmoles.
Promoter	Catalyst additive.
mmole	Amount of catalyst additive, mmoles.
MeOH (mL)	Amount of methanol used.
Pressure (psi)	Reaction pressure in psig.
H_2/CO	Syngas molar (volume) ratio.
Temp (°C)	Reaction temperature.
Time (h)	Reaction time in hours.
Additive	Catalyst additive.
mmoles	Amount of catalyst additive in mmoles.
SELECTIVITY (MOLE %)	Selectivities, based on methanol consumed.
DME	Dimethyl ether.
MEE	Methyl ethyl ether.
AcH	Acetaldehyde.
Et_2O	Diethyl ether.
EtOH	Ethanol.
MeOAc	Methyl acetate.
DMA	Dimethyl acetal.
EtOAc	Ethyl acetate.
MEA	Methyl ethyl acetal.
HOAc	Acetic acid.
EtOH	Selectivity to free ethanol.
EtOH Equiv	Selectivity to other ethanol equivalents.
Total EtOH	Total ethanol selectivity.
Total Acetic	Total selectivity to acetic acid.

Table 2. Comparison Run with C23 and C16 as Catalyst Charge

KGM-#	4-136A	5-29
Catalyst	C4	C23
mmole	2	2
Catalyst	$RuCl_3$	C16
mmole	4	4
Promoter	A28	A28
mmole	40	40
MeOH (mL)	40	40
Pressure (psi)	1000	1000
H_2/CO	2:1	2:1
Temp (°C)	140	140
Time (h)	2.5	2
Additive	A25	none
mmoles	2	-
SELECTIVITY (MOLE %)		
MEE	6.1	8.1
AcH	1.9	12.1
Et_2O	1.2	0.7
EtOH	68.9	55.5
MeOAc	10.2	14.5
DMA	0.3	1.7
EtOAc	4.5	2.3
MEA	0.2	0.4
HOAc	6.2	4.3
EtOH	69	55
EtOH Equiv	16	26
Total EtOH	85	82
Total Acetic	15	18

Experimental Procedure: B(a); Analytical Procedure: C(c); Key on page 27.

Table 3. Exposure of C23 to Catalytic Conditions

KGM-#	5-69
Catalyst	C23
mmole	0.308
Catalyst	none
mmole	0
Promoter	none
mmole	0
MeOH (mL)	15
Pressure (psi)	890
H_2/CO	2:1
Temp (°C)	140
Time	7 min
Additive	none
SELECTIVITY (MOLE %)	
MEE	0.0
AcH	6.0
Et_2O	0.0
EtOH	0.0
MeOAC	19.8
DMA	74.2
EtOAc	0.0
MEA	0.0
HOAc	0.0
AcH (Total)	80
HOAc (Total)	20

Experimental Procedure: B(c); Analytical Procedure: C(c);
Key on page 27.

Table 4. Catalytic Reaction Without Ruthenium

KGM-#	5-20
Catalyst	C4
mmole	8
Catalyst	none
mmole	-
Promoter	A28
mmole	80
MeOH (mL)	60
Pressure (psi)	1000
H_2/CO	2:1
Temp (°C)	140
Time (h)	2.5
Additive	A25
SELECTIVITY (MOLE %)	
MEE	0.0
AcH	36.9
Et_2O	0.0
EtOH	0.0
MeOAc	30.2
DMA	24.2
EtOAc	0.0
MEA	0.0
HOAc	8.7
AcH (Total)	61
HOAc (Total)	39

Experimental Procedure: B(a); Analytical Procedure: C(c); Key on page 27.

Figure 1. Gas Uptake vs. Time at Different C23 Charges.
Conditions: 4 mmole C16
40 mmole A28
40 mL MeOH
140°C
1000 psig 2:1 H_2/CO
Experimental procedure B(a)
Analytical procedure C(c).

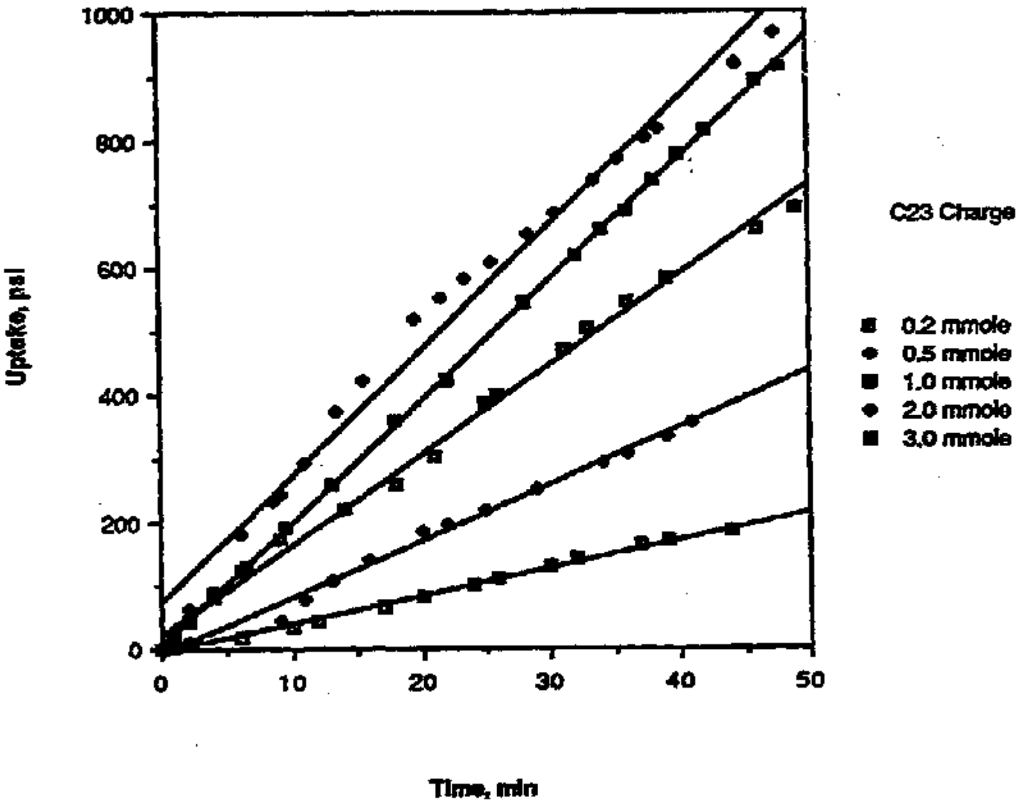


Figure 2. Initial Rate vs. C23 Charge.
Conditions: Same as Figure 1.

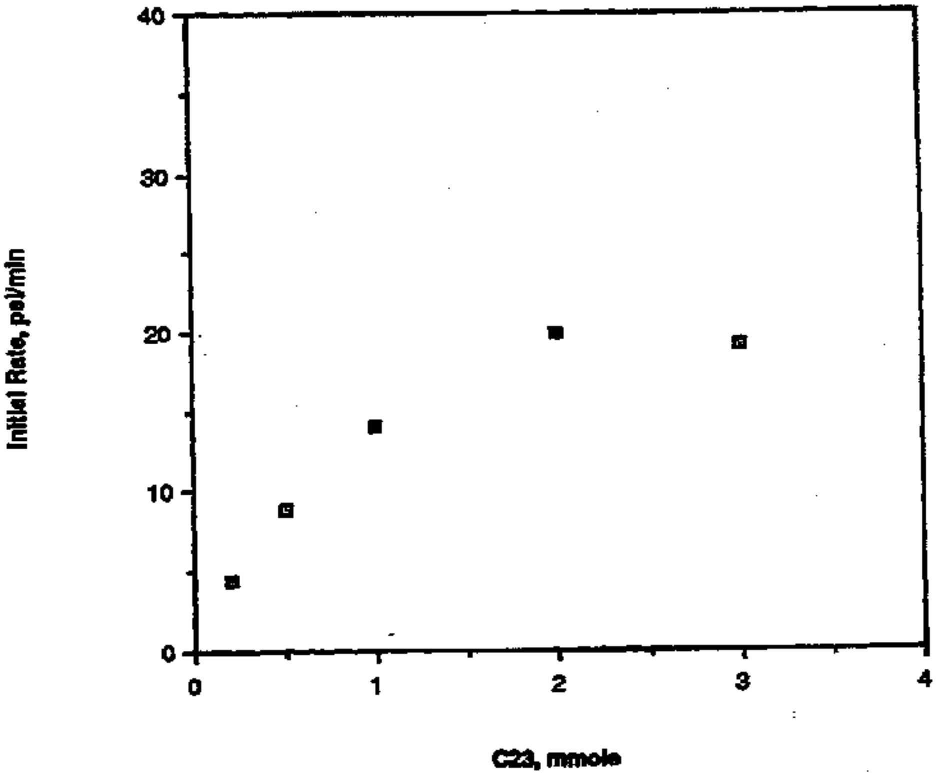


Figure 3. Selectivity as a Function of C23 Charge.
Conditions: Same as Figure 1.

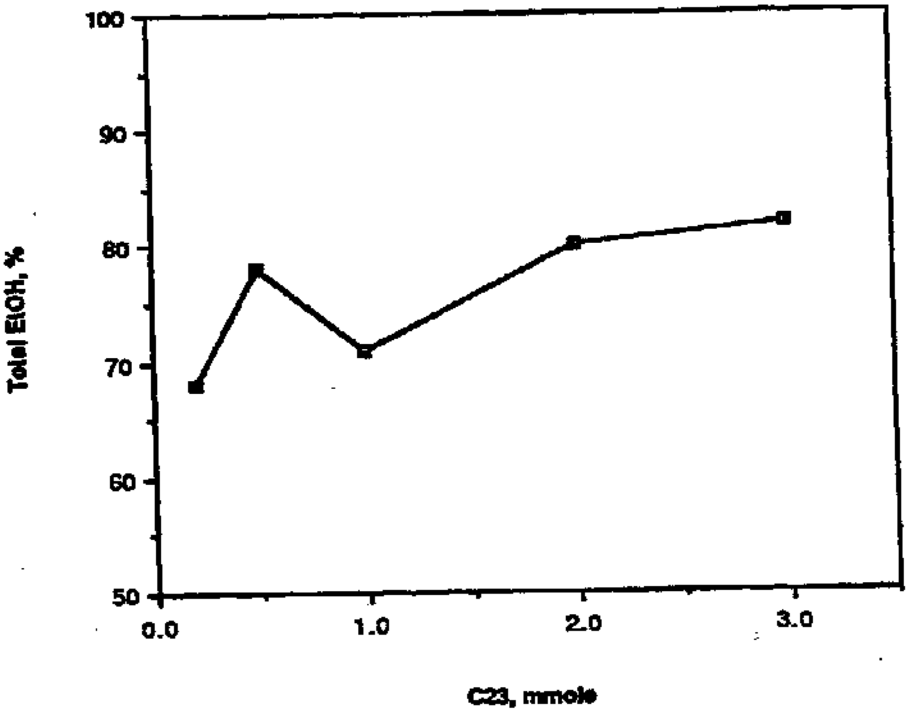


Figure 4. Uptake vs. Time at Different A28 Charges.
Conditions: 4 mmole C16
2 mmole C23
40 mL MeOH
140°C
1000 psig 2:1 H_2/CO
Experimental procedure B(a)
Analytical procedure C(c).

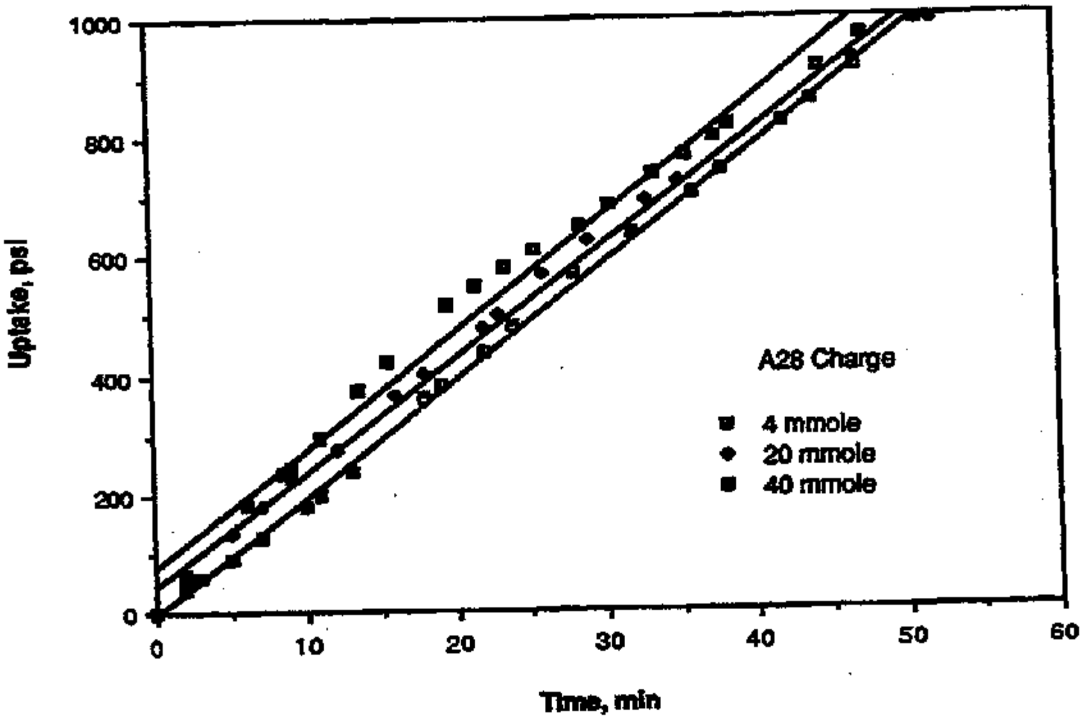


Figure 5. Initial Rate vs. A28 Charge.
Conditions: Same as Figure 4.

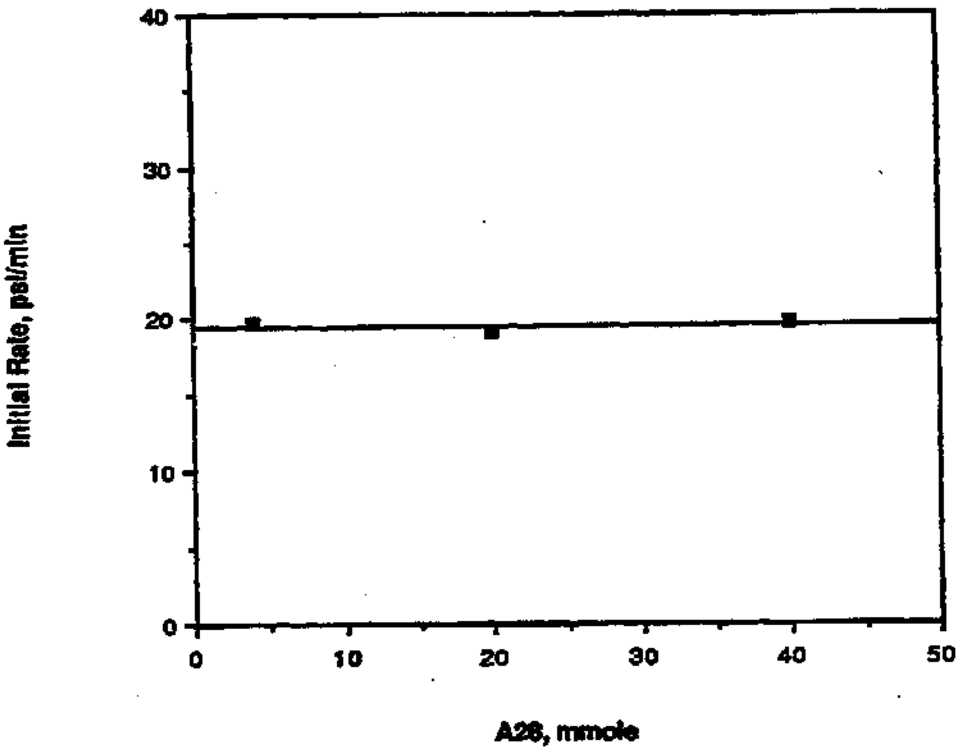
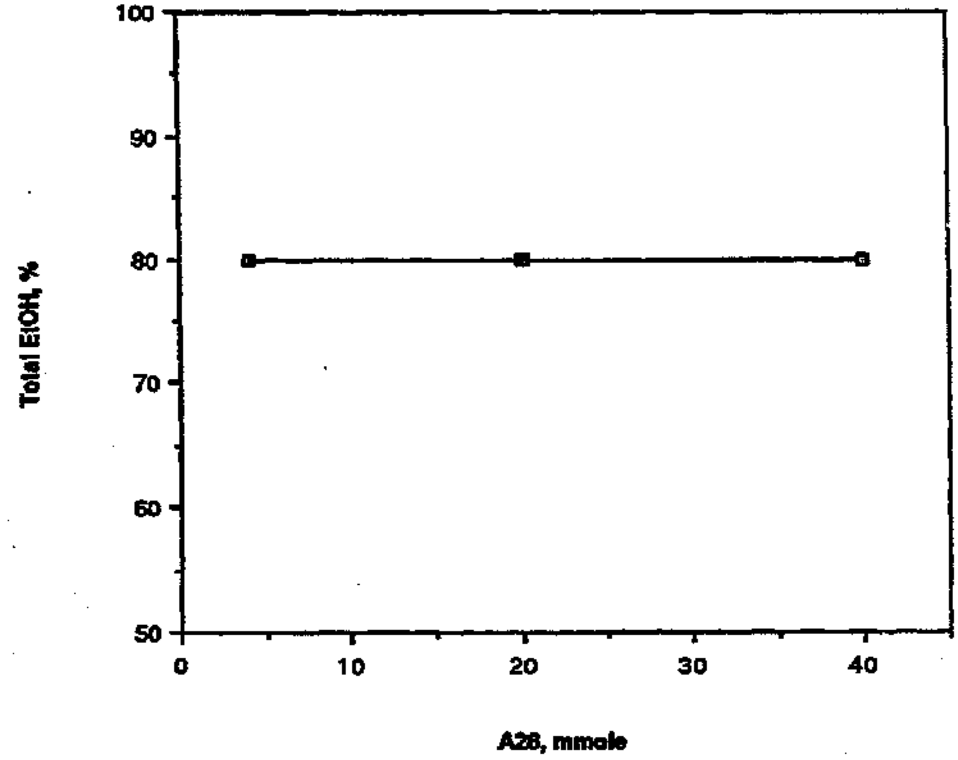


Figure 6. Selectivity as a Function of A28 Charge.
Conditions: Same as Figure 4.



5. Studies of New Additives

We have prepared three new additives (A108, A109, and A110) which are slightly different structurally from A25. These new additives were tested for methanol homologation activity and the results are shown in Table 5. Both additives A109 and A110 show a selectivity very close to that observed for A25. On the other hand A108 gives ethanol in very poor selectivity.

Table 5. Effects of Several Novel Catalyst Additives

KGM-#	5-46	5-87	5-101
Catalyst	C4	C4	C4
mmole	2	2	2
Catalyst	RuCl$_3$	RuCl$_3$	C16
mmole	4	4	4
Promoter	A28	A28	A28
mmole	40	0	40
MeOH (mL)	40	40	40
Pressure (psi)	1000	1000	1000
H$_2$/CO	2:1	2:1	2:1
Temp (°C)	140	140	140
Time (h)	1	2	1
Additive	A108	A109	A110
mmoles	2	2	2
SELECTIVITY (MOLE %)			
MEE	0.5	5.4	5.1
AcH	6.1	4.3	9.6
Et$_2$O	0.2	0.6	0.4
EtOH	2.5	54.9	43.7
MeOAc	74.1	21.9	27.0
DMA	1.4	0.3	0.5
EtOAc	0.3	4.7	4.4
MEA	0.1	0.1	0.1
HOAc	14.7	7.5	8.8
EtOH	2	55	44
EtOH Equiv	9	16	21
Total EtOH	11	71	65
Total Acetic	89	29	35

Experimental Procedure: B(a); Analytical Procedure: C(c);

Key on page 27.

B. Direct Syngas Conversion by Ruthenium Catalysts

1. Introduction

Because of the good catalytic activity of promoted homogeneous ruthenium catalysts for syngas conversion, we continued to investigate the effects of various additives to these catalysts. The goal of these experiments is to improve the behavior of the catalyst system at lower pressures. Improvements are being sought mainly in overall catalyst activity, with a lesser emphasis on selectivity to C_2+ alcohols and stability.

Recently, we found that when additives A16 and A92 were added to the catalyst system, not only was the activity increased, but more importantly, the production of higher alcohols increased significantly. Furthermore, the system is very selective in producing alcohols. Only small amounts of acetates or formates were observed. It is because of these good characteristics that we decided to investigate this system more closely this quarter.

We carried out some experiments at pressures lower than 5000 psi of syngas and found that the system still showed activity at pressures as low as 2000 psi. As expected, both the total activity and selectivity to higher alcohols declined as the pressure was lowered.

We also carried out experiments varying other components and conditions of the reaction, and in some instances made further improvements on the catalyst activity and selectivity.

2. Effects of Pressure

In this quarter we concentrated our efforts on examining the catalyst system of Ru/A16/KI/A92 more closely. Since this catalyst system showed relatively high activity at 5000 psi and 230 °C, we decided to look at its activity at lower pressures and the same temperature. The results are summarized in Table 6. As expected, the activity of the catalyst system decreases as a function of the operating pressure. From the results of these experiments, we were also able to get some information on the dependence of activity on the operating pressure. Figure 8 is a plot of ln(rate) vs. ln(pressure) and it shows a relationship close to linear. The slope of the line is close to 2 which signifies a second order dependence.

The selectivity to higher alcohols is apparently also a function of the pressure. As shown in Table 6, and also in Figure 7, the percentage of higher alcohols dropped from 35% to less than 5% by weight when going from 5000 psi to 2000 psi.

The ratio of H_2/CO is also important to the selectivity to higher alcohols. As shown in Figure 9, a CO-rich syngas (2:1 CO/H_2) is better for the formation of higher alcohols despite a decrease in the total activity of the catalyst system as compared to experiments using a 1:1 syngas. Both the total activity and the selectivity to higher alcohols decrease when hydrogen-rich syngas (2:1 H_2/CO) is used.

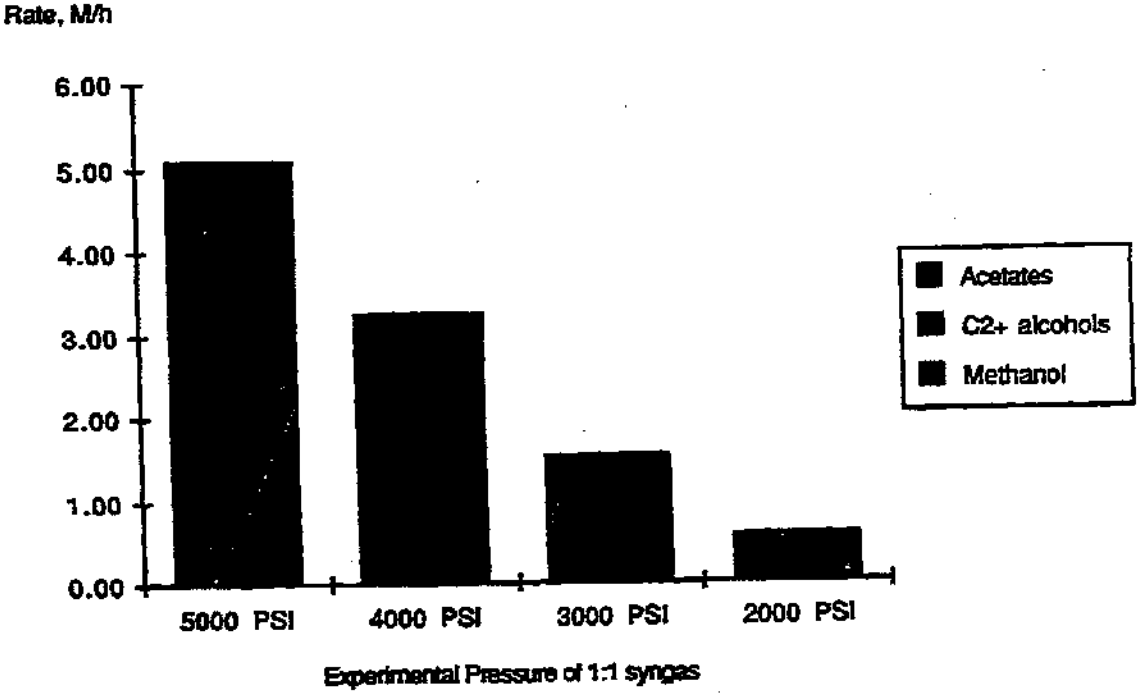
3. Effects of Solvents and Promoters

Solvent is also an important factor for the activity and selectivity of the system. We found that 1,3-dimethylethyleneurea was a very good solvent for the production of higher alcohols. The total activity of the system in this solvent is somewhat lower than the system in phenyl ether, but the rate to higher alcohols is much higher in this solvent. When one looks at the carbon efficiency, it is actually better. Similar results were obtained using N-methylpyrrolidone as solvent. Figure 10 shows a comparison of results for the catalyst system in several solvents.

We have been using KI as the source of iodide. Lately, we briefly experimented using LiI as the iodide source and found that it further increases the production of higher alcohols, especially in the polar solvent 1,3-dimethylethyleneurea. The total activity is almost unchanged (see Figure 11 for comparison). Methyl iodide retarded the activity of the catalyst system completely. Experimental and analytical details for these and the other experiments on direct syngas conversion with ruthenium catalysts are reported in Table 7.

We have done some analyses on the gas mixture in the reactor after the reaction was stopped. The results are shown in Table 8. We found that the formation of methane is very small when the solvent is phenyl ether or 1,3-DMEU. About 4% of the offgas is methane. The methane content is somewhat higher when using NMP as the solvent (about 10% of the offgas). The production of carbon dioxide is high especially when the production of C_{2+} alcohols is high (close to 30% of the off gas is CO_2). Carbon dioxide is likely the product of the water-gas shift reaction. Since water is produced in the formation of ethanol, larger amounts of CO_2 are therefore expected whenever ethanol is produced in larger quantities.

Figure 7. A Comparison of the Rate to Alcohols at Different Pressures for the Catalyst System of Ru/A16/KI/A92 in Phenyl Ether.



Experimental Conditions: 230 °C; 3.0 h; 1:1 CO/H_2; 14 mmoles [Ru]; 7 mmoles A16; 30 mmoles KI; 93 mmoles A92; 40 g Phenyl ether.

Figure 8. A Plot of Ln ($Rate_{total}$) vs. Ln (Pressure) Showing the Dependence on Pressure for the Catalyst System of Ru/KI/A16/A92.

Slope = 2.1

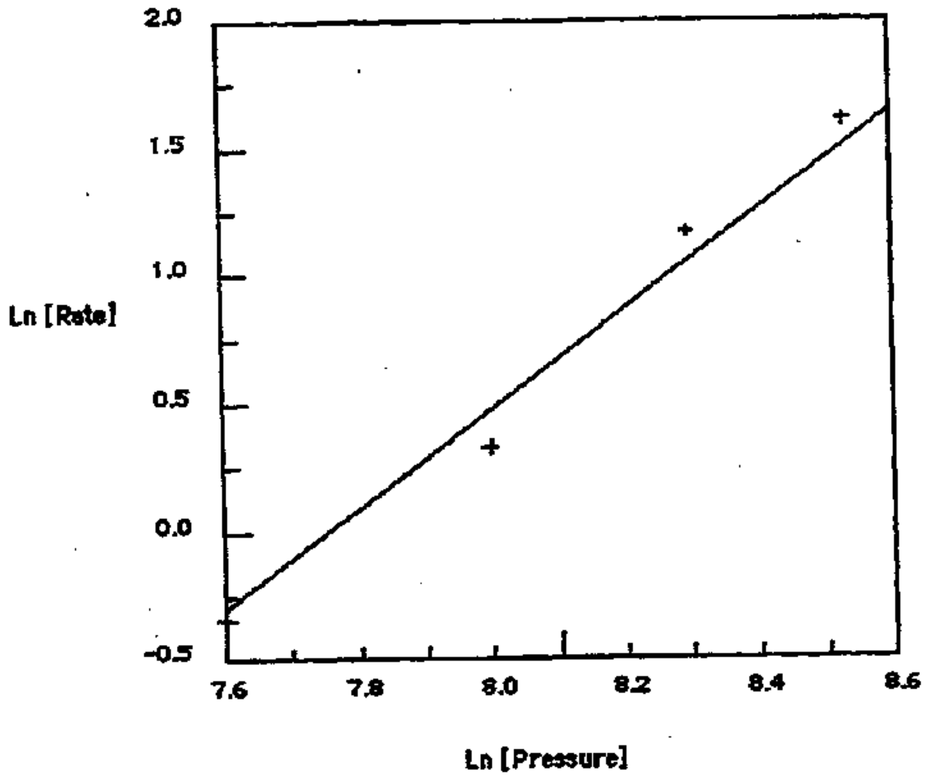
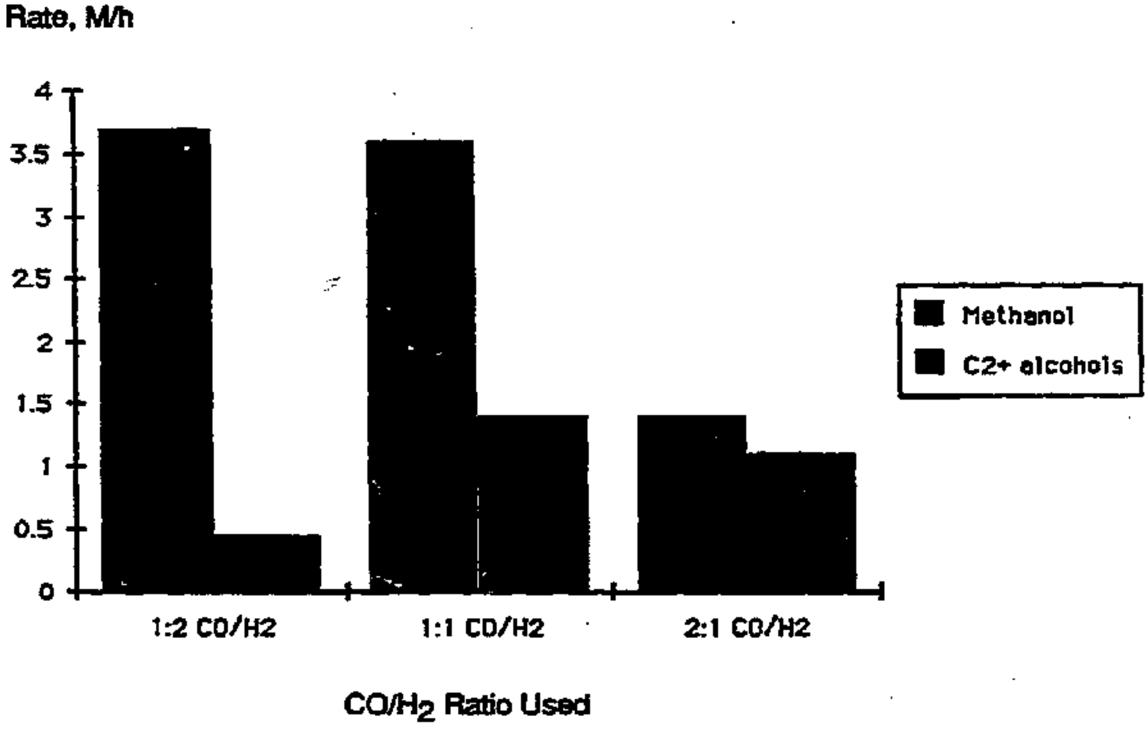
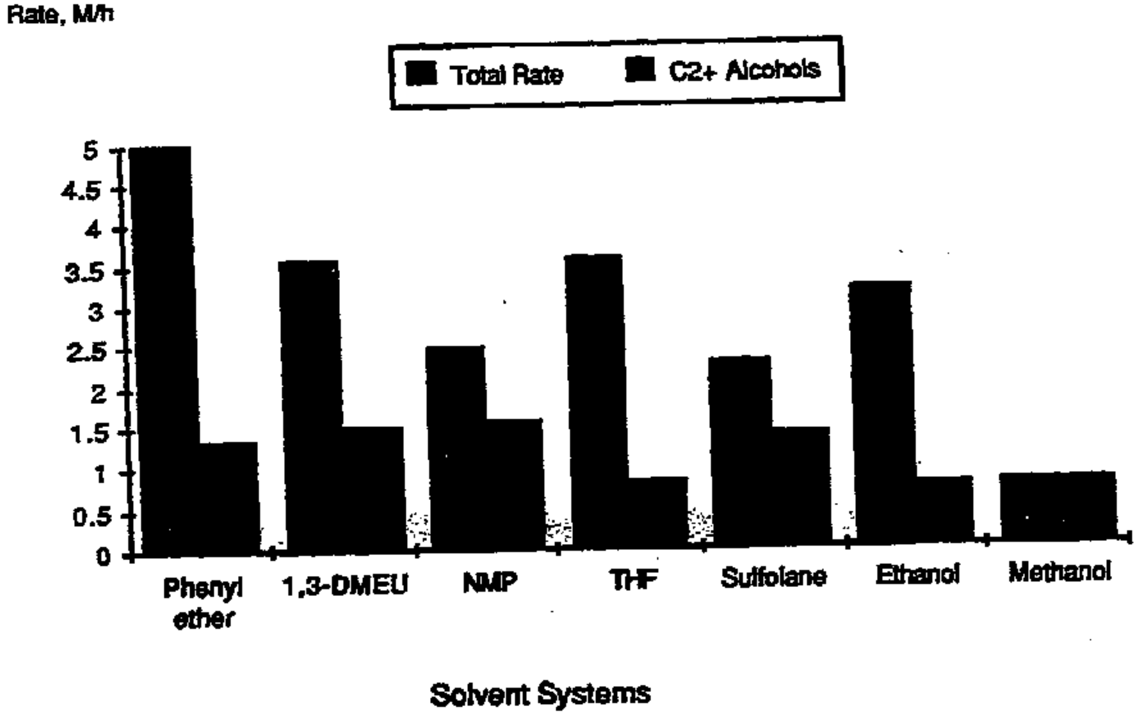


Figure 9. A Graphical Comparison of the Production of Methanol and C_{2+} Alcohols in Experiments Using Different Ratios of Syngas.



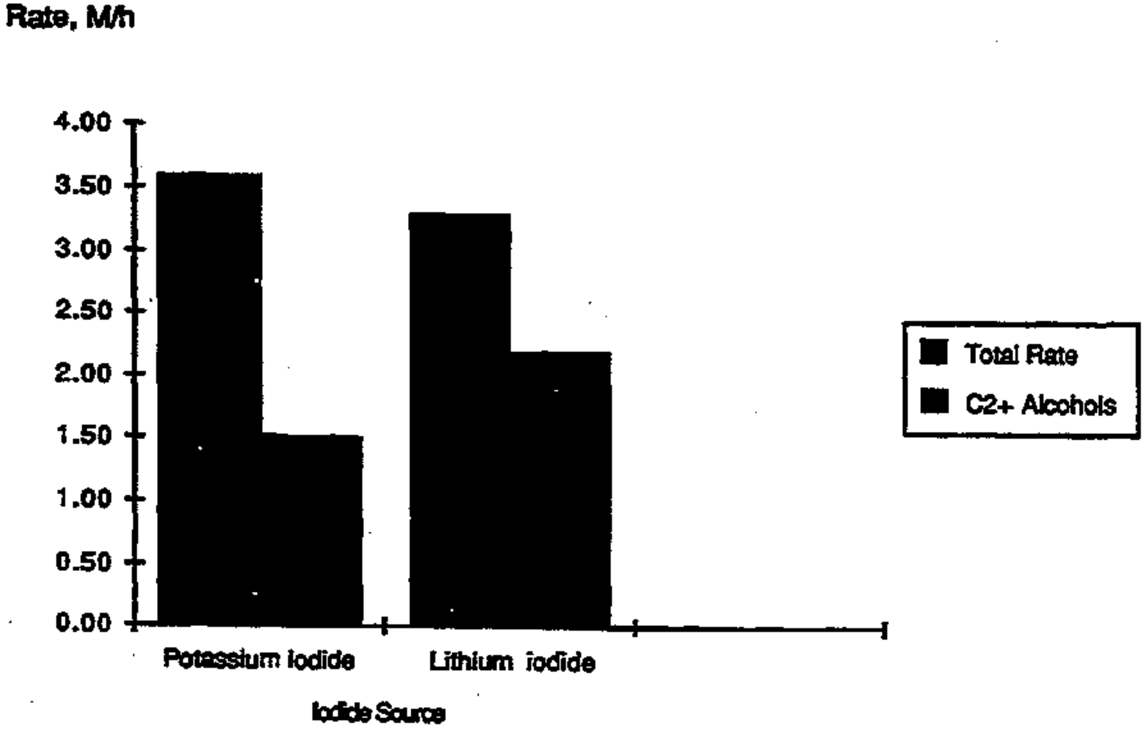
Experimental Conditions: 5000 psi; 230 °C; 3.0 h; 14 mmoles [Ru];
7 mmoles A16; 30 mmoles KI;
93 mmoles A92; 40 g of Phenyl ether.

Figure 10. A Graphical Comparison Between Several Solvent Systems for the Catalyst System of Ru/KI/A16/A92.



Experimental Conditions: 5000 psi; 230 °C; 3.0 h; 1:1 CO/H_2
14 mmoles [Ru]; 7 mmoles A16; 30 mmoles KI;
93 mmoles A92; 40 g of Solvent.

Figure 11. A Comparison of Rates and Selectivities for LiI and KI Promoters.



Experimental Conditions: 5000 psi; 230 °C; 3.0 h; 1:1 CO/H_2
14 mmoles [Ru]; 7 mmoles A16; 30 mmoles I^-;
93 mmoles A92; 40 g of 1,3-DMEU.

Table 6. Amounts of Products Formed at Different Pressures.

Conditions: 230°C, 4.7 mmoles of $Ru_3(CO)_{12}$, 7 mmoles of A16, 93 mmoles of A92, and 30 mmoles of KI in 37.5 mL of phenyl ether.

Pressure, psi	MeOH	C_{2+} ROH	Other Ox.	% ROH	% C_{2+} ROH	$Rate_{tot}$
5000	12.7 g	7.1 g	0.80 g	96%	35%	5.0 M/h
4000	8.4 g	4.6 g	0.1 g	99%	35%	3.2 M/h
3000	4.7 g	.64 g	0.1 g	98%	12%	1.4 M/h
2000	2.4 g	0.1 g	0.1 g	96%	4%	0.7 M/h

Key to Table 7

ID-#	
1 Catalyst	Catalyst precursor charged.
2 mmol	Amount of catalyst precursor used.
3 Solvent	Solvent used.
4 mL	Amount of solvent used, in mL.
5 Additive	Additive employed.
6 mmole	Amount of additive used.
7 Press., psi	Reaction pressure in psig.
8 Temp., °C	Reaction temperature.
9 Time, hrs.	Reaction time in hours.
10 H_2/CO	Syngas molar ratio.
11 MeOH, g	Amount of methanol produced, grams.
12 EtOH, g	Amount of ethanol produced, grams.
13 n-PrOH, g	Amount of n-propanol produced, grams.
14 n-BuOH, g	Amount of n-butanol produced, grams.
15 Tot.Prod., g	Weight of total products analyzed.
16 Rate, total, M/h	Total rate in moles/l solution/hr.
17 C_2+ alcohol %	Mole % of C_2+ alcohols in total product.

Table 7. Effects of A16 and A92 on the Ru/KI System in Various Solvent Systems

TWL-#	10-26	10-29	10-38
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmol	4.7	4.7	4.7
3 Solvent	Phenyl ether	Phenyl ether	Phenyl ether
4 mL	37.5	37.5	37.5
5 Additive	A16/KI/A92	A16/KI/A92	A16/KI/A92
6 mmole	7.0/30/93	7.0/30/93	7.0/30/93
7 Press., psi	4000	3000	2000
8 Temp.,°C	230	230	230
9 Time,hrs.	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH,g	8.4	4.7	2.4
12 EtOH,g	4.2	0.6	0.1
13 n-PrOH,g	0.4	0.1	0.0
14 n-BuOH,g	0.0	0.0	0.0
15 Tot.Prod.,g	13.2	5.6	2.6
16 Rate,total, M/h	3.2	1.5	0.7
17 C_{2+} alcohols %	27.0	9.0	3.0

Experimental procedure: B(b); Analytical procedure: C(b);
Key on page 48.

Table 7. Effects of A16 and A92 on the Ru/KI System in Various Solvent Systems (Cont'd)

	TWL-#	10-59	10-34	10-57
1	Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2	mmol	4.7	4.7	4.7
3	Solvent	Phenyl ether	Phenyl ether	Phenyl ether
4	mL	37.5	37.5	37.5
5	Additive	A16/KI/A92	A16/KI/A92	A16/KI/A92
6	mmole	7.0/30/93	7.0/30/93	7.0/60/158
7	Press., psi	5000	5000	5000
8	Temp.,°C	230	230	230
9	Time,hrs.	3.0	3.0	3.0
10	H_2/CO	2.0	0.5	1.0
11	MeOH,g	13.3	5.1	17.0
12	EtOH,g	2.3	4.7	3.6
13	n-PrOH,g	trace	1.0	0.3
14	n-BuOH,g	0.0	0.1	0.0
15	Tot.Prod.,g	15.6	11.1	21.2
16	Rate,total, M/h	4.1	2.9	5.5
17	C_{2+} alcohols %	20.0	50.0	13.0

Experimental procedure: B(b); Analytical procedure: C(b);
Key on page 48.

Table 7. Effects of A16 and A92 on the Ru/KI System in Various Solvent Systems (Cont'd)

TWL-#	10-40	10-41
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmol	4.7	4.7
3 Solvent	Phenyl ether	Phenyl ether
4 mL	37.5	37.5
5 Additive	A16/KI/A92/P(n-Bu)$_3$	A16/MeI/A92
6 mmole	7.0/30/93/4.4	7.0/71/93
7 Press., psi	5000	5000
8 Temp.,°C	230	230
9 Time,hrs.	3.0	3.0
10 H_2/CO	1.0	1.0
11 MeOH,g	9.0	*
12 EtOH,g	4.2	
13 n-PrOH,g	0.2	
14 n-BuOH,g	0.0	
15 Tot.Prod.,g	14.0	
16 Rate,total, M/h	3.3	
17 C_{2+} alcohols %	25.0	

Experimental procedure: B(b); Analytical procedure: C(b);
Key on page 48.

* No analysis done.

Table 7. Effects of A16 and A92 on the Ru/KI System in Various Solvent Systems (Cont'd)

TWL-#	10-47	10-71	10-48
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmol	4.7	4.7	4.7
3 Solvent	1,3-DMEU	1,3-DMEU	1,3-DMEU
4 mL	38.0	38.0	38.0
5 Additive	A16/KI/A92	A16/KI/A92	A16/KI/A92
6 mmole	7.0/30/93	7.0/30/158	7.0/30/93
7 Press., psi	5000	5000	3000
8 Temp.,°C	230	230	230
9 Time,hrs.	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH,g	7.5	7.7	7.6
12 EtOH,g	7.0	8.6	3.2
13 n-PrOH,g	1.1	1.4	0.5
14 n-BuOH,g	0.2	trace	trace
15 Tot.Prod.,g	16.2	18.0	11.4
16 Rate,total, M/h	3.6	4.0	2.8
17 C_{2+} alcohols %	42.0	47.0	25.0

Experimental procedure: B(b); Analytical procedure: C(b);
Key on page 48.

Table 7. Effects of A16 and A92 on the Ru/KI System in Various Solvent Systems (Cont'd)

TWL-#	10-63	10-73	10-69
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmol	4.7	4.7	4.7
3 Solvent	1,3-DMEU	1,3-DMEU	NMP
4 mL	38.0	38.0	40.0
5 Additive	A16/LiI/A92	A16/LiI/A92	A16/KI/A92
6 mmole	7.0/30/93	7.0/30/158	7.0/30/93
7 Press., psi	5000	5000	5000
8 Temp.,°C	230	230	230
9 Time,hrs.	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH,g	3.9	7.3	3.2
12 EtOH,g	9.9	6.1	7.6
13 n-PrOH,g	2.0	0.6	1.3
14 n-BuOH,g	0.0	0.0	0.0
15 Tot.Prod.,g	16.8	14.2	13.5
16 Rate,total, M/h	3.3	3.3	2.5
17 C_{2+} alcohols %	67.0	39.0	61.0

Experimental procedure: B(b); Analytical procedure: C(b);
Key on page 48.

Table 8. Analysis of Reactor Offgas After Catalytic Experiments

TWL-#	10-57	10-69	10-73
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmol	4.7	4.7	4.7
3 Solvent	Phenyl ether	NMP	1,3-DMEU
4 mL	37.5	40.0	38.0
5 Additive	A16/KI/A92	A16/KI/A92	A16/LiI/A92
6 mmole	7.0/60/158	7.0/30/93	7.0/30/158
7 Press., psi	5000	5000	5000
8 Temp.,°C	230	230	230
9 Time,hrs.	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 CO, Mole %	44	26	20
12 H_2, Mole %	36	33	46
13 CH_4, Mole %	4	11	4
14 CO_2, Mole %	16	30	30

Experimental procedure: B(b); Analytical procedure: C(b).

C. Direct Syngas Conversion by Heterogeneous Catalysts

1. Introduction

We have initiated work on the heterogeneously catalyzed system based on alkali-loaded molybdenum sulfide and cobalt-molybdenum sulfide catalysts. We began with a brainstorming session attended by about ten chemists or engineers from various areas at the UCC Technical Center. We are now working our way through the list of ideas which we hope will lead to a better understanding of the controlling factors in the production of alcohols versus hydrocarbons with these catalysts, such that we will thereby be able to develop an improved catalyst system.

2. Edge vs. Basal Plane Site Contribution to Catalysis

Several investigations by a variety of researchers have been carried out to determine if edge and basal plane sites exhibit different activity for hydrogenation, desulfurization and denitrification reactions. We are interested in determining if these different sites show differing activities for the conversion of syngas to alcohols and/or to hydrocarbons. We have ground two samples of MoS_2 in a mortar and pestle, one in water and one in air. We are in the process of determining by oxygen chemisorption if the edge site to basal plane site distribution has changed. If so, we will determine if there is a difference in activity. We saw no change in the samples by X-ray diffraction.

3. Particle Size Determination

We have prepared catalysts on molybdenum sulfide prepared by Climax Molybdenum Corp. and have noticed differences in the amount of impregnating solution taken up by different samples and possibly differences in the degree of wettability. We are investigating the variability of particle size, surface area, and pore structure of various samples of a particular MoS_2 preparation (AMAX-20). We took a 50 gm sample and sieved it into various fractions as shown in Table 9, calculated the weight percent of each fraction and obtained surface area and porosimetry measurements on three of these fractions and on a sample of unsieved material.

Table 9. Surface Area Measurements on Size-Fractionated MoS_2.

Mesh Size	wt %	Surface area (sq. m/gm)
10-20	17.37	72.9
20-30	20.1	
30-40	19.33	69.4
40-60	19.02	
60-80	7.04	
80-100	3.86	
-100	13.27	60.1
unsieved		70.2

The initial porosimetry determinations are in question because of difficulties in differentiating between interparticle pores and voids between particles. We are still working on this to determine if we can get any reliable information from porosimetry measurements.

4. Effect of Aqueous vs. Non-aqueous Impregnations

We were interested in determining if the use of non-aqueous impregnating solutions had any effect on the catalyst performance. We prepared two 0.75 moles K per mole MoS_2 catalysts via a stir-mix impregnation method. These catalyst preparations were identical, except that one used an aqueous solution of potassium acetate and the other used an anhydrous ethanol solution of potassium acetate. The results are shown in Table 10 along with the run conditions. If the differences in space velocity, catalyst density, and consequently conversion are taken into account, the results do not appear to be different. The rate to alcohols, however, is slower than expected based on prior results on similar catalysts. This may indicate that the base material has in some way degraded since it was last used ten months ago.

Table 10. Results of Aqueous and Non-Aqueous Impregnations

Run Number	22NEK4R2-6 (aqueous)	22NEK6R2-6 (non-aqueous)
Temp (°C)	300	300
Pressure (psig)	1200	1200
Space Velocity (1/1/h)	6600	5580
H_2/CO ratio	1	1
gms catalyst	0.8541	0.7695
Alcohol Rate lb/cf/h	13.36	10.52
% CO Conversion	9.92	7.63
C mole % alcohols	81.61	87.36
C mole % oxygenates	87.24	92.62
wt% C_{2+} alcohols	40.18	39.02
C_2/C_{2+} alcohol wt ratio	63.86	66.94

Experimental procedure: B(e); Analytical procedure: C(d).

D. Task 2 Summary

The catalyst lifetime studies with the methanol homologation system have been completed. Our most recent results confirm our previous suspicions that the halt in gas uptake during reaction is due to the buildup of volatile materials in the reactor. Methane, ethers, and acetaldehyde all contribute to a lowering of the syngas partial pressure during the course of the homologation. These studies show that within the timescale of our experiments (ca. 10 h), no catalyst decomposition is detected. Longer lifetime studies will need to be made in continuous type reactors rather than the batch reactors in which we now operate.

The two products (C16 and C23) isolated from the reactor at the end of the homologation experiments have now been conclusively identified. C16 is a complex of ruthenium, A28, and carbon monoxide. C23 is a complex of C4, A25, A28, and carbon monoxide. Together, these complexes account for > 95 % of the ruthenium, C4, and A25 charged to the reactor. In addition, we have shown that these complexes can be charged to the reactor instead of the normal catalyst charge and used to homologate methanol with no loss in activity or selectivity. C16 and C23 can again be isolated from the reactor in high yield. These observations strongly suggest that these complexes are active intermediates in the homologation reaction.

Our investigations into the mechanism of this reaction have also been very informative. We have shown that C23 may be directly responsible for the novel homologation activity of this catalyst. We have also shown that we may be operating above the solubility limit of this complex under the reaction conditions. If true, then we should be able to reduce the amount of C23 (or the additives required to form C23) in a catalyst charge while maintaining rate. Our kinetic data further show that we can lower the concentration of A28 by at least an order of magnitude with no loss in rate. Maintaining rate at lower catalyst/additive concentration significantly reduces operating cost and simplifies product separation.

The activity of the ruthenium catalyst system for direct conversion of syngas to alcohols decreases as a function of the operating pressure; approximately a second-order dependence was seen. The selectivity to higher alcohols is also a function of pressure, decreasing with pressure.

The ratio of H_2/CO is also important to the selectivity to higher alcohols. A CO-rich syngas (2:1 CO/H_2) is better for the formation of higher alcohols despite a decrease in the total activity of the catalyst system as compared to experiments using a 1:1 syngas. Both the total activity and the selectivity to higher alcohols decrease when hydrogen-rich syngas (2:1 H_2/CO) was used.

Solvent is another important factor for the activity and selectivity of the system. We found that 1,3-dimethylethyleneurea is a very good solvent for the production of higher alcohols with this system. We have also found that LiI as the iodide source further increases the production of higher alcohols over that observed with KI.

We have initiated work on the heterogeneously catalyzed system based on alkali-loaded molybdenum sulfide and cobalt-molybdenum sulfide catalysts. We are now working our way through a list of ideas which we hope will lead to a better understanding of the controlling factors in the production of alcohols versus hydrocarbons with these catalysts.

We are in the process of determining whether it is possible to change the edge site to basal plane site distribution in catalyst precursors, and whether this can change the catalyst performance.

We are also investigating the variability of particle size, surface area, and pore structure of various samples of a particular MoS_2 preparation. We are currently trying to determine whether we can get reliable information from porosimetry measurements.

We are interested in determining if the use of non-aqueous impregnating solutions can have an effect on catalyst performance. Two identical K-MoS_2 catalysts were prepared, except that one was prepared with an aqueous solution of potassium acetate and the other with an anhydrous ethanol solution of potassium acetate. The catalytic results with these materials do not appear to be significantly different.

II. TASK 3: Bench Scale Concept Evaluation

A. Introduction

Work in Task 3 during the first year of this contract involves engineering support for the chemical research, and seeks to quantify the economic impact of any developments to guide the research in the optimum direction. Economic evaluations of systems under investigation and a base case process for conversion of syngas to fuel alcohols are also included.

Task 3 work later in the contract period will involve bench-scale experiments with selected catalytic systems, the development of kinetic and empirical models, and continuing economic and process conceptualization studies.

The major efforts for this quarter have been in the definition of the base case economics and in support of the experimental program on heterogeneous catalysts. The work reported in the first quarter on preliminary economic guidance for research was reviewed and discussed with the researchers. No extension of the work or modification of the assumptions seemed necessary.

B. Support for Experimental Program

1. Heterogeneous Process

The problems revealed in the previous experimental work were:

(a) rates lower than commercially desirable, particularly for retrofit into an existing methanol reactor,

(b) catalyst deactivation, and

(c) increasing methane formation as the conversion increased and the proportion of higher alcohols increased.

Engineering support for this program has been focused on developing an understanding of catalyst preparation and whether modifications to the preparation procedure might improve performance, particularly in relation to (a) and (b).

One of the puzzling features of previous experimental work with the heterogeneous catalyst was that catalyst deactivation was evident in pilot plant experiments but was not reported in laboratory experiments in microreactors. Figure 12 is some recent data obtained using MoS_2 in a microreactor. (Reaction conditions were not constant throughout the run.) The dashed line is the equation

$$r = r_o / (1 + k\, r_o\, t)$$

This is the form obtained if catalyst activity decays by a second order process

$$dr/dt = -k\, r^2$$

Previous work has shown that this relationship fitted the data on deactivation in a pilot plant experiment. At present, this relationship is merely a convenient empirical equation. However, it is typical of the behavior expected if the activity decline is due to loss of surface area or active sites by sintering or recrystallization.

Deactivation was not evident in many of the previous microreactor experiments with this catalyst system because operating conditions were not held constant or the run time was short. It is recommended that selected catalysts be tested in microreactors for sufficient time to determine deactivation rates and hence to try to establish a relationship between catalyst preparation and deactivation behavior.

One factor which may affect catalyst deactivation is the loss of sulfur. Addition of the appropriate concentration of H_2S to the feed may thus be essential for long term operation.

Equilibrium H_2S/H_2 ratios have been measured over molybdenum disulfide prepared by thermal decomposition of ammonium tetrathiomolybdate at 400°C (*1*). These measurements indicate that the equilibrium H_2S concentration is about 0.1 ppm at 300°C for 2/1 H_2/CO. The equilibrium concentration decreases even further if the sample is heated to higher temperature.

The difference between these equilibrium measurements and our previous data on sulfur loss suggests several possibilities:

(a) our catalyst is substantially more disordered than the sample studied in reference (*1*),

(b) sulfur is lost as other compounds instead of or in addition to H_2S, or

(c) the presence of syngas reactions increases the rate of sulfur loss.

These possibilities will be explored further. The objective is to develop a method to predict the sulfur feed rate needed to maintain a steady-state catalyst sulfur content.

Catalyst literature has been reviewed in search of alternative preparation methods which might be useful, and some procedures have been identified.

The best catalysts have been amorphous, as determined by X-ray analysis. Amorphous materials are known to be unstable in the sense that further heating leads to recrystallization. High catalyst activity requires the use of a high area precursor, but much of the surface area is lost in the impregnation step.

It is possible that the alkali metal distribution obtained by impregnation might be very nonuniform. This would explain why a high loading has been found necessary (to cover all of the MoS_2 surface). The large reduction in surface area occurring during impregnation could be due simply to blocking of many of the pores during drying and salt decomposition.

The first possibility being investigated is that the impregnating solution does not wet the MoS_2 surface. Mercury porosimetry showed that MoS_2 has a large volume of small pores. The impregnation procedure is to pull vacuum on the MoS_2 powder, add aqueous salt solution, release vacuum and mix. The maximum pressure available to force liquid into the pores is thus one atmosphere. Calculation shows that this is insufficient to force water into the small pores if the surface does not spontaneously wet.

Different procedures intended to improve wetting will be tested. A direct test of wetting is needed, to avoid the need to prepare catalyst and evaluate for each alternative. A procedure which uses only direct weighings to determine the residual void volume per gram of MoS_2 has been recommended.

The drying step may also contribute to the nonuniform alkali metal distribution even after adequate wetting is achieved. A literature review is under way.

Our present working assumption is that the alkali metal must be present on the MoS_2 surface. Preparation of some test catalysts from thiomolybdate solutions containing alkali metal molybdates would test this assumption.

The present amorphous catalyst needs to be compared with catalysts prepared using finely divided crystalline MoS_2. This will show whether the amorphous structure is essential for catalyst activity or is simply a consequence of the present method for achieving high surface area. Comparison of deactivation rates should show whether deactivation is largely due to the amorphous structure. A literature search on ways of obtaining crystalline material of high surface area is underway.

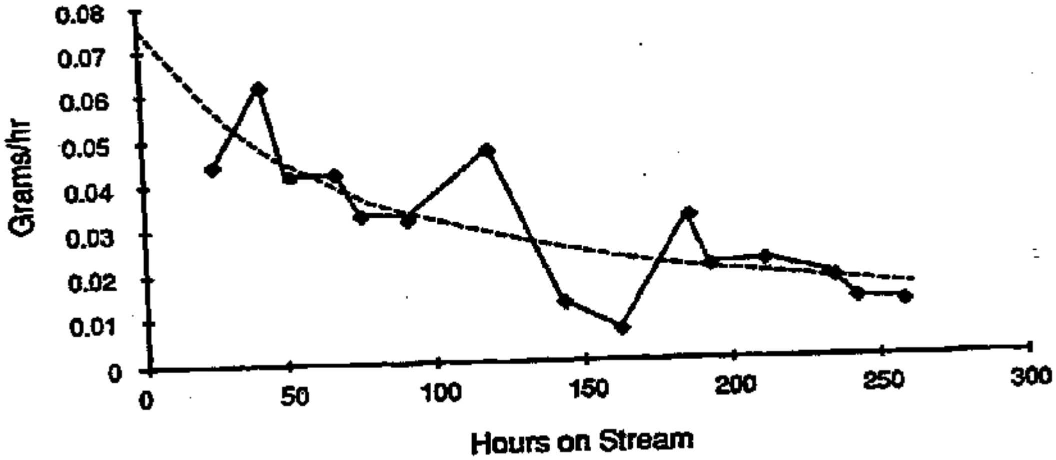
2. Methanol Homologation

In the methanol homologation batch experiments, the reaction rate slows down and appears to stop after several hours. Experimental data shows that the accumulation of methane is at least partly responsible for this effect. There is a substantial residual H_2 and CO content of the reactor gas and reaction is not limited by overall thermodynamic equilibrium. Examination of gas compositions at which rate stops (or decreases substantially) may give insight into the rate-determining step.

1. Bartovska, L., and Cerny, C., "The Influence of the Structure of Molybdenum Disulfide on its Reactivity." *Collect Czech. Chem. Commun.* **52**, 678 (1987).

2. Miremadi, B. K., and Morrison, S. R., "High Activity Catalysts from Exfoliated MoS_2." *J. Catal.* **103**, 334 (1987).

Figure 12. Microreactor Data Showing Catalyst Deactivation By A Second Order Process.

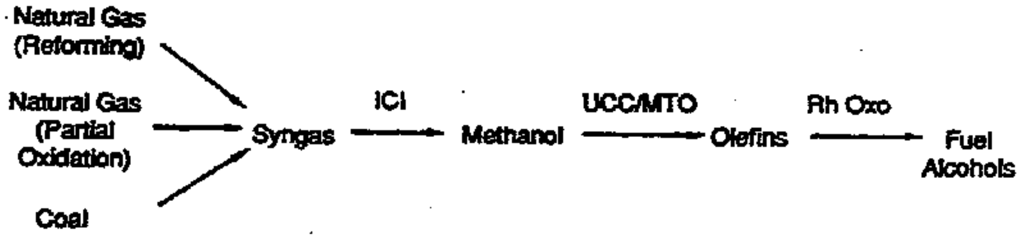


$dr/dt = k\, r^2$

------- $r = r_0 / (1 + k\, r_0\, t)$
$[r_0 = 0.075;\ k = 0.2]$

C. Base Case Economic Studies

A base case process for economic studies of making fuel alcohols from syngas has been developed. It uses existing technologies which have been demonstrated to be feasible or have already been commercialized. The process consists of the following steps:



Process economics for the two natural gas-based routes have been developed. With insights gained from this, an optimized and integrated multi-step process has been conceptualized which allows estimation of the lowest cost at which fuel alcohols can be produced. An "ideal" process has also been conceptualized which establishes a target production cost that new technology should strive for to be competitive. Next quarter, economics of the coal-based route will be developed.

A 60% methanol and 40% higher alcohol mix was assumed to be a suitable fuel alcohol blend for gasoline. The process economics are based on:

- 2500 tonnes/day methanol
- 2$/MMBTU natural gas
- 5¢/kwh electricity
- $4.5/1000 lbs of 900 psig steam
- Year: 1987
- 20% ROI; 10% depreciation

The natural gas reforming and oxidation steps (in this report and the previous Quarterly Report) are based on information from two sources. The material balances are from our own computer programs and experience. The investment data are taken from SRI Report No. 148 and have been scaled and slightly modified as appropriate.

Figure 13 shows the process flow diagram for production of fuel alcohols from syngas generated by reforming of natural gas. The hydroformylation and hydrogenation steps place constraints on the amount of methane that is in the syngas. This requires operation of the reformer at low pressure (~150 psia) and a higher steam to natural gas ratio than would normally be needed for methanol synthesis. The syngas compression costs are correspondingly higher. The syngas ratio produced is 5.9:1 and is adjusted for hydroformylation by CO_2 removal using a MEA unit followed by PSA for hydrogen removal. Part of the hydrogen is used in hydrogenation while the majority of it is burned as fuel. Finally the methanol refining train is considerably simplified since only water needs to be removed. The battery limits and the total utilized investments are $300 MM and $415MM respectively. The total production cost is $1.12/gal (raw material 28%, utilities 7%, period costs 19%, depreciation and ROI 46%).

Figure 14 shows the process flow diagram for production of fuel alcohols from syngas generated by partial oxidation of natural gas. Optimization shows that partial oxidation should be operated at a high pressure because the cost of natural gas compression is a fraction of the syngas compression costs and incremental oxygen compression costs are fairly small. The syngas produced has a ratio of 2.05:1 which is achieved by adding steam to the generator. The CO_2 in the inlet is removed by a MEA unit prior to methanol synthesis or hydroformylation. PSA is used to adjust the ratio for the latter. The feed to MeOH synthesis is stoichiometric, has low inerts, and very little CO_2. The impact of these variables on methanol synthesis utilities and raw material efficiencies is expected to be significant but was not evaluated for the purposes of this study. It is expected that this impact will be favorable to the economics. However, it was conservatively assumed that the economics were no better than for a conventional methanol synthesis. The product cost is estimated to be $1.11/gal (Raw material 26%, utilities 4%, period costs 21%, depreciation and ROI 49%). The total utilized and battery limits investments are $422 MM and $314 MM respectively. These costs are about the same as for the reforming cases. Why this is so becomes clear as one looks at the methanol product cost comparison for the two cases.

Methanol Production Cost (¢/lb)	Reforming	Partial Oxidation
Raw Material	4.79	3.01
Utilities	0.60	0.28
Period	0.66	1.28
ROI & Depreciation	2.07	4.01
	8.12	8.58
	56¢/gal	57¢/gal

The larger capital and period costs for partial oxidation are offset by a better raw material efficiency and lower utility costs.

An integrated multi-step process has been conceptualized (Figure 15) which improves the raw material efficiency but minimizes capital cost by reducing the size of the oxygen unit to as small as possible. This is done by using "autothermal" reforming which consists of reforming followed by catalytic partial oxidation. It reduces the amount of oxygen required, reformer steam needed and the shifting that is necessary. The compression costs are practically eliminated by running methanol synthesis close to 700 psia. The amount of water formed is controlled by the CO_2 slip from the MEA units, so no refining of methanol is necessary. The production cost for this process is estimated to be $0.90/gal with a battery limits investment of $250 MM.

Sensitivity of production costs to natural gas cost shows that, using reforming or partial oxidation of natural gas, $0.90/gal can be achieved if the natural gas price drops to $0.50/MMBTU.

Finally, an ideal process for making fuel alcohols was synthesized which helps establish a target production cost for emerging technologies to shoot for. As drawn in Figure 16, it consists of autothermal reforming coupled with either UCC or other technology for syngas conversion to higher alcohols. Investment estimates were generated by analogy to similar processes (e.g., UCC/MoS_2 investment = ICI Methanol investment). Other costs were generated by comparison of the other two cases and the integrated multi-step process. Production costs were thus estimated to be $0.65/gal. We have also estimated that processes using modified methanol catalysts to produce a fuel alcohol blend should be able to produce it for $0.65/gal. This, or its equivalent for a different economic basis, is the target production cost that emerging technologies must achieve in order to be competitive.

Figure 13. Fuel Alcohols From Natural Gas via Reforming.

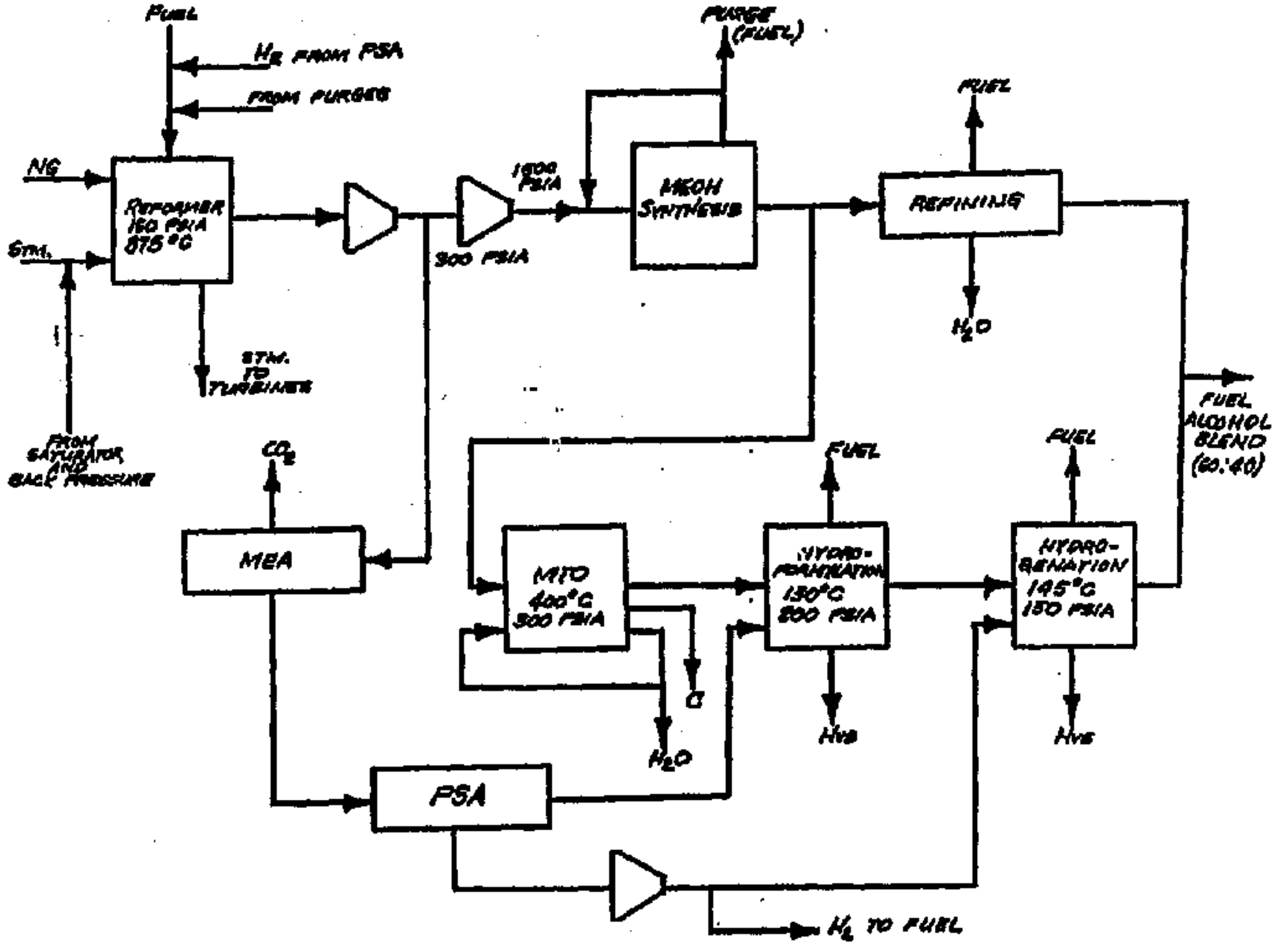


Figure 14. Fuel Alcohols From Natural Gas via Partial Oxidation.

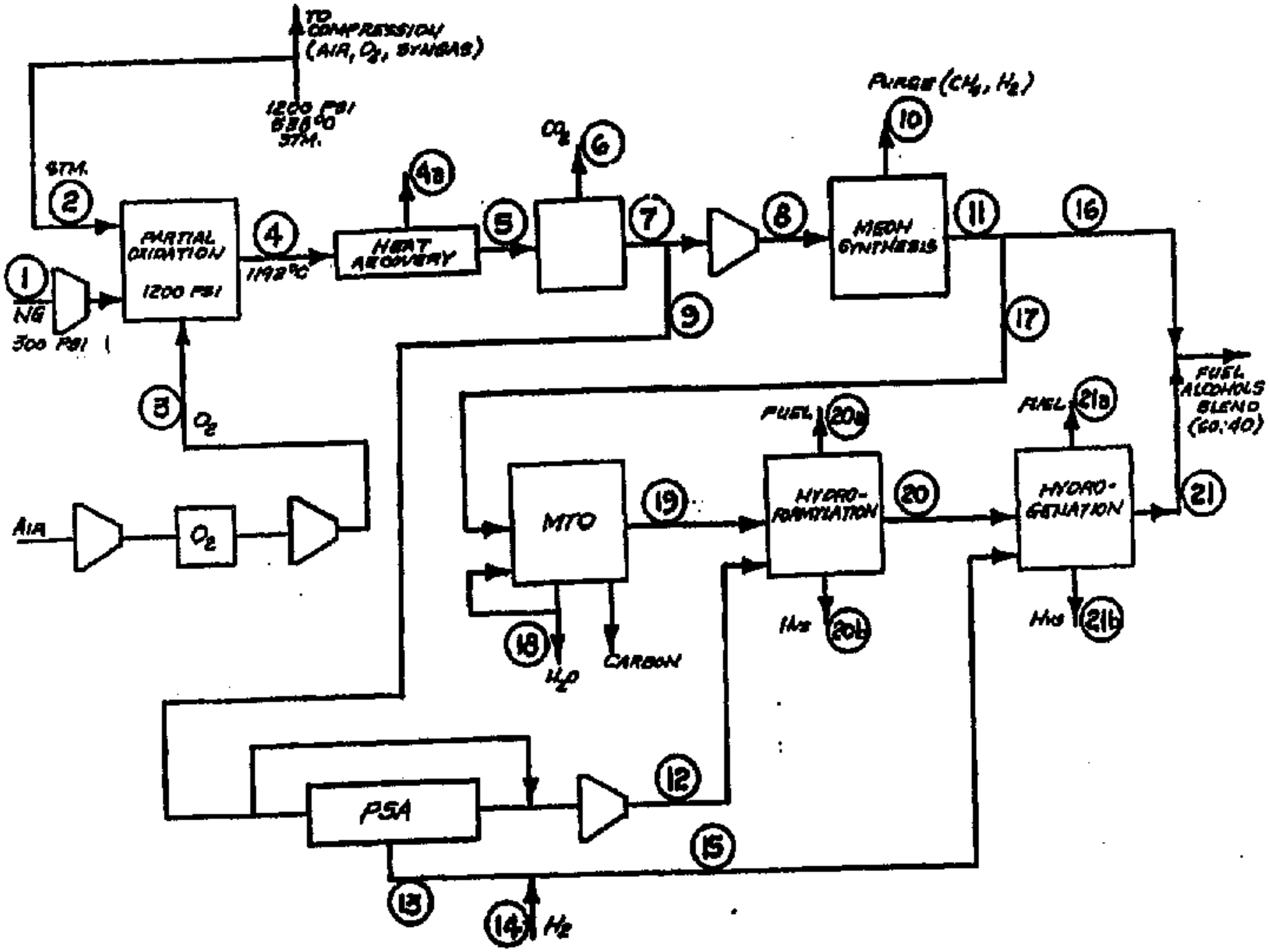


Figure 15. Integrated Process for Fuel Alcohols From Natural Gas.

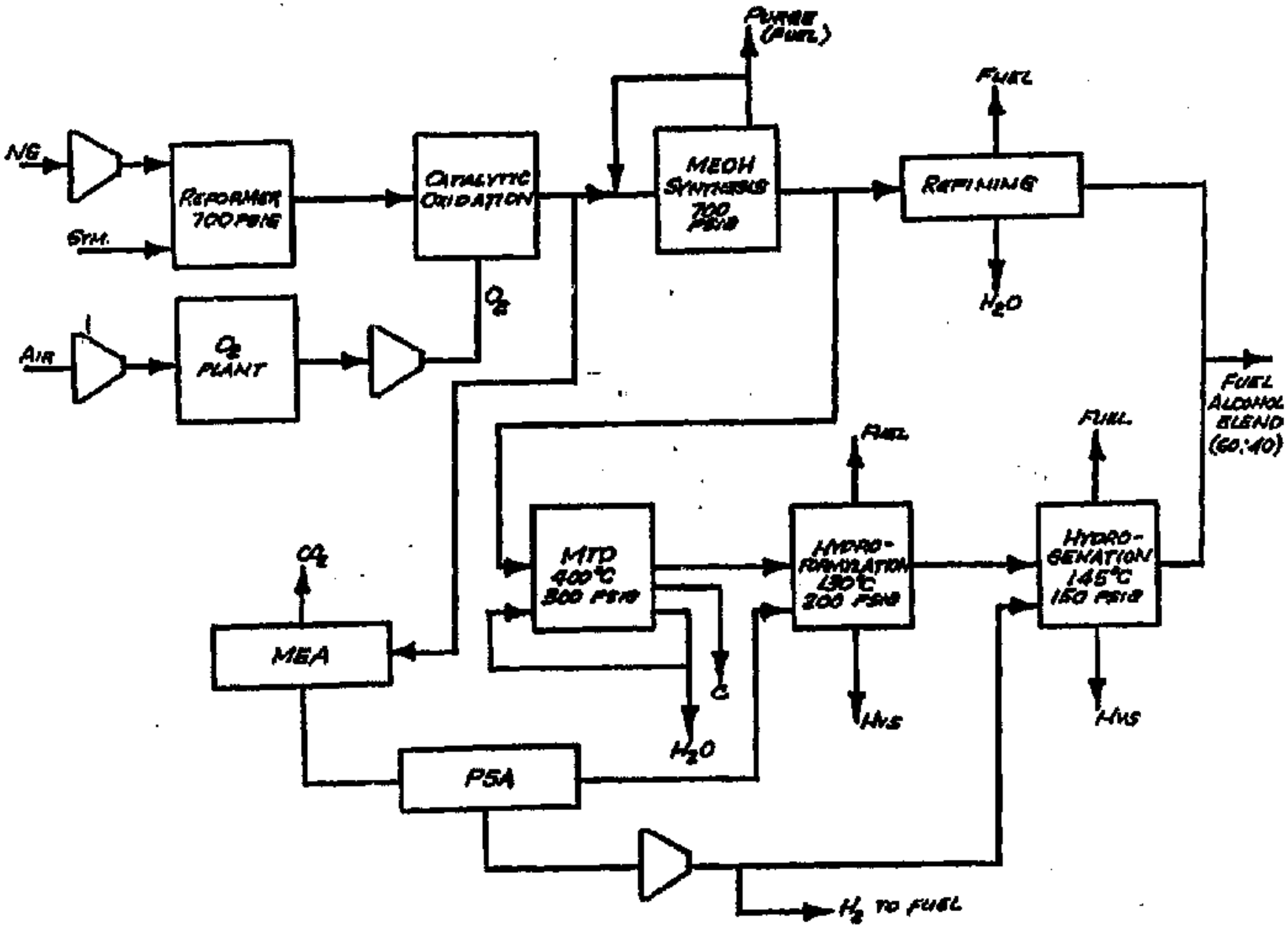
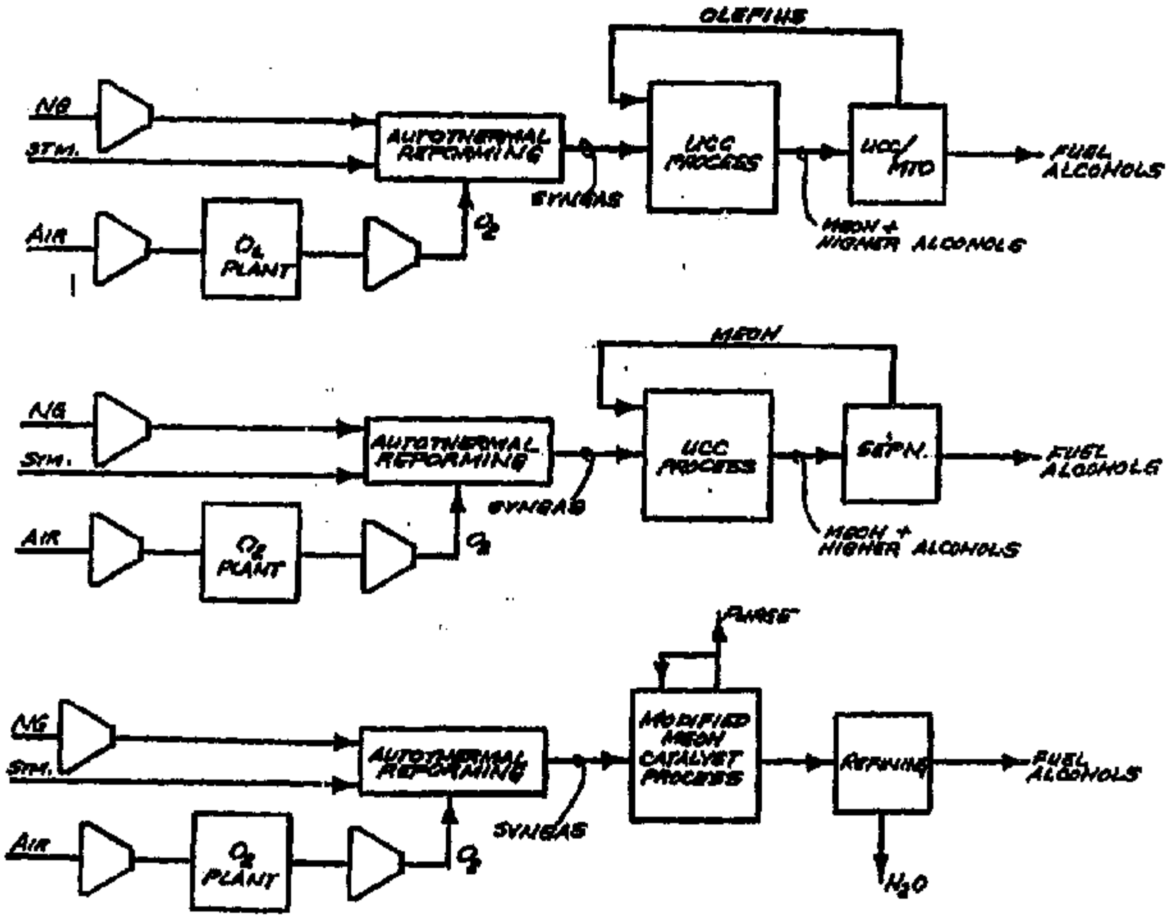


Figure 16. Ideal Process Schematics.



D. Task 3 Summary

The major efforts for this quarter have been in the definition of base case economics and in support of the experimental program on heterogeneous catalysts.

The problems revealed in the previous experimental work with the heterogeneous MoS_2 catalysts for conversion of syngas to alcohols included rates lower than commercially desirable, catalyst deactivation, and increasing methane formation as the conversion increased and the proportion of higher alcohols increased. Engineering support for this program has been focused on developing an understanding of catalyst preparation and whether modifications to the preparation procedure might improve performance.

The catalyst activity appears to decline in a second-order process typical of the behavior expected if the activity decline is due to loss of surface area or active sites by sintering or recrystallization.

One factor which may affect catalyst deactivation is the loss of sulfur. Addition of the appropriate concentration of H_2S to the feed may thus be essential for long term operation. We will attempt to develop a method to predict the sulfur feed rate needed to maintain a steady-state catalyst sulfur content.

Catalyst literature has been reviewed in search of alternative preparation methods which might be useful, and some procedures have been identified.

It is possible that the alkali metal distribution on the catalyst obtained by impregnation might be very nonuniform. The large reduction in surface area observed after impregnation could be due simply to blocking of many of the pores during drying and salt decomposition. The possibility is being investigated that the impregnating solution does not wet the MoS_2 surface. Different procedures intended to improve wetting will be tested. Alternative means to dry the material may also need to be explored to maintain uniform alkali metal distribution.

A base case process for economic studies of making fuel alcohols from syngas has been developed. It uses existing technologies which have been demonstrated to be feasible or have already been commercialized. The process consists of the following steps:coal or natural gas (reforming or partial oxidation) to syngas; syngas to methanol by ICI technology; methanol to light olefins by proprietary UCC technology using molecular sieves; olefins to alcohols by hydroformylation (with a homogeneous rhodium "oxo" catalyst) followed by hydrogenation. Process economics for the two natural gas-based routes have been developed. With insights gained from this, an optimized and integrated multi-step process has been conceptualized which allows estimation of the lowest cost at which fuel alcohols can be produced.

A 60% methanol and 40% higher alcohol mix was assumed to be a suitable fuel alcohol blend for gasoline. At a natural gas price of $2/MMBTU, the cost of producing this, by either partial oxidation or reforming, is $1.12/gal. The larger capital and period costs for partial oxidation are offset by its lower utility costs and better raw material efficiency in methanol synthesis.

An integrated process with autothermal reforming at 750 psia and methanol synthesis at 700 psia allows incorporation of the best features of reforming and partial oxidation as well as elimination of syngas compression. The production cost of fuel alcohols by this process is estimated to be $0.90/gal. This is, therefore, the lowest cost at which fuel alcohols can be produced by an integrated, multi-step process.

An "ideal" process has also been conceptualized which establishes a target production cost that new technology should strive for to be competitive. This process incorporates autothermal reforming for producing syngas followed by single- or two-step conversion to fuel alcohols using emerging technologies. The production costs for these are estimated to be $0.65/gal. This production cost, or its equivalent with another set of economic criteria, is the target that any new process should strive for in order to be competitive.

Next, economics of the coal-based route will be developed.