

#### 4.2.5 Task 2 Summary

##### *Cobalt Catalysts*

Investigations of cobalt catalysts have been conducted, with the effort concentrating on identifying suitable solvents to enhance the production of higher alcohols from syngas. Earlier work on homogeneous cobalt systems reported in the literature shows that cobalt catalysts can produce alcohol products, but rates are very low under practical conditions. A number of solvents have been studied, some in combination with additional promoters.

Three solvents were identified in these studies which appear to show improved production of higher alcohols, relative to standard runs conducted in toluene solvent. Since these higher alcohols may be formed by homologation of initially-formed methanol, studies were also carried out on the homologation of added methanol.

Further work was conducted with the three initially identified solvents found to enhance the production of higher alcohols. Only one solvent was found suitable for further research; 3,4,5-trimethoxytoluene appears to provide significantly enhanced activity for higher alcohol formation from syngas, as well as providing improved cobalt stability. In addition, systems based on this solvent were successfully applied to the homologation of methanol with homogeneous cobalt catalysts.

Continued studies of cobalt catalysts in this and other novel solvents indicated improved cobalt stability, which allowed the catalyst to remain active for longer periods of time and under a wider range of conditions. However, solvent decomposition was found to be a critical problem. The use of selected catalyst additives to counter this decomposition was not successful. Related experiments with rhodium catalysts showed good solvent stability in some cases, but catalyst activity was low.

Cobalt complexes with coordinated pentamethylcyclopentadienyl ligand were tested as catalyst precursors in attempts to produce a more stable catalyst. Although some alcohol product was formed under relatively mild conditions, spectroscopic studies after catalysis indicate that the initial complex has decomposed into other complexes.

### *Copper Catalysts*

It had been previously reported that various copper compounds in the presence of base are able to catalyze the conversion of  $H_2/CO$  into methanol and methyl formate under relatively mild conditions, 80-120°C and 500-2000 psi syngas. In our experience, this catalyst system produces a mixture of oxygenates at rates of about 1.5 mol/l/hr under these conditions. About half of the mixture is methanol, and no higher alcohols are observed.

Prior to the initiation of work on this contract, we discovered that the inclusion of various additives in this copper/base system produced substantial effects on the rate of the reaction. Rates to oxygenates of higher than 3 mol/l/hr have been observed in these modified systems. Again, about half of the product mixture is methanol, and no higher alcohols are observed. During this contract, we have studied the use of a range of conditions, solvents, and additives with the copper/sodium methoxide system to determine the most active catalyst. We have also studied the effect of several forms of copper and the use of various bases. The goal of this research has been to increase the catalytic activity and to alter the selectivity to produce higher alcohols.

Diethyl carbitol (DEC) solvent, which has been used for the majority of the runs, was far superior to several other solvents investigated. Even the addition of 5 mL of methanol to a run conducted in DEC was found to decrease activity to 25% of normal.

Additives  $SmCl_3$  and  $UCl_4$  gave significantly enhanced rates when they were present in amounts comparable to the amount of

copper charged. In contrast, other additives were found which virtually eliminated activity. When additive  $\text{SmCl}_3$  was used in conjunction with one of these additives, some activity was restored, but the rate remained depressed versus the copper/sodium methoxide only case.

Additional experiments were conducted using various different solvents and additives in an attempt to extend the lifetime of the catalyst and/or shift its selectivity. Some new products, including ethanol, have been observed in small amounts. However, no significant improvements in lifetime or product distribution were observed.

Experiments have also been conducted to determine how the products are formed in this system. One plausible route is the formation of a formaldehyde or formaldehyde-like intermediate. The other possibility involves hydrogenolysis of intermediate oxygenates. Piperidine has been included in normal catalytic runs to act as a trapping agent for a formaldehyde intermediate. Formaldehyde is known to react with amines to give methylamines, and this has been shown to occur in this system using paraformaldehyde. Since in a standard run with piperidine added, little N-methylpiperidine formation is observed, it seems unlikely that much free formaldehyde is formed in this system. Unfortunately, there are several complicating factors which cloud the issue. The copper catalyst rapidly carbonylates the piperidine to give N-formylpiperidine thus removing the trapping agent from the system; one of the major oxygenates formed in the system reacts with piperidine even in the absence of catalyst to give N-formylpiperidine; and exposure of the  $\text{CuX}$  to methanol prior to attainment of reaction conditions has been found to entirely inhibit activity. Thus one cannot test whether the copper catalyst will produce N-methylpiperidine from methanol and piperidine, which would be another possible source of the N-methylpiperidine.

Since solids are present in the catalyst solutions following typical runs, an attempt was made to determine whether the catalysis is homogeneous or heterogeneous in nature. Solids were

removed via filtration, and both the solids and the filtrates were tested for continued activity alone and with added sodium methoxide. In all cases, no activity remained.

The solids have been examined and found to contain sodium formate and probably copper metal. Similar solids obtained by reaction of copper(I) iodide and sodium methoxide at 100°C under one atmosphere syngas still contain methoxide rather than formate, are highly air sensitive and display moderate catalytic activity under standard conditions of temperature and pressure. After reaction at higher pressure, the solids no longer contain methoxide, but contain instead formate, and are no longer active. The unreactive solids contain copper metal, but work with cupric methoxide has shown that copper metal is probably not the active catalyst.

A copper hydride species formed by  $\beta$ -hydride elimination from copper(I) methoxide is believed to be the active copper catalyst species. The reactivity of the complex bis(triphenylphosphine) copper(I) tetrahydroborate in the presence of methoxide as well as the high activity of independently synthesized copper hydride in the presence of methoxide point to the involvement of both a copper hydride species and methoxide in the catalytic system. Copper hydride also showed some activity with sodium ethoxide, which is not normally a suitable base for this system.

Deactivation of the catalyst system seems to be closely tied to loss of methoxide and formation of formate. Water in the solvent was suspected to play a role in this transformation, but work in carefully dried diethyl carbitol and tetrahydrofuran has demonstrated that water is not the problem. A related catalyst system, CuCRA, containing copper(I) iodide, sodium hydride and sodium t-pentoxide, was investigated and found to be unreactive under the usual conditions.

Because of the practical limitations of this copper catalyst system--the problems of deactivation and low yields of higher alcohols--work on this approach was concluded.

### *Iron Catalysts*

An investigation of an iron-based system reported to produce methanol under very mild conditions casts doubt on the reliability of the literature results. Although a variety of experimental procedures have been investigated, it has not been possible to reproduce the reported production of methanol under one atmosphere of pressure. Serious flaws in experimental procedures and interpretations were found. Experiments carried out under higher pressures with the components of the reported electrocatalytic system also were not successful in syngas conversion. Attempts to use logical extensions of the system have not been found to yield active catalysts under higher syngas pressure.

### *Other Catalysts*

A variety of novel metal complex-solvent combinations have been investigated for their syngas conversion activity. Although some of these systems produced alcohol products, the activities were low in all cases.

$(C_5Me_5)Re(CO)_3$  and  $PdCl_2/NaOMe$  were also tested for catalytic activity. Even at  $310^\circ C$ , the rhenium complex showed only minimal activity, forming traces of hydrocarbons. The palladium/base catalyst was inactive under standard conditions for the copper/base catalyst.

Two experiments were done to investigate a literature report claiming conversion of  $H_2/CO$  to methanol under conditions of one atmosphere and  $20^\circ C$ . The catalyst was a metalloporphyrin/colloidal platinum/ligand combination in a variety of solvents. We were unable to observe any product formation under conditions similar to those reported.

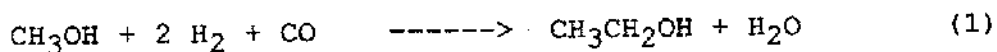
### 4.3 Task 3 - Further Study of Superior Catalysts

The objective of Task 3 was to investigate in more detail the characteristics and chemistry of catalyst systems identified in Tasks 1 and 2 as having the most potential for further development. The activities to be included in this task were both of a fundamental chemical nature and a process-oriented nature. These approaches have been pursued on the novel low-pressure homologation system, discovered in Task 1, which converts methanol to ethanol upon reaction with syngas.

#### 4.3.1 Ruthenium-Based Catalysts for Methanol Homologation

##### 4.3.1.1 Introduction

Homologation of methanol yields ethanol according to equation 1. The reaction is traditionally carried out with a Co-Ru-I



catalyst at 160 to 180°C and 3000 to 6000 psig. The ethanol rates are typically 3 to 6 moles/l/hr (M/hr) and selectivities are at best 85%. In our earlier work in this contract under Task 1, we discovered a novel ruthenium-based catalyst that allows the reaction to be carried out at significantly lower pressure. For example, ethanol selectivities of 80% can be obtained at operating pressures below 1500 psig. The reduced reaction pressure made possible by this catalyst is a significant breakthrough in methanol homologation technology. Since methanol is readily obtained from synthesis gas this catalyst may provide a practical low pressure route to ethanol and possibly other higher alcohols.

Under Task 3, studies of the catalyst chemistry have been carried out with an emphasis on the involvement of catalyst

additives and precursors in the catalytic chemistry. Fundamental chemical studies have also been directed toward a better understanding of the chemical steps involved. At the same time, studies were conducted to characterize the system by studying its responses to various process variables. Since a large number of variables were potentially important, a series of statistically designed experiments was planned and completed.

#### 4.3.1.2 Scale-up of the Methanol Homologation System

In preparation for performing designed sets of experiments with the ruthenium-based methanol homologation system, a number of experiments were performed in a 300 mL autoclave, probing various aspects of the reactivity of the scaled-up system. The results of the experiments are summarized in Table 61.

In the larger volume system the rates to ethanol and its equivalents generally total about 1 M/hr and the selectivities are in the 70 to 80 percent range. There is some indication, run G-103, that high catalyst concentrations can reduce selectivity. In run G-106 the effect of low temperature on reactivity was investigated. The reaction was begun at 100°C and the temperature increased in 10° increments. The catalyst activity was very low at 100 and 110°C, but moderate activity began at 120°C. At 130 and 140°C maximum activity was observed. This suggested a lower practical limit of 125°C. Run G-107 was performed at 125°C and did show good activity, but the selectivity was lower than in run G-106, perhaps because of differences in the catalyst concentration.



Key to Table 61

SGHAM-G-#

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1 Catalyst	Compound added as catalyst precursor.
2 mmol	Amount of catalyst precursor, mmoles.
3 Cocatalyst	Compound added as cocatalyst.
4 mmol	Amount 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 Press., psi	Reaction pressure in psig.
11 H <sub>2</sub> /CO	Syngas molar (volume) ratio.
12 Temp., °C	Reaction temperature.
13 Time, hr	Reaction time in hours.
14 Uptake, psi	Gas uptake in psi.
15 EtOH Rate	Rate to ethanol, M/hr.
16 EtOH Eq. Rate	Rate to ethanol equivalents, M/hr.
17 Other Ox. Rate	Rate to other oxygenates, M/hr.
18 EtOH Sel., wt. %	Weight percent selectivity to ethanol plus equivalents.

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Table 61. Scale-up of the Methanol Homologation System

SGHAM-G-#	102	103	104	105	106	107
1 Catalyst	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>	RuCl <sub>3</sub>
2 mmol	4	12	12	12	12	9
3 Cocatalyst	C4	C4	C4	C4	C4	C4
4 mmol	2	6	3	3	3	3
5 Additive	A25	A25	A25	A25	A25	A25
6 mmol	2	6	6	6	6	6
7 Promoter	A28	A28	A28	A28	A28	A28
8 mmol	40	120	120	120	120	60
9 MeOH, mL	150	150	150	150	150	150
10 Press., psi	1000	1000	1000	1000	1000	1000
11 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1	2:1	2:1
12 Temp., °C	140	140	140	140	140 <sup>a</sup>	125
13 Time, hr	2.77	0.92	3.77	2.50	2.80	3.13
14 Uptake, psi	3500	870	5240	3380	3200	3410
15 EtOH Rate	0.71	0.23	0.66	0.74	0.67	0.47
16 EtOH Eq. Rate	0.52	0.36	0.33	0.37	0.40	0.45
17 Other Ox. Rate	0.28	1.13	0.24	0.35	0.10	0.09
18 EtOH Sel., wt. %	70.8	25.8	74.2	67.9	81.1	73.5

Experimental procedure: B(15); Analytical procedure: C(9); Key on page 232.

<sup>a</sup> Temperature increased in 10° increments from 100°C to 140°C.

#### 4.3.1.3 Statistically Designed Experiments

There are many variables which may affect the performance of the methanol homologation system. These include temperature, pressure, syngas ratio, and concentrations of ruthenium, A28, C4, and A25. With this many variables it would be very time-consuming to investigate separately the effects of each one on the homologation reaction. Therefore it was decided to run statistically designed experiments, specifically a two-level factorial, in order to establish which variables were most important and in what direction to move in order to obtain optimum results.

For the first designed set it was decided to examine six variables in eight experiments. The variables examined were temperature, pressure, concentration of C4, and the ratios of ruthenium, A28, and A25 to C4. It had been established that the lowest temperature at which reasonable rates are observed is 125°C, so this was set as the lower temperature limit. The upper temperature was set at 155°C. The pressure was varied between 1200 and 3500 psi. The amount of C4 was varied from 2 mmole to 6 mmole. The ranges for the ratios of ruthenium and A25 to C4 were 1:1 to 3:1. The ratio of A28 to C4 was varied from 20:1 to 60:1. The syngas ratio was held constant at  $H_2/CO = 2:1$  and the reactions were run for a fixed time of three hours. The results of the first designed set are reported in Table 62.

As can be seen in Table 62, a wide range of reactivity was observed. The total rate to ethanol and equivalents ranged from 0.27 to 2.46 M/hr. The mole percent selectivity to ethanol ranged from 24% to 79%. The last three runs reported, G-118, 123, and 125, are center point runs, run at the average level of each variable. These runs should give an indication of the reproducibility of the system under these conditions. Significant variations can be seen, particularly between run G-118 and the two later runs. This lack of reproducibility may have arisen from

equipment problems or from changes in the reagents used, since two reagents had to be replaced during the designed set. Whatever the cause, this poor reproducibility was also reflected in the fact that quantitative correlations could not be made between the variable levels and the results of the experiments. Qualitative examination of the data suggested that rate and/or selectivity are helped by low levels of C4 and A28 and high levels of pressure, ruthenium, and A25. High temperature seemed to help the rate to ethanol but hurt the selectivity.

Based on the results from the first designed set, a second designed set was formulated. In order to simplify interpretation of the results, two more variables were fixed. The level of C4 was fixed at 2 mmole and the pressure was fixed at the maximum economically feasible level, 1500 psi. Experience with the first designed set suggested that the upper temperature of 155°C was too high, so the temperature range was decreased to 125 to 140°C. Likewise, the 60:1 level of A28 to C4 seemed too high, so this range was decreased to 20:1 to 40:1 (40 and 80 mmole). The range of ratios of ruthenium and A25 to C4 was kept constant, and since C4 was fixed at 2 mmole, this range became 2 to 6 mmole for both ruthenium and A25. The results from the second designed set are reported in Table 63.

The modifications for the second designed set appear to have helped reproducibility. Run G-130 was repeated since its uptake seemed unusually low. The repeat run, G-137, was almost exactly the same in all respects. The other data were apparently just as good, since quantitative correlations were obtained. Some examples of the correlations are listed below.

Rate to Ethanol + Equivalents:

$$\text{Rate} = -2.71 + 0.0265 \times \text{Temp} + 0.0925 \times \text{Ru/C4} - 0.075 \times \text{A25/C4}$$
$$r^2 = 0.91$$

Weight Percent Selectivity:

$$\text{Selectivity} = -19.9 + 0.665 \times \text{Temp} + 2.873 \times \text{Ru/C4} -$$
$$4.00 \times \text{A25/C4} + 2.448 \times (\text{Ru/C4} - 2) (\text{A25/C4} - 2)$$

$$r^2 = 0.95$$

Mole Percent Selectivity:

$$\text{Selectivity} = 115.6 - 0.359 \times \text{Temp} + 2.962 \times \text{A25/C4}$$
$$r^2 = 0.72$$

The values of  $r^2$ , reflecting the "goodness of fit" of the correlations, ranged from 0.72 to 0.99. It should be noted that the two selectivities, weight percent and mole percent, are affected oppositely by temperature and A25 levels. The selectivity of the methanol homologation reactions has previously been reported on a weight percent basis. However, during the second designed set it was noticed that some experiments which produced very little other oxygenates nevertheless gave very poor weight percent selectivities to ethanol. Upon examining the method of selectivity calculation it was found that one product which is an ethanol equivalent was being produced in large quantities and that its high molecular weight caused it to lower the apparent selectivity of the reaction. In order to circumvent this problem the selectivity was calculated on a mole percent basis. Since each equivalent of ethanol then counted equally, the high molecular weight product did not affect the selectivity

calculation (see for example runs G-130 and 137). It should also be noted that the weight percent calculation does not include methane produced during the reaction since its small weight has little effect on the calculated selectivity. However, the methane had a large effect on the mole percent calculation and so it is included in the mole percent selectivity. For this reason and the above problem with high molecular weight ethanol equivalents, it is felt that the mole percent selectivity is a truer representation of the selectivity of the homologation reaction.

The dependence of the rate to ethanol and equivalents on temperature and Ru/C4 ratio at a constant A25/C4 ratio of 1:1 is presented graphically in Figure 7. The contours of constant rate demonstrate that the major factor in determining the rate is temperature, with a smaller effect derived from the Ru/C4 ratio. The mole percent selectivity under the same conditions is presented in Figure 8. The vertical lines signify a lack of dependence of selectivity on Ru/C4 ratio. Overlaying the two graphs reveals that areas of highest rate do not correspond to highest selectivity. This relationship is clearly visible upon examination of the equations from which the plots were derived. High rate to ethanol requires high temperature and ruthenium and low A25, while high mole percent selectivity is achieved at low temperature and high A25. This inability to obtain both the highest rate and selectivity under the same conditions may represent a fundamental limitation of the methanol homologation system. However, it must be remembered that these limitations apply only within the range of variables investigated in this designed set. It may be that under different conditions a high rate can be obtained without sacrificing selectivity.

Table 64 reports a few other experiments performed on the basis of the results from the designed sets. In run G-124, the optimum catalyst composition for high selectivity was examined at high temperature, 155°C. This high temperature not only gave rise to very poor selectivity, but also caused rapid deactivation of the catalyst. The initial rate of gas uptake was high, but the

rate of uptake rapidly declined, resulting in a very low total gas uptake. Run G-138 was similar to G-134 except that A25 was increased, which should have led to higher selectivity at the expense of a lower rate to ethanol. The equations previously discussed predicted a rate of 1.05 M/hr and a selectivity of 74.2%. The selectivity matched the prediction exactly, but the rate was 1.33 M/hr, 27% higher than predicted.

In an attempt to boost selectivity while maintaining a high rate, the syngas ratio was changed to  $H_2/CO = 3:1$ . Three experiments were run at this ratio, runs G-139, 140, and 141. The total pressure was varied from 1200 psi (ca. same partial pressure of  $H_2$  as G-138) to 2000 psi (same partial pressure of CO as G-138). In each case the rate to ethanol was lower, probably because of more rapid catalyst deactivation. The selectivity to liquid products was higher with  $H_2/CO = 3:1$ , but the rate of methane production was much higher and this led to an overall decrease in mole percent selectivity to ethanol.

Key to Tables 62, 63, and 64

SGHAM-G-#

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1 mmol Ru	Amount of Ru added as RuCl <sub>3</sub> .
2 mmol A28	Amount of A28 added.
3 mmol C4	Amount of C4 added.
4 mmol A25	Amount of A25 added.
5 MeOH, mL	Amount of methanol used, mL.
6 Pressure, psi	Reaction pressure in psi.
7 H <sub>2</sub> /CO	Synthesis gas volume (molar) ratio.
8 Temp., °C	Reaction temperature.
9 Time, hr	Reaction time in hours.
10 Uptake, psi	Gas uptake in psi.
11 Rate to EtOH	Rate to ethanol, M/hr.
12 Rate to EtOH Eq.	Rate to ethanol equivalents, M/hr.
13 Rate to Other Ox.	Rate to other oxygenates, M/hr.
14 Tot. EtOH Sel., wt. %	Weight percent selectivity to ethanol plus equivalents in liquid products.
15 Tot. EtOH Sel., mol. %	Mole percent selectivity to ethanol plus equivalents; calculation includes methane detected in gas phase.

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Table 62. Results of First Methanol Homologation Designed Set

SGHAM-G-#	113	114	115	116
1 mmol Ru	2	6	6	6
2 mmol A28	120	360	120	40
3 mmol C4	2	6	2	2
4 mmol A25	6	6	2	2
5 MeOH, mL	150	150	150	150
6 Pressure, psi	1200	3500	1200	3500
7 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
8 Temp., °C	125	125	155	125
9 Time, hr	3.00	3.00	3.00	3.00
10 Uptake, psi	1260	9610	2220	3850
11 Rate to EtOH	0.03	0.59	0.20	0.45
12 Rate to EtOH Eq.	0.30	0.38	0.41	0.22
13 Rate to Other Ox.	0.05	0.78	0.25	0.11
14 Tot. EtOH Sel., wt. %	50.8	47.9	60.0	78.7
15 Tot. EtOH Sel., mol. %	75.0	29.6	47.7	79.1

Experimental procedure: B(15); Analytical procedure: C(9); Key on page 239.

Table 62. Results of First Methanol Homologation Designed Set  
(Cont'd)

SGHAM-G-#	119	120	121	122
1 mmol Ru	18	2	6	18
2 mmol A28	120	40	120	360
3 mmol C4	6	2	6	6
4 mmol A25	18	6	6	18
5 MeOH, mL	150	150	150	150
6 Pressure, psi	1200	3500	1200	3500
7 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
8 Temp., °C	125	155	155	155
9 Time, hr	3.00	3.00	3.00	3.00
10 Uptake, psi	4000	14060	1050	10110
11 Rate to EtOH	0.63	1.39	0.02	0.32
12 Rate to EtOH Eq.	0.36	1.07	0.25	0.87
13 Rate to Other Ox.	0.12	0.37	0.32	0.47
14 Tot. EtOH Sel., wt. %	78.1	81.0	31.8	66.7
15 Tot. EtOH Sel., mol. %	71.4	64.1	24.5	46.3

Experimental procedure: B(15); Analytical procedure: C(9); Key on page 239.

Table 62. Results of First Methanol Homologation Designed Set  
(Cont'd)

SGHAM-G-#	118	123	125
1 mmol Ru	8	8	8
2 mmol A28	160	160	160
3 mmol C4	4	4	4
4 mmol A25	8	8	8
5 MeOH, mL	150	150	150
6 Pressure, psi	2400	2400	2400
7 H <sub>2</sub> /CO	2:1	2:1	2:1
8 Temp., °C	140	140	140
9 Time, hr	3.00	3.00	3.00
10 Uptake, psi	11510	9470	9540
11 Rate to EtOH	1.29	1.04	1.06
12 Rate to EtOH Eq.	0.68	0.79	0.63
13 Rate to Other Ox.	0.33	0.23	0.23
14 Tot. EtOH Sel., wt. %	80.8	85.8	84.5
15 Tot. EtOH Sel., mol. %	69.9	61.7	62.4

Experimental procedure: B(15); Analytical procedure: C(9); Key on page 239.

Table 63. Results of Second Methanol Homologation Designed Set

SGHAM-G-#	128	129	130	137	131
1 mmol Ru	2	2	2	2	2
2 mmol A28	40	80	80	80	40
3 mmol C4	2	2	2	2	2
4 mmol A25	2	2	6	6	6
5 MeOH, mL	150	150	150	150	150
6 Pressure, psi	1500	1500	1500	1500	1500
7 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1	2:1
8 Temp., °C	125	140	125	125	140
9 Time, hr	3.00	3.00	3.00	3.00	3.00
10 Uptake, psi	2400	3500	1510	1550	3420
11 Rate to EtOH	0.19	0.47	0.07	0.04	0.31
12 Rate to EtOH Eq.	0.54	0.43	0.38	0.40	0.55
13 Rate to Other Ox.	0.05	0.11	0.04	0.06	0.12
14 Tot. EtOH Sel., wt. %	63.9	74.2	53.6	49.6	60.8
15 Tot. EtOH Sel., mol. %	71.3	64.4	78.5	78.5	73.3

Experimental procedure: B(15); Analytical procedure: C(9); Key on page 239.

Table 63. Results of Second Methanol Homologation Designed Set  
(Cont'd)

SGHAM-G-#	132	133	134	135	136
1 mmol Ru	4	6	6	6	6
2 mmol A28	60	80	40	40	80
3 mmol C4	2	2	2	2	2
4 mmol A25	4	2	2	6	6
5 MeOH, mL	150	150	150	150	150
6 Pressure, psi	1500	1500	1500	1500	1500
7 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1	2:1
8 Temp., °C	132	125	140	125	140
9 Time, hr	3.00	3.00	3.00	3.00	3.00
10 Uptake, psi	3570	3150	5770	2550	5050
11 Rate to EtOH	0.49	0.36	0.92	0.23	0.73
12 Rate to EtOH Eq.	0.46	0.36	0.31	0.38	0.36
13 Rate to Other Ox.	0.11	0.12	0.28	0.08	0.20
14 Tot. EtOH Sel., wt. %	69.8	65.8	74.5	60.6	73.0
15 Tot. EtOH Sel., mol. %	78.0	74.8	71.5	79.9	74.0

Experimental procedure: B(15); Analytical procedure: C(9); Key on page 239.

Table 64. Other Methanol Homologation Experiments

SGHAM-G-#	124	138	139	140	141
1 mmol Ru	6	6	6	6	6
2 mmol A28	40	40	40	40	40
3 mmol C4	2	2	2	2	2
4 mmol A25	6	6	6	6	6
5 MeOH, mL	150	150	150	150	150
6 Pressure, psi	1200	1500	2000	1200	1600
7 H <sub>2</sub> /CO	2:1	2:1	3:1	3:1	3:1
8 Temp., °C	155	140	140	140	140
9 Time, hr	3.00	3.00	3.00	3.00	3.00
10 Uptake, psi	1580	5430	3900	1360	2480
11 Rate to EtOH	0.18	0.84	0.55	0.19	0.36
12 Rate to EtOH Eq.	0.28	0.49	0.37	0.25	0.34
13 Rate to Other Ox.	0.22	0.31	0.10	0.05	0.08
14 Tot. EtOH Sel., wt. %	50.6	71.9	81.5	66.0	74.7
15 Tot. EtOH Sel., mol. %	41.6	74.2	53.8	55.6	58.1

Experimental procedure: B(15); Analytical procedure: C(9); Key on page 239.

Figure 7. Contours of Constant Rate to Ethanol, M/hr

Methanol Homologation Design II  
A25/C4 = 1  
Pressure = 1500 psi, C4 = 2 mmol

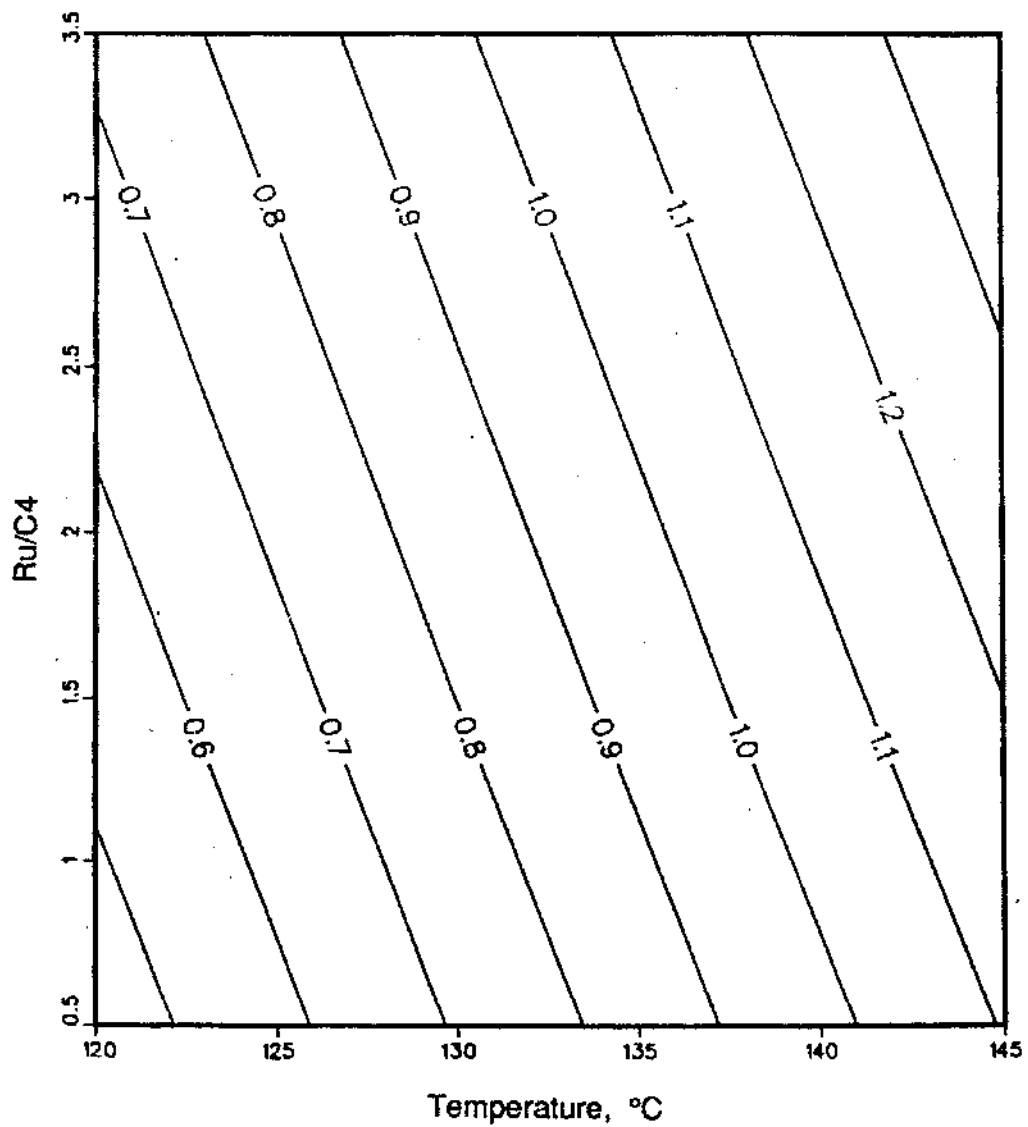


Figure 8. Contours of Constant Ethanol Selectivity, Mol%

Methanol Homologation Design II  
A25/C4 = 1  
Pressure = 1500 psi, C4 = 2 mmol

