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## **OPTIMUM HIGHER ALCOHOL MIXTURES FOR FUELS** FROM SYNGAS: SEVENTH QUARTERLY TECHNICAL **PROGRESS REPORT, APRIL-JUNE 1986**

UNION CARBIDE CORP., SOUTH CHARLESTON, WV. RESEARCH AND DEVELOPMENT DEPT

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U.S. DEPARTMENT OF COMMERCE Technology Administration National Technical Information Service Springfield, VA 22161 SEVENTH QUARTERLY TECHNICAL PROGRESS REPORT DOE CONTRACT DE-AC22-84PC70022 OPTIMUM HIGHER ALCOHOL MIXTURES FOR FUELS FROM SYNGAS

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JULY 30, 1986

ENGINEERING, MANUFACTURING AND TECHNOLOGY SERVICES DIVISION UNION CARBIDE CORPORATION RESEARCH AND DEVELOPMENT DEPARTMENT SOUTH CHARLESTON, WEST VIRGINIA

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> TECHNICAL PROGRESS REPORT DE-AC22-84PC70022

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Seventh Quarterly Report April - June 1986

### Optimum Higher Alcohol Mixtures for Fuels from Syngas

#### Patent Hold

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#### PATENT STATUS

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Patents cleared by Chicago on August 11, 1986

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### I. CONTRACT OBJECTIVE

¢ The objective of the contract is to develop and evaluate novel homogeneous catalytic systems for the selective conversion of low ٥.  $H_2/CO-ratio$  syngas to alcohol <sup>5</sup>fuel extenders.

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#### II. SCHEDULE

The contract work was originally planned for the 24-month period from October 1, 1984 through September 30, 1986. Our present plan is to continue the work, on a no-cost extension, through January 31, 1987.

Work on the project is divided into three tasks.

Task 1 is the study and development of a ruthenium-based catalytic system for alcohol production discovered at Union Carbide. The effects of reaction components, including additives, co-catalysts, and solvents, on catalyst productivity and selectivity are being investigated. Task 1 work will continue throughout the contract period.

Task 2 is the search for novel syngas conversion catalysts with improved performance. The major direction has been toward metal systems not previously known to have significant catalytic activity in homogeneous CO hydrogenation reactions. Work on Task 2 will be pursued only at a low level during the remainder of the contract, as concepts for investigation are developed.

Task 3 is a more detailed study of the most promising catalyst systems identified in Tasks 1 and 2. Investigations are to be carried out on both fundamental and process levels. Work in Task 3 is proceeding on the novel methanol homologation system discovered under this contract.

## III. ORGANIZATION

The production of optimum higher alcohol mixtures for fuels from syngas by homogeneous catalysts is the goal of a research and development program conducted by the Engineering, Manufacturing and Technology Services Division of Union Carbide Corporation.

The work is performed at Union Carbide Corporation's South Charleston Technical Center, South Charleston, West Virginia 25303.

Principal investigator is Dr. B. Duane Dombek.

Program manager is Dr. Donald C. Best.

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## IV. SUMMARY OF PROGRESS

A. Task 1: Modification of Ruthenium Catalyst System

Because of their reactivity and selectivity in syngas-based reactions producing higher alcohols, ruthenium catalysts are being investigated more thoroughly in Task 1 of this contract. Research has been done on several ruthenium-based catalyst systems during this quarter.

The screening of several types of additives with ruthenium catalyst systems has been continued. The basic objective of this effort is to modify the catalyst systems so that higher alcohols can be produced directly from syngas. Efforts are therefore directed toward increasing the total activity of the systems so  $\int_{1}^{1}$ that a lower operating pressure can be realized. At the same time, studies are being directed toward increasing the C<sub>2</sub>+ alcohol selectivity of the systems:

Much of the effort is being concentrated on the ruthenium carbonyl/molten phosphonium salt system. However, the iodidepromoted ruthenium system in NMP is also being investigated. Several catalyst additives have been observed to have beneficial effects on these ruthenium systems. As described in the last quarterly report, a novel metal-containing additive has been found to significantly enhance both the rate of syngas conversion and the yield of higher alcohols. Additionally, the use of this additive has been found to allow operation at pressures lower than previously used; experiments at 3000 psi gave better performance than some runs at 5000 psi not using the additive. Experiments have now been conducted with the synthetic precursors of this additive to see whether they may form the catalytic promoter under reaction conditions. Although a beneficial effect is observed, it is not as great as when the preformed additive is employed.

Modifications of this additive have also been investigated. Use of related compounds has so far given results inferior to those previously obtained. The introduction of electron-donating or electron-withdrawing groups sometimes can cause significant changes in catalyst behavior. In this case, neither gave an increase in activity, although changes in selectivity were evident.

Organic ligands similar to those included in some of the metal-containing additives tested have also been used as catalyst additives. In several cases, enhanced selectivities and activities to higher alcohols were observed.

These experiments were carried out according to Procedures B(a) and B(b) of Appendix B. Product analyses were conducted using Procedure C(a) of Appendix C. A more complete description of these experiments and tables of data are given in Appendix D.

B. Task 3: Further Study of Superior Catalysts

Further investigations have been carried out in an effort to gain basic information on the catalytic chemistry involved in the novel methanol homologation system discovered earlier in this project. Logical extensions of this system are also under investigation, based on the knowledge already gathered. Experiments in this basic investigation of the homologation system were conducted following Procedure B(c) of Appendix B, and analytical determinations were carried out according to Procedure C(b) of Appendix C.

Earlier work in this project has shown the importance of two specific catalyst additives in the new homologation system. Work has now been done to attempt to use additives similar to one of these, both to learn about the essential characteristics of the additive and to try to further enhance the rate and selectivity. Of a number of similar additives tried, three have been found to promote the formation of ethanol at selectivities approaching those earlier observed. It is not yet clear what properties of these

additives are important in determining the catalyst activity.

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Several experiments were carried out with added solvents (in addition to the methanol normally used). Although earlier work with cobalt-based homologation systems showed increased selectivity with added solvents, these experiments did not result in increased selectivity. However, the reactant methanol is from a practical standpoint the solvent of choice for this reaction.

Because of the many variables involved in the methanol homologation system, it was felt that the best approach to gaining an understanding of how each affects the behavior of the system was ≥ through statistically designed experiments. These experiments would allow the determination of which variables were most important for obtaining high conversion rates of methanol to ethanol with high selectivity, and at what levels optimum results could be obtained. A first designed set of experiments explored the effects of six variables: temperature, pressure, ruthenium, and the amounts of three additives. The experiments did not generate data of sufficient quality for quantitative correlations to be made, but did suggest conditions under which a second designed set might be more successful. The second designed set varied only temperature, ruthenium, and two additives, over somewhat narrower ranges. This designed set provided excellent quantitative correlations between the variables studied and the rate and selectivity of ethanol production. Unfortunately, the results showed that conditions for highest rate and highest selectivity are mutually exclusive within the range of variables investigated. The highest rate to ethanol is achieved at high temperature and high ruthenium. The highest selectivity requires low temperature.

The experiments of the designed sets were carried out. according to Procedure B(d) of Appendix B. Analyses were performed as described in Procedure C(c) of Appendix C. Further experimental information and tables of data are presented in Appendix D.

## V. CHANGES

There were no contract changes during this quarter. A request has been filed for a four-month no-cost extension to cover the period from October 1. 1986 to January 31. 1987.

## VI. FUTURE WORK

Work during the next quarter will continue on Task 1, with the goal of improving ruthenium catalysts for the direct, selective conversion of syngas to alcohols.

Additional work on Task 2 will be carried out as concepts , "worthy of experimental investigation are developed. Work in this task seeks to discover novel types of catalysts for the conversion of syngas to fuel alcohols.

Work on Task 3 will continue. This task involves the more thorough investigation of system(s) identified in Tasks 1 and 2 as the most deserving of further work. The system presently under investigation is the novel ruthenium-based methanol homologation system discovered under this contract.

C. Best D.

Program Manager

## APPENDIXES

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By S. L. Gipson, T. W. Leung, and P. W. Wegran

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### Appendix A. USE OF CODE SYSTEM

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A code system is being used in this report and throughout the contract period to identify proprietary data or information which may be the subject of future patents. The code system consists of three classifications, each member of which is assigned a number.

Category A encompasses additives, such as ligands, retal complexes, or salts, which apparently function as catalyst promoters.

Category C consists of catalysts or co-catalysts

Category S includes solverts for catalytic reactions.

Use of the code syster has been approved by the Chief Office of Patent Counsel, U.S. Department of Energy, 9800 South Cass Avenue, Argonne, Illinois 60439.

The following coded information is included in this report:

A8: ·	A catalyst additive
A25:	A catalyst additive
A261	A catalyst additive
A36:	A catalyst additive
A4-A58:	Catalyst additives
A59-A-2:	Metal-containing catalyst additives
A-3-A-8:	Organic catalyst additives
A <sup>-</sup> 9-A80:	Metal-containing catalyst additives
C18:	A catalyst precursor
54:	A reaction solvent
\$22-527 :	Peaction solvents

### Appendix B. PROCEDURES FOR CATALYST TESTING

Catalyst tests carried out under this contract have been assigned reference numbers of the form SGHAM-X-y, where the character X identifies the appropriate researcher and the numeral y specifies the serial number of the experiment.

#### PRÒCEDURE B(a).

Into a specially designed glass liner, the catalyst and additive(s) were charged along with 15.0 g of  $P(n-Bu)_4Br$ . The glass liner was then placed into a 150 mL rocker bomb autoclave. The system was pressurized with nitrogen to 80 psig and vented, a total of three times. The system was then pressurized with syngas to 200 psig, vented, pressurized to 1000 psig syngas and tested for possible leaks. Then it was heated to 230°C and pressurized to 5000 psig (or other specified pressure) for a desired period (usually 3.0 hr) with adjustment of pressure back to the specified level as uptake of gas occurred. After the desired time of reaction, the system was vented and purged with nitrogen. The glass liner was taken out and the content analyzed by GC methods.

PROCEDURE B(b)

In experiments which used NMP as the solvent, the catalyst and additives were charged into a 150 mL Hastelloy C magnedrive autoclave along with the solvent under argon. The reactor was sealed, pressurized with 80 psi of nitrogen, and vented. It was then pressurized to 300 psi with syngas and then vented. This purging was then repeated once more before the system was pressurized to 1000 psi of syngas. At this point, the system was

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tested for possible leaks. It was then heated to the desired temperature. After the desired temperature was reached, the system was pressurized to the desired level with syngas. The temperature and pressure were then kept constant for the desired reaction period. Afterwards, the reactor was rapidly cooled to room temperature by a cool water jacket.

PROCEDURE B(c).

A 100 cc Hastelloy magnedrive autoclave was used for catalyst testing. The cleaned autoclave was purged with nitrogen, charged with the reactants, sealed and pressured to 400 psig with synthesis gas of the desired composition. The reactor was maintained at 400 psig for 10 minutes to check for leaks. The reactor was then heated to the desired temperature and pressured with synthesis gas to 25 psi above the specified pressure. The pressure was maintained within ± 25 psi of the operating pressure by repressurizing as necessary. After the experiment was completed, the reactor was cooled to 20°C. The gas was vented and the liquid products were collected in a chilled bottle fitted with a septum. The reactor was washed with various solvents until the rinses appeared clean. The reactor was periodically disassembled and cleaned, as required.

PROCEDURE B(d).

Catalyst testing was performed in a 300 mL Hastelloy C magnedrive autoclave. The cleaned autoclave was purged with nitrogen, charged with reactants, liquids first, then solids, sealed and pressured to 600 psi with synthesis gas of the desired composition. This pressure was held for 15 minutes to ensure that there were no leaks. The temperature was then raised to the desired operating temperature and the pressure raised to the desired\_operating pressure. The pressure was maintained to within the

± 200 psi by repressurizing as necessary. All experiments were run for three hours. After completion of the run the reactor was cooled to below 20°C and a gas sample was taken. The reactor was slowly vented and the product collected in a crown-capped bottle precooled to 0°C. The reactor was washed with several solvents, then disassembled and washed further.

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## Appendix C. PROCEDURES FOR PRODUCT ANALYSIS

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PROCEDURE C(a)

Liquid organic product analyses were performed on a Hewlett-Packard gas chromatographic instrument, model 5840A, equipped with a 30m x 0.32mm Durabond 1701 capillary column with initial temperature and final temperature set at 25 and 280°C, respectively.

PROCEDURE C(b).

Liquid product analyses were performed on a Varian 3700 capillary gas chromatograph equipped with a Durabond 1701 30m x 0.32mm capillary column.

PROCEDURE C(c).

Liquid product analyses were performed on a Hewlett-Packard HP5890A gas chromatograph using a DB 1701 30m x 0.32mm capillary column attached to a flame ionization detector. Products were quantified using acetonitrile as an internal standard. Gas samples were analyzed using a Carle Analytical Gas Chromatograph, Series S.

## Appendix D. EXPERIMENTAL DATA

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	c.	Effects of Crganic Additives	-	· · ·	-				r	,	,	30
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## II. TASK 3: Further Study of Superior Catalysts

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c.	Catalyst	Studi	les	. <b>.</b>		•	•	•		,	•				•	ŗ				40
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E,	Summary			<b>.</b> .		,					,				,	·				-1

### I. TASK 1: Modification of Ruthenium Catalyst Systems

A. Introduction

The good characteristics of ruthenium-based catalysts for syngas conversion were the basis for further investigation of these catalysts under Task 1 of this project. Ruthenium catalysts studied earlier in the contract have shown good activity, selectivity to higher alcohols, and catalyst stability at pressures of about 6000 psi. Efforts are continuing to improve the catalyst characteristics at lower pressures, both through catalyst screening studies and through a better understanding of the catalytic process.

The screening of several types of additives with ruthenium catalyst systems has therefore been continued. The basic objective of this effort is to modify the catalyst systems so that higher alcohols can be efficiently produced directly from syngas. Efforts are therefore directed toward increasing the total activity of the systems so that a lower operating pressure could be realized. At the same time studies are being directed toward increasing the  $C_2^+$  alcohol selectivity of the systems.

Much of the effort is being concentrated on the ruthenium carbonyl/molten phosphonium salt system. However, the iodidepromoted ruthenium system in NMP is also being investigated. Following the discovery that additive A38 can increase the catalyst activity as well as the production of  $C_2^+$  alcohols, a number of additives with structures similar to A38 were discovered to have similar catalytic characteristics. A particular additive was found to increase the production of n-propanol, especially in the molten phosphonium salt system. Furthermore, it was demonstrated that the addition of synthetic precursors of A38 to the molten phosphium salt system gave catalytic effects very similar to those of A38. These experiments were carried out according to Procedures

B(a) and B(b) of Appendix B. Product analyses were conducted using Procedure C(a) of Appendix C.

B. Effects of Metal-Containing Additives in Ruthenium Systems

We previously reported that the use of a novel metalcontaining additive, A38, in the catalyst system of ruthenium carbonyl/molten phosphonium salt causes the activity of the system to increase substantially. Even at the relatively low syngas pressure of 3000 psi, the activity of the system was quite respectable. It has now been demonstrated that by adding the precursors of A38, for example, A57/A58 or A16/A58, to the catalyst system of Ru<sub>3</sub>(CO)<sub>12</sub>/molten phosphonium salt, effects similar to A38 were observed. However, A38 remainsma superior additive to its precursors. Results of these experiments are presented in Table I.

When an experiment was carried out under 2:1  $H_2/CO$  syngas, the activity of the system dropped compared to that seen under 1:1 syngas. This suggests that a higher CO partial pressure is essential for the homologation step(s).

Modification of the ligand has not yet led to a further g increase in the activity of the catalyst system. For example, A59, A60, and A61 are modifications of A38, but they do not provide catalytic results as good as A38. Nevertheless, one particular modification did yield some interesting results. When A62 was added to the molten salt system, it caused the system to produce more propanol than previous systems. Electron-donating groups on this ligand seem to retard the homologation steps of this particular system, while electron-withdrawing groups caused the system to produce other oxygenates.

The screening of metal-containing compounds discussed earlier as catalyst additives to the phosphonium salt system is almost completed. Additives A63-A68 "seemed to have either a slight positive effect or no effect on the activity and the selectivity to higher alcohols. A69 did not affect the activity but increased the

formation of ethanol moderately. A70, A71, and A72 retarded the catalyst activity severely. Results of these experiments are given in Table I.

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These experiments were carried out according to Procedures B(a) and B(b) of Appendix B. Product analyses were conducted using Procedure C(a) of Appendix C. Key to Tables I and II.

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Catalŷst precursor [charged ∩1 Catalyst 2 mmole Amount of catalyst precursor used Solvent used 5 E 3 Solvent . 4 m̃⊾/g Amount of solvent used, in mL or grams ... . 5 Additive Additive employed e 6 mmole Amount of additive used Reaction pressure in psig • 7 Press.,psi 8 Temp., C Reaction temperature ; 9 °, 9 Time, hrs. Reaction time in hours 10 H<sub>2</sub>/CO Syngas molar ratio 0 29

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11 MeOH,gAmount of methanol produced, in grams12 EtOH,gAmount of ethanol produced, in grams13 n-PrOH,gAmount of n-propanol produced, grams14 n-BuOH,gAmount of n-butanol produced, grams15 CH <sub>3</sub> CHO,gAmount of acetaldehyde produced, grams16 Other Ox.,gAmount of other oxygenates produced, grams17 Total Prod.,gWeight of total products analyzed18 % C <sub>2</sub> + alcoholsWeight percent of C <sub>2</sub> and higher alcohols19 C <sub>2</sub> +/C <sub>1</sub> ratioWt. ratio of C <sub>2</sub> and higher products to C <sub>1</sub>			-		<b>`</b>
12 EtOH,gAmount of ethanol produced, in grams13 n-PrOH,gAmount of n-propanol produced, grams14 n-BuOH,gAmount of n-butanol produced, grams15 CH <sub>3</sub> CHO,gAmount of acetaldehyde produced, grams16 Other Ox.,gAmount of other oxygenates produced, grams17 Total Prod.,gWeight of total products analyzed18 % C <sub>2</sub> + alcoholsWeight percent of C <sub>2</sub> and higher alcohols19 C <sub>2</sub> +/C <sub>1</sub> ratioWt. ratio of C <sub>2</sub> and higher products to C <sub>1</sub>		11	MeOH,g	Amount	of methanol produced, in grams
13 n-PrOH,gAmount of n-propanol produced, grams14 n-BuOH,gAmount of n-butanol produced, grams15 $CH_3CHO,g$ Amount of acetaldehyde produced, grams16 Other Ox.,gAmount of other oxygenates produced, grams17 Total Prod.,gWeight of total products analyzed18 % C <sub>2</sub> + alcoholsWeight percent of C <sub>2</sub> and higher alcohols19 C <sub>2</sub> +/C <sub>1</sub> ratioWt. ratio of C <sub>2</sub> and higher products to C <sub>1</sub>		12	EtOH, g	Amount	of ethanol produced, in grams
14 n-BuOH,gAmount of n-butanol produced, grams15 CH3CHO,gAmount of acetaldehyde produced, grams16 Other Ox.,gAmount of other oxygenates produced, grams17 Total Prod.,gWeight of total products analyzed18 % C2+ alcoholsWeight percent of C2 and higher alcohols19 C2+/C1 ratioWt. ratio of C2 and higher products to C1		13	n-PrOH,g	, Amount	of n-propanol produced, grams
15 $CH_3CHO,g$ Amount of acetaldehyde produced, grams16 Other Ox.,gAmount of other oxygenates produced, grams17 Total Prod.,gWeight of total products analyzed18 % C2+ alcoholsWeight percent of C2 and higher alcohols19 C2+/C1 ratioWt. ratio of C2 and higher products to C1	ए ७	14	n−BuOH, g	Amount	of n-butanol produced, grams
16 Other Ox.,gAmount of other oxygenates produced, grams17 Total Prod.,gWeight of total products analyzed18 % $C_2$ + alcoholsWeight percent of $C_2$ and higher alcohols19 $C_2$ +/ $C_1$ ratioWt. ratio of $C_2$ and higher products to $C_1$		15	сн <sub>3</sub> сно, д	Amount	of acetaldehyde produced, grams
17 Total Prod., g Weight of total products analyzed $\int_{0}^{1}$ 18 % C <sub>2</sub> + alcohols Weight percent of C <sub>2</sub> and higher alcohols 19 C <sub>2</sub> +/C <sub>1</sub> ratio Wt. ratio of C <sub>2</sub> and higher products to C <sub>1</sub>		16	Other Ox.,g	Amount	of other oxygenates produced, grams
18 % C <sub>2</sub> + alcohols Weight percent of C <sub>2</sub> and higher alcohols 19 C <sub>2</sub> +/C <sub>1</sub> ratio Wt. ratio of C <sub>2</sub> and higher products to C <sub>1</sub>		17	Total Prod.,g	Weight	of total products analyzed 🧃
19 $C_2 + / C_1$ ratio Wt. ratio of $C_2$ and higher products to $C_1$	·	18	$C_2$ + alcohols	Weight	percent of $C_2$ and higher alcohols
	:	· 19	C <sub>2</sub> +/C <sub>1</sub> ratio	Wt. ra	tio of $C_2$ and higher products to $C_1$

Table I. Effects of D	Metal-Contain:	ing,Additives
∽ SGHAM-L-#	1-123	1-129
1 Catalyst	Ru <sub>3</sub> (CO) <sub>12</sub> .	Ru <sub>3</sub> (CO) <sub>12</sub>
"2 mmole	1.25	1.25
3 Solvent	P (n <sub>7</sub> Bu) <sub>4</sub> Br	P (n-Bu) <sub>4</sub> Br
4 mL/g	÷ 15.0g	15.0g
5 Additive	A16	A16/A58
6 mmole	. 3.0	. 3.0/3.0
7 Press., psi	5000	5000
8 Temp., C 🐪	230	230 🚊
9 Time, hrs	3.0	3.0
10 H <sub>2</sub> /CO	1.0	1.0
- · u	n 7,1	
11 MeOH,g	. 0.89	2.7
12 EtOH,g	1.70	3.1
13 n-PrOH,g "	0.59	1.0
14 n-BuOH,g	0.0	0.26
15 CH <sub>3</sub> CHO <sub>f</sub> g	trace	0.25
16 Other Ox.,g	9.4	5.7
17 Total Prod., g	12.6	13.0
18 % C <sub>2</sub> + alcohols	18	34
19 C <sub>2</sub> +/C <sub>1</sub> ratio	13	3.8

See page 19 for key.

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5GHAM-L-#	1-119	1-131
1 Catalyst	Ru <sub>3</sub> (CO) <sub>12</sub>	Ru <sub>3</sub> (CO) <sub>12</sub>
2 mmole	1.25	1.25
3 Solvent	P (n-Bu) <sub>r4</sub> Br	P(n-Bu) <sub>4</sub> Br
4 mL/g	15.0g	15.0g
5 Additive	A57	A57/A58
6 mmole	3.0	3.0/3.0
7 Press.,psi	5000	° 5000
8 Temp., C	230	230
9 Time, hrs	3.0	3.0
0 H <sub>2</sub> /CO	1.0	. 1.0 .
<u>ء</u>	•	
1 MeOH,g	, <b>0.15</b>	1.0
2 EtOH,g	0.26	2.7 ~ <sup>2</sup>
3 n-PrOH, g	trace	0.80
4 n-BuOH, g	0.0	0.36
5 CH <sub>3</sub> CHO,g	trace	0.20
6 Other Ox.,g	3.4	5.4
7 Total Prod.,g	3.8	. 10.5
8 % C <sub>2</sub> + alcohols	6.8	37
9 C <sub>2</sub> +/C <sub>1</sub> ratio	_	9.5

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SGHAM-L-#	2-79 "	3-29	
			1. x
1 Catalyst	$Ru_3(CO)_{12}$	$= Ru_3(00)_{12}$	
2 mmole	. 1.25	1.25	
3 Solvent	P (n-Bu) <sub>4</sub> Br	P (n-Bu) <sub>4</sub> Br	į,
4 mL/g	15.0g	, 15.0g	
5 Additive	A59	A60	•
6 mmole	° 3.0 :	3.0 .	
7 Press.,psi	5000	5000	
8 Temp., C	230.	230	
9 Time, hrs	3.0	3.0	4
10 н <sub>2</sub> /со	1.0	. 1.0	
	.*	,	
ll MeOH,g	1.9	2.5	
12 EtOH,g	3.3	3.1	
13 n-PrOH,g	1.2	0.96	
14 n-BuOH,g	0.38	0.30	
15 CH <sub>3</sub> CHO,g	0.26	0.31	2
16 Other Ox.,g	5.3	4.1	•
~17 Total Prod.,g	12.3	· 11.2	
18 % C <sub>2</sub> + alcohols	40	39	
19 C <sub>2</sub> +/C <sub>1</sub> ratio	5.5	3.4	

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See page 19 for key.

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SGHAM-L-#	2-810	ວ້
	2,02	3-19
1 Catalyst	Ru <sub>3,</sub> (CO) <sub>12</sub>	Ru <sub>3</sub> (CO) 12
2 mmole 15	1.25	1.25 .
3. Solvent	NMP	<sup>*</sup> NMP
4 mL/g	30.0 mL	, 3Ó.0 mL
5 Additive	KI/A59	KI/A61
6 mmole	9.0/3.0	9.0/3.0 ×
7 Press., psi	6000	6000
8 Temp., C	230	230
9 Time, hrs	3.0	3.0 <sup>-</sup>
10 н <sub>2</sub> /се	1.0	1.0
0	e	
11 MeOH,g	2.3	. 2.5
12 EtOH,g	3.3	2.4
13 n-PrOH,g	0.41	0.14
14 n-BuOH, g	trace	trace
1:5 CH <sub>3</sub> CHO,g <sup>1)</sup>	1.9	1.4
16 Other Ox.,g	1.9	1.4 .
17 Total Prod.,g	<b>_9.9</b>	7.9
18 % C <sub>2</sub> + alcohols		32
19 C <sub>2</sub> +/C <sub>1</sub> ratio	3.3	2.2

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SGHAM-L-#	2-55	2-103
1 Catalyst	, <sup>' [</sup> Ru <sub>3</sub> (CO) <sub>12</sub>	. Ru <sub>3</sub> (CO) <sub>12</sub>
2 mmole	<b>.1.25</b>	1.25
3 Solvent	P (n-Bu) 4Br	P(n-Bu) <sub>4</sub> Br
4 mL/g	15.0g	15.0g
5 Additive	A38	A38
6 mmole	3.0	3,0
7 Press., psi	5000	5000 .
8 Temp., C	230	ິ 230 ຸ 🧸
9 Time, hrs	3.0	3.0
- 10 H <sub>2</sub> /CO	1.02	2.0
ll MeOH,g	2.8	3. <sup>7</sup> 1
12 EtOH,g	5.4	3.48
13 n-PrOH,g	1.1	0.43
14 n-BuOH,g	0.34	trace
15 СН <sub>3</sub> СНО, д 📜	0.10	0.25
16 Other Ox.,g	· ~ 7.7	2° <b>.</b> 5
17 Total Prod.,g	17.8	10.4
18 % C <sub>2</sub> + alcohols	38	38
19 C <sub>2</sub> +/C <sub>1</sub> ratio	5.4	1.8
See page 19 for key.	•	

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SGHAM-L-#	3-24	<sup>-</sup> 3-28 <u>-</u>	2-106
l Catalyst	Ru <sub>3</sub> (CO) 12	Ru3 CO 12	Ru3 CO 12
2 mmole	1.25	1.25	1,25
3 Solvent	P(n-Bu) <sub>4</sub> Br	Pn-Bu <sub>4</sub> Br	P/n-Bu <sub>4</sub> Br
4 mL'g	<u>1</u> 5.0g	15.0g	- 15.0g
5 Additive	A62	A79 ≈	- <b>A8</b> 0
6 mmole	3.5	3.0	3.5
- Press.,psi	5000	5000	5000
8 Iemp., C	230	230	=230
9 Time, hrs	3.0	_3.0	3.0
10 H <sub>2</sub> /CO	1.0	1.0	- 1.0
ll MeOH.g	1.76	2.03	0.56
12 EtOH,g	3.55	2.69	<u> </u>
13 n-PrOH,g	1.4	0.92	_0.36
14 n-BuOH, g	0.58	0.32	0.41
15 СН <sub>З</sub> СНО, д	0.18	0.23	° 0.16
⊃ 16 Other Ox.,g	5.8	4.52	⁻.2 <u></u> =
1 <sup>-</sup> Total Prod.g	13.3	10.7	9.86
18 % C <sub>2</sub> - alcohols	42	3-	20
19 C <sub>2</sub> -/C <sub>1</sub> ratio	6.6	4.3	- <u>-</u> 1 <sup>i-</sup>
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See page 19 for key.

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SGHAM-L-##	3-52	3-11	3-40
l Catalyst	Ru <sub>3</sub> (CO) <sub>12</sub>	• Ru <sub>3</sub> (CO) <sub>12</sub>	. Ru <sub>3</sub> (CO) <sub>12</sub>
2 mmole	1.25	1.25	1.25
3 Solvent	P (n-Bu) <sub>4</sub> Br	P(n-Bu) <sub>4</sub> Br	<sup>•</sup> P(n-Bu) <sub>4</sub> Br
4 mL/g	ء 15.0g «	15.0g -	15 <u>.</u> 0g .
5 Additive	none	A70	A65
6 mmole	· – ·	- 1.5	1.5
7 Press.,psi	5000	5000	5000
8 Temp., °C	230	230 .	2,30
9 Time, hrs	· 3.0	3.0	. 3 <b>.</b> 0
10 н <sub>2</sub> /со	1.0	1.0	1.0
			-
11 MeOH,g	3.0 ;	1.6	2.4
12 EtOH,g	1.7	1.4 *	3.0
13 n-PrOH,g	0.32	0.12	0.24
14 n-BuOH,g	trace	o trace	trace
15 <sup>°</sup> CH <sub>3</sub> CHO,g	0.1 *	trace	0.29
16 Other Ox.,g	0.27	trace	.0.55
17 Total Prod.,g	5.4	3.1 🛸 "	б.4
18 % C <sub>2</sub> + alcohols	39	_ ·	51
$19 C_2 + 7 C_1$ ratio	0.8	<del>-</del> ,	1.7

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SGHAM-L-# 1 Catalyst 2 mmole 3 Solvent 4 mL/g 5 Additive 6 mmole 7 Press.,psi 8 Temp., °C 9 Ťime,hrs 10 H <sub>2</sub> /CO	3-44 Ru <sub>3</sub> (CO) <sub>12</sub> 1.25	3-46  Ru <sub>3</sub> (CO) <sub>12</sub>	3-50
1 Catalyst 2 mmole 3 Solvent 4 mL/g 5 Additive 6 mmole 7 Press.,psi 8 Temp., °C 9 Ťime,hrs 10 H <sub>2</sub> /CO	Ru <sub>3</sub> (CO) <sub>12</sub> 1.25	Ru <sub>3</sub> (CO) <sub>12</sub>	Buo <sup>(</sup> (CO) 4 0
2 mmole 3 Solvent 4 mL/g 5 Additive 6 mmole 7 Press.,psi 8 Temp., °C 9 Ťime,hrs 10 H <sub>2</sub> /CO	1.25		: 13,007,12
3 Solvent 4 mL/g 5 Additive 6 mmole 7 Press.,psi 8 Temp., *C 9 Ťime,hrs 10 H <sub>2</sub> /CO		1.25	1.25
4 mL/g 5 Additive 6 mmole 7 Press.,psi 8 Temp., °C 9 Ťime,hrs 10 H <sub>2</sub> /CO	P (n-Bu) <sub>4</sub> Br	P (n-Bu) <sub>4</sub> Br	P(n-Bu) <sub>4</sub> Br
5 Additive 6 mmole 7 Press.,psi 8 Temp., °C 9 Ťimè,hrs 10 H <sub>2</sub> /CO	15 <sup>°</sup> .0g	15.0g	15.0g
6 mmole 7 Press.,psi 8 Temp., °C 9 Ťime,hrs 10 H <sub>2</sub> /CO	A63	A66	A64
7 Press.,psi 8 Temp., <sup>•</sup> C 9 Ťimė,hrs 10 H <sub>2</sub> /CO	1.5	1.5 ·	1,.2
8 Temp., °C 9 Ťimė, hrs 10 H <sub>2</sub> /CO	<sup>``</sup> 5000	5000	5000
9 Ťimė, hrs 10 H <sub>2</sub> /CO	230 🐰	. 230	230
10 H <sub>2</sub> /CO	3.0	3.0	3.0 oʻ'
د .	1.0	1:0	1.0
		e .	c
11 MeOH,g	2.5	2.7	2.7
12. EtOH, g	3.1 '	3.3	3.0
13 n-PrOH,g	0.24	0.23	0.2
14 n-BuOH,g . "	trace	trace "	trace
15 CH <sub>3</sub> CHO,g	0.29	0.35	0.28
.16 Other Ox.,g	0.55	0.69	0.52
17 Total Prod.,g	6.7	7.3	6.7
18 <sup>.</sup> % C <sub>2</sub> + alcohols	50	48	48
19 C <sub>2</sub> +/C <sub>1</sub> ratio	1.7	1.7	1.5
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See page 19 for key. . .

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SGHAM-L-#	\\ 4-82	3-56	3-62
1 Catalyst	Ru <sub>3</sub> (CO) <sub>12</sub>	Ru <sub>3</sub> (CO) <sub>12</sub>	Ru <sub>3</sub> (CO) 12
2 mmole	1.25	1.25	1.25
3 Solvent	P(n-Bu) <sub>4</sub> Br	P (n-Bu) <sub>4</sub> Br	P(n-Bu) <sub>4</sub> Br
4. mL/g	15.0g	15.0g	15.0g
5 Additive	A67	A68	A69 ·
6 mmole	1.5	· 1.5	1.5
7 Press.,psi	- 5000 ·	5000 <sup>on</sup>	5000
8 Temp., °C	230	230	230
9 Time, hrs	3.0	3.0	3.0
10 H <sub>2</sub> /CO	1.0	1.0	1.0
11 MeOH,g	2.7	3,4	1.8
12 EtOH,g	2.9	2.1	2.9
13 n-PrOH,g	0.18	0.19	0.27
14 n-BuOH,g o	trace	• 0.0	0:0
15 CH3CHO,g	0.26	0.20	0.31
16 Other Ox.,g	0.73	0.40	0.50
17 Total Prod.,g	6.8	6.3	5.8
18 % C <sub>2</sub> + alcohols	45 ·	36	55
`19 C <sub>2</sub> +/C <sub>1</sub> ratio	1.5	0.9	2.2

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Table I. Effects of Metal-Containing Additives (Cont'd.)

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SGHAM-L-#	3-34	4-78
1 Catalyst	Ru <sub>3</sub> (CO) <sub>12</sub>	Ru <sub>3</sub> (CO) <sub>12</sub>
2 mmole	1.25	1.25
3 Solvent	P(n-Ėu) <sub>4</sub> Br	P(n-Bu) <sub>4</sub> Br
4 mL/g	15.0g ·	15.0g
5 Additive	A71	A72
6 mmole	. <sup>1</sup> .5	1.5
7 Press., psi	5000	5000 '
8 Temp., C	230	230
9 Time, hrs	3.0 °	3.0
10 H <sub>2</sub> /CO	<u>1</u> .0	1.0
lı .	·	8
<sup>2</sup> 11 MeOH,g	1.4	NA <sup>a</sup>
12 EtOH,g	1,5	NA <sup>a</sup>
13 n-PrOH,g	0.25	NAa
14 n-BuOH,g	trace	NA <sup>a</sup>
15 СН <sub>3</sub> СНО,д	. 0.13	NAa
16 Other Ox., g	0.30	NA <sup>a</sup> ,
17 Total Prod.,g	3.6	NA <sup>a</sup>
18 % C <sub>2</sub> + alcohols	49	NA <sup>a</sup>
19 C <sub>2</sub> +/C <sub>1</sub> ratio	1.6	NA <sup>a</sup>

a Not analyzed; very small amounts of products formed.

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See page 19 for key.

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#### C. Effects of Organic Additives

When organic additive A58 was added to the ruthenium catalyst systems, both the molten phosphonium salt system and the iodide-promoted catalyst in NMP were found to produce more  $C_2$  products, such as ethanol. The enhancement was particularly notable for the NMP system. Increased activities were also observed. Electron-withdrawing groups substituted on the additive seem to increase both the activity and the selectivity to higher alcohols in the NMP system, while electron-donating groups have the opposite effect. A76 had a slight negative effect on the catalyst activity in NMP solvent, but the production of ethanol and propanol increased significantly. Interestingly, no effect was observed in either system when the closely related A73 was added. Results of these experiments are reported in Table II.

The addition of A77 or A78 to the NMP system affected the activity slightly. Also, the yield of C<sub>2</sub>+ alcohols dropped to only about 10% (from about 20% when no additive was added) by weight of total product.

It has become clear that benzimidazole, an additive previously reported as A40, is not stable at 230°C under catalytic conditions; it decomposes to o-phenylenediamine and some  $C_1$  fragment, most likely formic acid. Large quantities of o-phenylenediamine were observed by GC in these catalytic runs. Interestingly, o-phenylenediamine in low concentration was shown to be a mild promoter for the formation of certain oxygenates by these catalyst systems. At high concentrations, however, it retarded the catalyst activity. The enhanced production of certain oxygenates when benzimidazole was used as additive may have resulted from the hydrogenation of the  $C_1$  fragment formed from benzimidazole decomposition. Results of these experiments are reported in Table II.
These experiments were carried out according to Procedures B(a) and B(b) of Appendix B. Product analyses were conducted using Procedure C(a) of Appendix C.

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SGHAM-L-#	3-17	2-65	1-109
1 Catalyst	Ru <sub>3</sub> (CO) <sub>12</sub>	Ru <sub>3</sub> (CO) <sub>12</sub>	Ru <sub>3</sub> (CO) <sub>12</sub>
2 mmole	1.25	1.25	1.25
3 Solvent	NMP	NMP	NMP
4 mL/g	30 /mL	3 <u>0</u> mL	30 mL
5 Additive	KI	KI/A58	KI/A58
· · ·	۲ ۱ ۱	1.	
6 mmole	9.0	9.0/1.9	. 9.0/3.0
7 Press.,psi	<u>،</u> 6000	6000	6000
8 Temp., C	230 .	<u>,</u> 230	230
9 Time, hrs	3.0	3.0	3.0
10 н <sub>2</sub> /со	1.0	1.0 4	1.0
11		2 2	2 6
II MeOH,g	3.1	3.3	3.0
12 EtOH,g	0.86	2.1	× 1.5
13 n-PrOH,g	/ trace		0.10
14 n-BuOH,g	trace	trace	
15 СН <sub>З</sub> СНО, g	0.10	1.3	. 1.5
16 Other Ox.,g	0.47	1.2	0.89
17 Total Prod.,g	4.53	. <b>8.0</b> .	7.6
18 % C <sub>2</sub> + alcohols	: 19	28	21
19 $C_2 + / C_1$ ratio	0.46	1.4	1.1

Table II. Effects of Organic Additives in Ruthenium Systems

See page 19 for key.

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SGHAM-L-# 3-58 2 1 Catalyst Ru2(CO) 12 Ru	4-46 $3 (CO)_{12}$ Ru <sub>3</sub> (CO) <sub>1</sub> $2 2 2.2^{\frac{3}{2}}$ P NMP	-
1 Catalyst Ru <sub>2</sub> (CO) <sub>12</sub> Ru	$\begin{array}{c} \begin{array}{c} \text{Ru}_{3} (\text{CO})_{12} \\ \text{Ru}_{3} (\text{CO})_{1} \\ \text{Ru}_{3} (\text{CO})_{1} \\ \text{2} \\ \text{2} \\ \text{2} \\ \text{P} \\ \end{array} \end{array}$	2
	2.2 <sup>%</sup> P NMP	
2 mmole 2.2 2	P NMP	
3 Solvent NMP NM		
4 mL/g '50 mL 50	mL 50 mL	
5 Additive KI KI	/A74 KI/A75	
6 mmole 19 1	9/2.5 19/2.6	
7 Press.,psi 6000 6	000 6000	•
8 Temp., °C 230 2	30 230 `	
9 Time, hrs 3.0 3	.0 3.0	•
10 H <sub>2</sub> /CO 1.0 1	0 1.0	
· · · · · · · · · · · · · · · · · · ·		
11 MeOH,g 4.2 4	3.3	
12 EtOH,g 1.1	1.0 2.3	
13 n-PrOH,g 0.15	0.23	
14 n-BuOH,g 0.0 t:	race trace	
15 CH <sub>3</sub> CHO,g 0.47	1.0 0.57	
16 Other Ox.,g 0.33	0.73 0.63	h
17 Total Prod., g 6.3 1	0.6 7.0	
18 % C <sub>2</sub> + alcohols 20 4	3	
19 C <sub>2</sub> +/C <sub>1</sub> ratio 0.5	1.5 1.1	

Table II. Effects of Organic Additives in Ruthenium Systems (Cont'd.)

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See page 19 for key.

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(Cont'd.	· <b>)</b>	a <sup>2</sup> -	÷ 8
ं SGHAM-L-#	2-96	3-23	4-52
1 Catalyst	Ru <sub>3</sub> (CO) 12	Ru <sub>3</sub> (CO) <sub>12</sub>	Ru <sub>3</sub> (CO) 12
2 mmole	1.25	" 1.25	1.25
3 Solvent	NMP	NMP	NMP
4 mL/g	30 mL	50 mL	50 mL
5 Additive	KI/A73	KI/Benz <sup>a</sup>	KI/o-Phen <sup>b</sup>
6 mmole	9.0/2.3	9.0/51	9.0/4.6
7 Press.,psi	<sup>*</sup> 6000	6000	6000
8 Temp., C	230	230	230
9 Time, hrs	3.0	3.0	3.0
10 H <sub>2</sub> /CO	1.0 0 2.	1.0	1.0
11 MeOH,q	3.02	-3.9	3.8
12 EtOH,q	0.56	0.73	2.0
13 n-PrOH, g	trace	trace	0.24
14 n-BuOH, g	trace	0.0	. trace
15 CH <sub>3</sub> CHO,g	/. 0 <b>.1</b> 0	trace	0.61
16 Other Ox.,g	0.35	2.8	0.9
17 Total Prod.,g	4.0	7.5 <sup>C</sup>	7.6
18 % C <sub>2</sub> + alcohols	14	10	* 30
19 C <sub>2</sub> +/C <sub>1</sub> ratio	0.33	°.9	1.0
<sup>a</sup> Benzimidazole			e.
<sup>b</sup> o-Phenylenediam	nine	٢	
c In this experim	ment, 3.7g (37	mmole) of o-ph	nenylenediamine
was detected by	GC.		
See page 19 for	key.		
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Table IT. Effects of Organic Additives in Ruthenium Systems

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Table II. Effects of Organic Additives in Puthenium Systems Cont'd.

	SGHAM-L-#	4-54	4~58
	1 Catalyst	Ru <sub>3</sub> (CO) <sub>12</sub>	Ru3 (CO 12
-	2 mr.ole	1,25.	- 1.25
	3 Solvent	P(n-Bu <sub>4</sub> )Br	NMP
	4 mL∕g	15.0 g	50 rL
	5 Additive	o-Phen <sup>a</sup>	KI o-Phen <sup>a</sup>
	6 rumole	9.0	9.0 9.3
	<pre>Press.,psi</pre>	5000	6000
	8 Terp., C	230	_ 230 _
:	9 Tire, hrs	3,.0	3.0
	10 H <sub>2</sub> /CO	1.0	1.0
	11 MeOH.g	2.1	3.4
	12 EtOH.g	1.3	1.8
•	13 n-PrOH-g	0:18	0.21
	14 n-BuOH-g	trace	trace
	15 СН <sub>З</sub> СНО, д	trace	0,28
	16 Other Ox.,g	0.84	1.2
	1 <sup>-</sup> Total Prod.g	4.42	6.9
	18 % C2+ alcohol:	s 33	51
•	19 C <sub>2</sub> ± C <sub>1</sub> ratio	1.1	1.0

a o-Phenylenediarine

See page 19 for key.

Table II	. Effects	of	Organıc	Additives	ìn	Futheniur	Systens
	Cont'd	-					

SGHAM-L-#	3-32	3-48	3-64
1 Catalyst	Ru <sub>3</sub> (CO 12	Ru3 CO 12	Ru <sub>3</sub> CO 12
2 rrole	2.2	2.2	2.2
3 Solvent	NMP	NMP	NMP
4 rL g	50 g	50 mL	50 mL
5 Additive	KI A-6	KI A	KI A-8
6 mrole	19 2.5	19 2.0	19 2
<pre>Press.,psi</pre>	6000	6000	6000
8 Terp C	230	230	230
9 Tire, hrs	3.0	3.0	30
10 н <sub>2</sub> СО _=	1.0	1.0	1.0
11 MeOH g	2.2	4.1	4.8
12 EtOH g	2.1	0.50	0.59
13 n-PrOH.g	01	trace	trace
14 n-BuOH-g	trace	trace -	trace
15 СН <sub>З</sub> СНО-д	trace	trace	trace
16 Other Ox.,g	0.42	trace	trace
1 <sup>-</sup> Total Prod.g	5、4	4.б	5.4
18 % C2 <sup>+</sup> alcohols	52	11	ii
19 C <sub>2</sub> - C <sub>1</sub> ratio	1.5	0.12	0.13

See page 19 for key

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D. Task 1 Summary

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As reported in the previous quarter, the use of a novel metalcontaining additive, A38, in the catalyst system of ruthenium carbonyl/molten phosphonium salt causes the activity of the system to increase substantially. Even at the relatively low syngas pressure of 3000 psi, the activity of the system was quite respectable. We have now found that addition of the precursors of A38 to a ruthenium catalyst system gives similar, but slightly inferior, results.

Modification of the organic portion of additive A38 has not yet led to a further increase in the activity of the catalyst system. Nevertheless, one particular modification did yield some interesting results; A62 caused the system to produce more propanol than previous systems. Electron-donating groups in the additive seem to retard the homologation steps of this particular system, while electron-withdrawing groups caused the system to produce other oxygenates.

The addition of organic additive A58 was found to enhance the production of  $C_2$  products such as ethanol; increased activities were also observed. Electron-withdrawing groups substituted on the additive seem to increase both the activity and the selectivity to higher alcohols, while electron-donating groups have the opposite effect. Additive A76 had a slight negative effect on the catalyst activity, but the production of ethanol and propanol increased significantly.

It has become clear that benzimidazole, an additive reported by others to be a useful promoter for ruthenium catalysts, is not stable at 230°C under catalytic conditions. It decomposes to o-phenylenediamine and some  $C_1$  fragment, most likely formic acid. Interestingly, o-phenylenediamine in low concentration was shown to be a mild promoter for the formation of certain oxygenates by these catalyst systems. At high concentrations, however, it retarded the catalyst activity. The enhanced production of certain oxygenates

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when benzimidazole was used as additive may have resulted from the hydrogenation of the C<sub>1</sub> fragment formed from benzimidazole

decomposition.

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#### II. TASK 3: Further Study of Superior Catalysts

### A. Introduction

The objective of Task 3 is 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 included in this task are both of a fundamental chemical nature and a process-oriented nature.

Work which has been done this quarter in Task 3 falls into c both categories. The system presently under study is the novel low-pressure homologation system which converts methanol to ethanol upon reaction with syngas. Fundamental chemical studies are being directed toward a better understanding of the chemical steps involved. At the same time, studies are being carried out to characterize the system by studying its responses to various process variables. A series of statistically designed experiments has been corpleted, and the results are presented below.

B. Methanol Homologation

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

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 $CH_{3}OH + 2 H_{2} + CO = ----> CH_{3}CH_{2}OH + H_{2}O$ 

catalyst at 160 to 180°C and 3000 to 6000 psig. The ethanol rates are typically 3 to 6 moles 1 hr M hr) and selectivities are at best 85%. In our work, we have discovered a novel ruthenium-based catalyst that allows the reaction to be carried out at significantly lower pressure. For example, ethanol selectivities of 80% are obtained at operating pressures below 1500 psig with a

- catalyst consisting of A9-Pu-A25-A28.

C. Catalyst Studies

Earlier work in this project has shown that catalyst additives A9 and A25 are critical components of the catalyst. In the absence of one or both; the homologation reaction is not observed. Additives similar to A25 were prepared and examined in our earlier work. In general, catalysts containing additives other than A25 = were found to be markedly less active, and ethanol selectivities were less than 40%. We have continued to study alternative additives and our current results are reported in Table III. All cf the runs reported in Table III were carried out at 9°5 psig with H<sub>2</sub> CO = 2:1

In run 18-109 with A26, the reaction consured 300 psi in rinutes and then stopped. The terperature was very difficult to control due to the exothermic nature of the reaction. Lower terperature runs 118-110 and 18-112) resulted in better terperature control. In each case gas consurption was low and in 18-112 the ethanol selectivity was only 9.1%. Additives A4<sup>-</sup> 18-54. EtoH = 64.8% . A3<sup>-</sup> 18-116. EtoH = 60.2% and A53 21-16. EtOH = 71.6% resulted in catalysts that yielded ethanol with selectivities >60%. The catalyst containing A53 approaches the activity and ethanol selectivity obtained with A25. The results with A4<sup>-</sup>, A3<sup>-</sup> and A53 deronstrate that additives other than A25 will work. However, at this tire it is not clear what property structural or electronic of the additive determines the overall activity.

Several experiments were carried out with  $H_2$  CO = i:l at various temperatures and pressures. The results are reported in Table IV. Neither the operating pressure nor the arount of C<sup>-</sup> utilized had ruch impact on the ethanol selectivity. The highest ethanol selectivity 50.1%, was obtained at 140°C and 500 psig. Decreasing the pressure decreased the activity as judged by the amount of gas consured per unit time

The homologation reaction was carried out with various solvents at constant catalyst composition and reaction conditions. The results are reported in Table IV. For comparison, run 17-19 (no solvent, same reaction conditions) is included in Table IV. In these experiments the methanol:solvent ratio was 1:1 by volume. Except for S22 (18-87, EtOH = 70.9%) the ethanol selectivities are markedly less than in the no-solvent case. There is no correlation of catalyst activity or product selectivity with solvent polarity. It was anticipated that the ethanol selectivity would increase by the addition of a solvent. This effect has been observed in the cobalt-catalyzed reductive carbonylation of methanol. In that case, it was thought that the metal-acyl intermediate ("CH<sub>3</sub>C(O)M", equation 2) reacts with H<sub>2</sub> or methanol to yield acetaldehyde or methyl acetate, respectively.



CH2OH

k2

"CH3C (O) M"

CH<sub>3</sub>C(O)H acetaldehyde

CH<sub>2</sub>C(O)OCH<sub>2</sub>

methyl acetate

(2)

A solvent decreases the methanol concentration whereas the H<sub>2</sub> concentration (assuming the H<sub>2</sub> partial pressure remains constant) remains relatively unchanged. The net effect is that the reaction of the acyl intermediate "CH<sub>3</sub>C(O)M" with H<sub>2</sub> becomes more favored  $(k_1[H_2] > k_2[CH_3OH])$  and the amount of acetaldehyde increases. The decreased catalyst activity and ethanol selectivity (except S22) may indicate that the solvent is not acting as a simple diluent in the homologation reaction.

Several runs were carried out with a catalyst consisting of A9-C6-C<sup>-</sup>-A25-A28. The results are listed in the corprehensive table Table V: 18-41. 68. <sup>-</sup>0. <sup>-</sup>3. <sup>-</sup>5, and <sup>-</sup>6. It was thought that C6. in combination with C<sup>-</sup>, would lead to a better acetaldehyde hydrogenation catalyst and higher etharol selectivities. Pun 18-41 resulted in an ethanol selectivity of 80% which is 8% higher than for the corresponding run without C6 1<sup>-</sup>-19. Table IV. Increasing A25 (18-<sup>-</sup>3 or C<sup>-</sup> 18-<sup>-</sup>0, or decreasing C<sup>-</sup> 18-68 resulted in ethanol selectivities less that <sup>-</sup>0% Further work with the A9-C6-C<sup>-</sup>-A25-A28 catalyst is necessary to understand the origins of these effects.

A corprehensive list of the experiments carried out in this part of the project during the quarter is given in Table V All of these experiments were carried out according to Procedure B c of Appendix B and analyzed according to Procedure C b of Appendix C

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Table III. Effects of Catalyst Composition Changes

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	۰. <sup>۰</sup>	Temp.,	• EtOH
SGHAM-W-#	Catalysts, molar ratio	·•C	Sel.,%
	<u>!</u>		
18-51	A9:C7:A8:A28 = 1:2:2:20	165	43.3
18-53	A9:C7:A53:A28 = 1:2:1:20	140	19.3
18-105	A9:C7:A54:A28 = 1:2:2:20	140 .	3.6
18-109	A9:C7:A26:A28 = 1:2:2:20	140 .	6.6
<u>1,</u> 8–110	A9:C7:A26:A28 = 1:2:2:20	· 115	not analyzed
18-112	À9:C7:A26:A28 = 1:2:2:20	95	9.1
18-113	A9:C7:A55:A28 = 1:2:2:20	140	. 26.2
18-115	A9:C7:A36:A28 = 1:2:2:20	140	32.2
18-50	A9:C7:A36:A28 = 1:2:3:20	165	not analyzed
18-54 "	A9:C7:A47:A28 = 1:2:1.5:20	140	64.8
18-56	A9:C7:A48:A28 = 1:2:2:20	. 140	24.8
18-59 <sub>s</sub>	A9:C7:A49:A28 = 1:2:2:20	140	17.0
18-60	A9:C7:A49:A28 = 1:2:1.35:20	120	37.9
18-114	A9:C7:A50:A28 = 1:2:2:20	140	15.4
18-116	A9:C7:A37:A28 = 1:2:2:20	140	60.2
18-121	A9:C7:A37:A28 = 1:2:2:20	. 150 '	12.5
18-122	A9:C7:A51:A28 = 1:2:2:20	140	9.4
18-123	A9:C7:A52:A28 = 1:2:2:20	140	4.8
21-16	A9:C7:A53:A28 = 1:2:2:20	140	71.6

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Table IV. Effects of Solvents and Reaction Conditions

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	•		Temp.,	Pressure,	• .	EtOH
SGHAM-W-#	A9:C7:A25:A28	Solvent	• • C	psig	н <sub>2</sub> /со	Sel.,%
18-97	1:2:2:20		140	<u>-</u> 975	1:1	45.2
118-100	1:2:2:20	<b></b>	140	750	1:1	41.8
18-102	1:1:2:20		140	750	1:1	41.0
21-28	1:0.5:2:20		140	750	1:1	41.7
21-25	· 1:2:1:20		140	500	1:1	50.1
4			c	,		
					•	Ť
17-19	1:2:2:20	none	140	975	2:1	72.7
18-85	1:2:2:20	S4	140	975	2:1	57.3
18-87	1:2:2:20	<b>S2</b> 2	140	975	2:1	70.9
18-91	1:2:2:20	S23	140	975	2:1	14.9
18-94	1:2:2:20	S24	140	975	2:1	56.5
21-30	1:2:2:20	S.2.5	140	975	2:1	45.
21-35	1:2:2:20	S26	140	975	2:1	44.4
21-39	1:2:2:20	s27	140	975	2:1	0.

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# Key to Table V.

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# SGHAM-W-#

1 Catalyst	Compound added as catalyst precursor
2 mmole	Amount of catalyst precursor, mmoles
3 Cocatalyst	Other compound added as cocatalyst
4 mmole	Amount of cocatalyst added
5 Additive -	Catalyst additives employed
6 mmole	Amount of catalyst additive
7 Promoter	Other promoter employed
8 mmole	Amount of promoter
9 MeOH(mL)	Amount of methanol used
10 Solvent	Reaction solvent employed
11 mL .	Volume of solvent used
12 Pressure, psi	Reaction pressure in psig
13 H <sub>2</sub> /CO	Syngas molar (volume) ratio
14 Temp., C	Reaction temperature
15 Time, hr	Reaction time in hours
16 Uptake,psi	Gas uptake in psi
17 Product Sel.8	Molar, selectivity to products:
18 EtOH	Free ethanol
19 EtOH Eq.	Ethanol equivalents
20 Total EtOH	Total ethanol
v 21 Other Oxy.	. Other oxygenates
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SGHAM-W-#	18-41	18-44	18-46
1 Catalyst	 A9	A9	A9
2 mmole	2.00	0.50	0.50
3 Cocatalyst	c6/c7	C7	C7
4 mmole	2/2	1.00	1.00
<sup>&gt;</sup> 5 Additive	A25	A25	A25
6 mmole	4.00	1.00	2.00
7 Promoter	A28	A28	A28
8 mmole	20.00	10.00	. 10.00
9 MeOH (mL)	40.00	40.00	40.00
10 Solvent	none	none	none
11 mL	0.00	0.00	0.00
12 Pressure, psi	975	975	975
13 H <sub>2</sub> /CO	° 2:1 ′	2:1	2:1
15 Temp., 'C	140,	165	165
16 Time, hr	<b>5.</b> 75	,2.50	2.20
017 Uptake,psi	3200	1097	1090
18 Product Sel.8	, Ş		
1,9 EtOH	50.23	° 29.51	31.94
20 EtOH Eq.	29.60	31.63	27.01
21 Total EtOH	79.83	61.13	58.96
22 Other Oxy.	20.17	38.87	41.04

Table V. Comprehensive Table of Homologation Experiments

See page 45 for key.

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Table V. Comprehensive Table of Homologation Experiments • . ۴.

(Cont'd.)

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SGE	IAM-W-#	18-48	18-50	18-51	18-53
1	Catalyst	A9	A9	A9	 'A9
, 2	mmole	0.25	0.50	0.50	2.00
'З	Cocatalyst	C7	C7 👾	C7	C7
4	mmole	0.75	1.00	1.00	4.00
5	Additive	A25	A36	- A8	A53
6	mmole	0.50	1.50	1.00	. 2.00
7	Promoter	A28	· A28	A28	A28 <sup>.</sup>
8	mmole	7.50	10.00	10.00	40.00
9	MeOH (mL)	40.00	40.00	40.00 "	. 40.00
10	Solvent	none	none	none	none
11	mL ÷	0.00	0.00'	0.00	0.00
12	Pressure,psi	975	975	975	975
.13	H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
14	Temp., 'C	165	165	. 140	. 140
15	Time, hr	1.50	2.50	1.50	0.75
16 ©	Uptake, psi	450 <sup>·</sup>	490	620	450
17	Product Sel.8		÷		•
18	EtOH	21.46	: NA <sup>a</sup>	15.94	7.67
19	EtOH Eq.	21.16	NAa	27.36	11.64 <sup>°</sup>
20	Total EtOH	42.62	NA <sup>a</sup>	43.30	19.31
21	Other Oxy.	57.38	· <sub>NA</sub> a	56.70	80.69

<sup>a</sup> Not analyzed; solution lost during recovery process. ń

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See page 45 for key.

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	(Cont'd	.)		v	' <b>.</b>
SGH	АМ-W-#	18-54	18-56	18-59	18-60
1	Catalyst	· A9	A9 '	A9	A9
2	mmole	2.00	2.00	2.00	1.00
3	Cocatalyst	C7·,	C7 *	C7	C7 ੂ
4	mmole	4.00	. 4.00	4.00	2.00
5	Additive .	A47	A48	A49	A49
6	mmole	2.50	4.00	2.20	01.35
7	Promoter	A28	A28	A28	A28
8	mmole	40.00	40.00	40.00	28.00
9	MeOH (mL)	40.00	40.00	40.00	40.00
10	Solvent	none	none	none	none
11	mL.	0.00	0.00	:0.00	• 0.00
12	Pressure, psi	975	975	975	975
13	H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
14	Temp., C	140	· 140	-140	120
15	Time, hr	2.00	1.00	1.00	2.50
16	Uptake, psi	1596	445	977	758
17	Product Sel.%		•		*
.18	EtOH	39.09	.75 <sup>#*</sup>	1.44	15.14
19	EtOH Eq.	25.71	23.13	15.56 ·	22.80
.20	Total EtOH	64.81	24.87	17.00	37.95
2.1	Other Oxy.	35.19	, 75.13	83.00	62.05

Comprehensive Table of Homologation Experiments

See page 45 for key.

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Table V.

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SGE	IAM-W-#	18-68	18-70 "	18-75	18-76
1	Catalyst	A9;		··A9	A9 «
2	mmole .	2,00	2.00	2.00	2.00
3	Cocatalyst	C6/C7	26/C7	C7	C6
4	mmole	4/1	، <sup>8</sup> /4 ,	S 1.00	<u>.</u> 4.00
5	Additive	- A25	A25	A25	A25.
б	mmole	4.00	. 4.00	- . 4.00	4.00
7	Promoter	A28	A28	A28	A28
8	.mmole	40.00	40.00	, 40 <b>.</b> 00	40.00
9	MeOH (mL)	40.00	40.00	40.00	40:00
10,	Solvent	none	none	none	none
11	mL	0.00	0.00	·0.00	0.00
12	Pressure, psi	975	975 ·	975	.975
13	H <sub>2</sub> /CO ∞	2:1	2:1	2:1	2:1
14	Temp., C	140 :	140	140.	<u> </u>
15	Time, hr	2.75 '	2.50	2.75	2.20
16	Uptake,psi	2330	1700 :	\$ 850	610
17	Product Sel.	i 1	-		·
18	EtOH	47.46	37.05	12.10	. 1.77
¥19	EtOH Eq.	22.24	28.45	42.22	45.33
20	Total EtOH	69.69	65.50	54.32	47.10
21	Other Oxy.	30.31	34.50	45.68	52.90

Table V. Comprehensive Table of Homologation Experiments

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(Cont'd.)

See page 45 for key.

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GHAM-W-#	18-73	18-85	18-87	18-91
1 Catalyst	A9	A9	· ` ` A9	 A9
2 mmole	2.00	2.00	2.00	2.00
-3 Cocatalyst	C6/C7	C7	C7	C7 (*
4 mmole	4/4	4.00	4.00	4.0 ·
5 Additive	A25	A25	A25	A25
6 mmole	8.00	<sup>220</sup> 4.00	4.00	4.00
7 Promoter	A28,	A28	A28	A28
8 mmole	40.00	40.00	. 40.00	40.00
9 MeOH(mL)	40.00	. 20.00	20.00	20.00
10 Solvent	none	S4	° \$22	\$23 <sub>.</sub>
11 mL	0.00	20.00	20.00	20.00
12 Pressure, psi	975	975	÷ 975	975
13 H <sub>2</sub> /CO	2:1	2:1	- 2:1	2:1
- 14 Temp., C	140	140	. 140	140
15 Time, hr	1.00	2.00	2.00	_2.00
.16 Uptake, psi	1450	1540	2030	380
		·. ·		
17 Product Sel.*	5	с.	•	۰. ۱
18 EtOH	37.39	30.23	45.75	6.83
19 EtOH Eq.	29.71	27.06	25.20	* 8.11
20. Total EtOH	67.10	57.30	70.94	14.94
21 Other Oxy.	32.90	42.70	29.06	85.06

See page 45 for key.

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, SGI	IAM-₩-# <sup>с3</sup> .	18-94	18-97	18-100		18-102
ົຸ1	Catalyst	A9	A9 .	A9		A9
. 2	mmole .	2,.00	2.00	2.00		2.00
-3	Cocatalyst	C7	· C7	C7 (		C7
4	mmole	4.00	4.00	·4.00		2.00
5	Additive	A25	A25	A25 (	÷.	A25
6	Mole	4.00 <sup>-</sup>	4.00	4.00	•	4.00
7	Promoter	. A28	A28	์ A28		A28
8	mmole ·	40.00	40.00 .	40.00		20.,00
√°9	MéOH (mL)	20.00	40.00 · ·	40.00		40.00
10	Solvent	Ş24	none	о́попе	ŝ	none
11	mL	20.00	0.00	0.00	· -	0.00
o <sup>12</sup>	<sup>'</sup> Pressure, psi	975	975	. 750		750
13	н <sub>2</sub> /со	2:1	1:1	1:1	4	1:1
14	Temp., C	140	140	140		140
-15	Time; hr	2.00	2.00	24.30		2.50
<sup>,</sup> 16	,Uptake, psi	. 1720	2568	2100		1980
•	77 F	Ŷ			c.	s
· 17	Product Sel.*		· · ·	2		
18	EtOH -	25.60	19.48	19.25		19.98
19	EtOH Eq.	30.98	25.80	22.57		21.02
۰. <mark>2</mark> 0	Total EtOH	56.58	45.27	41.82		41.00
21	Other Oxy.	43.42	54.73	58.18		59.00

Table V. Comprehensive Table of Homologation Experiments (Cont'd.) ;

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See page  $45^{1}$  for key.

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SGF	IAM-W-#	18-105	18-109	18-110	18-112
1	Catalyst	 A9	A9	A9	A9
2	mmole <sup>:</sup>	2.00	2.00	2.00	2.00
3	Cocatalyst	C7 ·	C7	C7	C7
4	mmole	4.00	4.00	4.00	4.00
5	Additive	A54	A26	A26	~ Å26
6	mmole	4.00	4.00	4,00	4.00
7	Promoter	A28	A28	A28	A28
8	mmole	-20.00	20.00	20.00	20.00
9	MeOH(mL)	40.00	40.00	40.00	40.00
10	Solvent	none	none	none	none
11	mL	.0.00	0.00	0.00	0.00
12	Pressure, pŝi	975	975	975	975
13	H <sub>2</sub> /CO	2:1	2:1	2:1	· 2:1
14	Temp., C	140	140	115	95
15	Time, hr	1.00	1.00	1.00	1.50
16	Uptake,psi	300	300	Ź70	477
17	Product Sel 2	• ,	ي بو		0
′ ± ′ ۱۹	E+OH	, 0.00	<u>"</u> О.ОО	NA <sup>a</sup> .	1,81
10	EtOH Eq	3 61	6 62	NAa	7.34
20	) Total Etor	3 61	6 62	NAa	9,15
20		06.30	03 30	лтл а	00.95

Table V. Comprehensive Table of Homologation Experiments (Cont'd.)

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<sup>a</sup> Not analyzed; solution lost during recovery process.

See page 45 for key.

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Table	v.	Comprehensive	Table	of	Homologation	Experiments	
		(Cont'd.)					

SGHAM-W-#	18-113	18-114	18-115	18-116
1 Catalyst	; A9	A9	A9	A9
2 mmole	2.00	2.00	2.00	2.00
3 Cocatalyst	C7	C7	C7	C7 २
:4 mmole	4.00	4.00	4.00	4.00
5 Additive	A55 -	A50 · ·	A36 .	- A36
6 mmole	4.00	4.00	4.00	4.00
7 Promoter	A28	A28	A28	A28
8 mmole.	20.00	20.00	20.00	20.00
9 MeOH (mL)	40.00	40.00	40.00	40.00
10 Solvent	none	none	none	none
,11 mL .	0.00	0.00	0.00	0.00
12 Pressure, psi	975	, 975	975	·975
"13 H <sub>2</sub> /CO	2:1	2:1	2:1	2:1
14 Temp., C	140	140	140	140
15 Time, hr	1.40	1.00	1.00	2,40
16 Uptake,psi	. 490	431 。	650	7
17 Product Sel.		1		
18, EtOH	13.06	1.89	15.07	34.10
19 · EtOH Eq.	13.15	13.57	17.15	26.10
20 Total EtOH	26.21	15.45	32.22	60.21
21 Other Oxy.	73.79	84.55	67.78	39.79

See page 45 for key.

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Table V. Comprehensive Table of Homologation Experiments (Cont'd.)

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SGHAM-W-#	18-121	18-122	18-123
1 Catalyst	A9	A9	A9
2 mmole	1.70	2.00	2.00
3 Cocatalýst	C7.	C7	C7
4 mmole	3.40	4.00	4.00
5 Additive	A36	A51	` A52
6 mmole	3.40	2.00	4.00
7 Promoter	A28	A28	A28
8 mmole	20.00	20.00	20.00
9 MeOH(mL)	40.00	40.00	40.00 .
10 Solvent	none	none	none
11 mL	0.00	0.00	0.00
12 Pressure,psi	975	975	975
13 H <sub>2</sub> /CO	2:1	2:1	2:1
14 Temp., °C	150	140	140
15 Time, hr	1.00	1.00	0.50
16 Uptake,psi	100	240	200
• 17 Product Sel.	5		
18 EtOH	1.85	0.74	0.67
19 EtOH Eq.	10.70	8.63	4.13
20 Total EtOH	12.56	9.37	4.81
21 Other Oxy.	87.44	90.63	95.19
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See page 45 for key.

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SGHAM-W-#	21-16	21-21	21-25
1 Catalyst	A9	C18	 · A9
2 mmole .	2.00	1.00	. 2.00
3 Cocatalyst	_ C7	C7	<sup>•</sup> C7
4 mmole	4.00	4.00	e 4.00
5 Additive (	A47	. A47 ·	· A25
, 6 mmole	4.00 4	4.00	2.00
.7 Promoter	A28	A28	A28
8 mmole	20.00	20.00	20.00
9 MeOH (mĽ)	40.00	40.00	°40.00
10 Solvent	none	none	none
11 mL	0.00	0.00	0.00
12 Pressure, psi	975	975	500
13 H <sub>2</sub> /CO	2:1	2:1	1:1
14 Temp., °C	140	140	140
15 Time, hr	4.50 .	2.75	2.00
16 Uptake,psi	1900	, 585	1085:
17 Product Sel %		2	
18 EtOH	46.45	28.46	24.09
19 EtOH Eq.	25.14	26.86 ***	25.92
20 Total EtOH	71.60	55.32	50.01
21 Other Oxy.	28.40	44.68	49.99

Table V. Comprehensive Table of Homologation Experiments -(Cont-d.) 6 . .

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SGHAM-W-#	21-28 .	21-30	21-35	21-39
1 Catalyst	A9	A9	A9	A9
2 mmole	2.00	2.00	2.00	,2.00
3 Cocatalyst	C7	C7	C7	C7
4 mmole	1.00	4.00	<sup>:</sup> 4.00	4.00
5 Additive	A25	A25	A25	A25
6 mmole	4.00	4.00	4.00	4.00
7 Promoter	A28	A28	A28	A28
8 mmole	20.00	20.00	20.00	20.00
9 MeOH (mL)	40.00	20.00	20.00	20.00
10 Solvent	none	S25	S26	ι S27
11 mL	0.00	c 20.00	20.00	20.00
12 Pressure,psi	<sup>·</sup> 750՝	975	<sup>-</sup> 975	975
13 H <sub>2</sub> /CO	1:1	2:1	2:1	2:1
14 Temp., C	140	140	140	140
15 Time, hr	1.75	2.00	2.00	1.00
16 Uptake,psi	2050	.1000 .	1490	320
17 Product Sel.8	÷	÷		
18 EtOH	21.14	16.97	14.00	0.00
19 EtOH Eq.	20.65	28.70	30.45	0.00
20 Total EtOH	41.79	45.67	44.45	. 0.00
21 Other Oxy.	58.21	54.33	55.55	100.00

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(Cont'd.)

Table V. Comprehensive Table of Homologation Experiments

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See page 45 for key.

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#### D. 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, A9, 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 A9, and the ratios of ruthenium, A28, and A25 to A9. 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 A9 was varied from 2 mmole to 6 mmole. The ranges for the ratios of ruthenium and A25 to A9 were 1:1 to 3:1. The ratio of A28 to A9 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 VI.

As can be seen in Table VI, 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

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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 Å9 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 A9 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 A9 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 A9 was kept constant, and since A9 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 VII.

The modifications for the second designed set appear to have helped reproducibility. Run G-130 was <sup>c</sup>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 Methane:

Rate =  $-0.63 + 0.00752 \times \text{Temp} - 0.03875 \times \text{Ru/A9} - 0.05375 \times$ A25/A9 =  $0.03375 \times (\text{Ru/A9} - 2)(\text{A25/A9} - 2)$ 

 $r^2 = 0.99$ 

Rate to Ethanol + Equivalents:

Rate =  $-2.71 + 0.0265 \times \text{Temp} + 0.0925 \times \text{Ru/A9} - 0.075 \times \text{A25/A9}$  $r^2 = 0.91$ 

Weight Percent Selectivity:

Selectivity =  $-19.9 + 0.665 \times \text{Temp} + 2.873 \times \text{Ru/A9} - 4.00 \times A25/A9 + 2.448 \times (\text{Ru/A9} - 2) (A25/A9 - 2)$ 

 $r^2 = 0.95$ 

Mole Percent Selectivity:

Selectivity = 115.6 - 0.359 x Temp + 2.962 x A25/A9  $r^2 = 0.72$ 

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

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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/A9 ratio at a constant A25/A9 ratio of 1:1 is presented graphically in Figure I. The contours of constant rate demonstrate that the major factor in determining the rate is temperature, with a smaller effect derived from the Ru/A9 ratio. The mole percent selectivity under the same conditions is presented in Figure II. The vertical lines signify a lack of dependence of selectivity on Ru/A9 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 This inability to obtain both the highest rate and A25. 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 significantly different conditions a high rate can be obtained without sacrificing selectivity.

Table VIII 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 VI-VIII.

12 Rate to EtOH Eq.

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13 Rate to Other Ox.

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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
З	mmol A9	Amount of A9 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
:	1	
°11	Rate to EtOH	Rate to ethanol, M/hr

Rate to ethanol, M/hr Rate to ethanol equivalents, M/hr 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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SGHAM-G-# +	113.	114	115	116 <u>-</u>
1 nr.ol Ru	2 .	ତ	<u>6</u>	- 6
2 r-ol A28	120	360.,	120	40
3 r=01 A9	. 2	6	. 2	2
4 mrol A25 5	6	- б	· 2	2
5 MeOH nL	150	150	. 150	f 150
6 Pressure, psi	1200 -	3500	1200 -	3500
- н <sub>2</sub> со	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 Pate to EtOH	0,03	0.59	0.20	0.45
12 Pate to EtOH Eq.	0 30	0.38	0.41	0,22
13 Pate to Other Ox.	0,05	09	0.25	.0,11
14 Iot. EtOH Sel., wt. %	50.8	49	60.0	-8,-
15 Tot. EtOH Sel. rol %	-5.0	29.6	4	-9.1

Table VI. Pesults of First Methanol Hopologation Designed Set

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See page 62 for key.

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(Cont'd.)		, ,	ū	2
SGHAM−G−# <sup>-</sup>	119	120	, 121	122
1 mmol Ru	18	2	6	:18 <u>;</u>
2, mmol A28	120	• 40	. · 120o	360
3 mmol A9	6 <sup>`</sup>	ົ2	6	6
4 annol 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°
Ч. — — — — — — — — — — — — — — — — — — —	, . ,	• · ·		**
11 Rate to EtOH	0.63	1.39	0.02	0.32
12 Rate to EtOH Eq.	0.36	ຼໍ່ 1.0ຸ7	• 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
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Results of First Methanol Homologation Designed Set

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Table VI.

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ст. Ст.	SGHAM-G-#	118	123	125	
1	mmol Ru	 8	8	8	
· 2	mmol A28	1.60	160	160	
3	mmol A9	4	4	. 4 -	-
4	mmol A25	. 8	8	8	
<sup>°</sup> 5	MeOH, mL	150	150	150	
б	Pressure, psi	2400	2400	2400	
. 7	H <sub>2</sub> /CO	2:1	2:1	2:1	
8	Temp., C	140	140	140	
و ب	Time, hr	3 <sub>¦</sub> .00	3.00	. 3:00	ల
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	Jot. EtOH Sel., mol. %	69.9	<i>.</i> 61.7	62.4	

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

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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 A9	2 ~	. 2	2	2	2
4 mmol A25	2 *	· 2	6	6.	. 6
5 MaOH, mL <sup>1</sup> o	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 pime, 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	Ó.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
				<u>-</u> 5	
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Table VII. Results of Second Methanol Homologation Designed Set

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Ø	SGHAM-G-#	132	133	134	135	~136
		~~~	·	 C		6
1	mmol Ru	4	к. <u>6</u> т.	ø	0	0
2	mmol A28	60	`80 °	40	40	∘ 80
3	mmol A9	2	. 2	2	2	. 2
4	mmol A25	· 4	2 :	2	÷ 6	6
5	MeŎH, mL	150	150	150	150	1,50
6	Pressure, psi	1500	1500	1500	1500	. 1500
7	и н <sub>2</sub> /со	2:1	2:1	2:1	2:1	2:1
۰ . ٤	B Temp., C	132	125	140	125	140
. 9	Time, hr	3.00	3.00	3 <u>. 0</u> 0	3.00	3.00
10	) Uptake, psi	357Ö	3150 ·	5770	2550	5050
; }						
1:	L Rate to EtOH	0.49	0.36	0.92	0.23	0.73
1:	2 Rate to EtOH Eq.	0.46	0.36	0.31	0.38	0.36
1:	3 Rate to Other Ox.	0.11	0.12	0.28	0.08	0.20
1.	4 Tot. EtOH Sel., wt.%	69.8	65.8	74.5	60.6	73.0
1:	5 Tot. EtOH Sel., mol. %	78:0	74.8	71.5	. 79.9	74.0

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

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Table VIII. Other Methanol Homologation Experiments

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6	,				
SGHAM-G-#	124	138	139	140	141
1 mmol Ru	6	`	6	б <u>.</u>	6،
2 mmol A28	<sup>;</sup> 40	40	40	40	40
3 mmol A9	2	2	2	2	2
4 mmol A25	6	6	б	6	6
5 MeOH, mL	150 <sup>÷</sup>	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
		τ	_		
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 <b>.</b> 8	55.6	58.1

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Task 3 Summary

Research in Task 3 has been conducted on the novel methanol homologation system which produces ethanol and other products under relatively low pressures. Studies of the catalyst chemistry have been carried cut, with an emphasis on the involvement of catalyst precursors in the catalytic chemistry. The effects of using related and different catalyst precursors have been investigated, and these studies are continuing.

Earlier work in this project has shown the importance of specific catalyst additives in the new homologation system. Further work has now been done to attempt to use additives similar to one of these, A25, both to learn about the essential characteristics of this additive and to try to further enhance the rate and selectivity with a different additive. Of a number of similar catalyst additives tried, three have been found to promote the formation of ethanol at selectivities approaching those earlier observed for A25. It is not yet clear what properties of these  $\ell$  additives are important in determining the catalyst activity, but research is continuing.

Several experiments were carried out with added solvents (in addition to the methanol normally used). Although previously studied cobalt-based homologation systems show increased selectivity with added solvents, experiments with our ruthenium-based system did not result in increased selectivity. However, the reactant methanol is in any case the solvent of choice for this reaction.

Because of the many variables involved in this methanol homologation system, it was felt that the best approach to gaining an understanding of how each affects the behavior of the system was through statistically designed experiments. These experiments would allow the determination of which variables were most important for obtaining high rates of conversion of methanol to ethanol with high selectivity. A first designed set of experiments

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did not generate data of sufficient quality for quantitative correlations to be made, but did suggest conditions under which a second designed set might be more successful. The second designed set provided excellent quantitative correlations between the variables studied and the rate and selectivity of ethanol production. The results showed that conditions for highest rate and highest selectivity are mutually exclusive within the range of variables investigated. The highest rate to ethanol is achieved at high temperature, high ruthenium, and low A25 levels. The highest selectivity requires low temperature and high A25. Further experiments are underway to try to further enhance the reaction rate while maintaining selectivity by using modifications of the present catalyst system.

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