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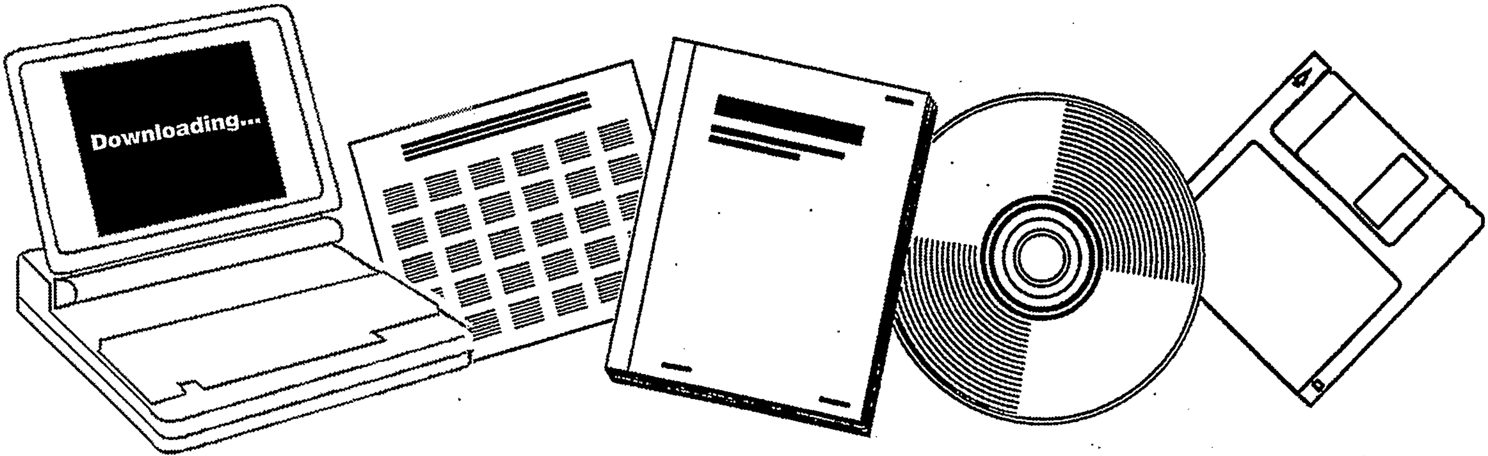
OPTIMUM HIGHER ALCOHOL MIXTURES FOR FUELS FROM SYNGAS: TECHNICAL PROGRESS REPORT, JULY-SEPTEMBER 1986

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

27 OCT 1986



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EIGHTH QUARTERLY TECHNICAL PROGRESS REPORT
DOE CONTRACT DE-AC22-84PC70022
OPTIMUM HIGHER ALCOHOLS MIXTURES FOR FUELS FROM SYNGAS

OCTOBER 27, 1986

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

DOE/PC/70022--T4

DE87 005640

TECHNICAL PROGRESS REPORT
DE-AC22-84PC70022

Eighth Quarterly Report
July - September 1986

Optimum Higher Alcohol Mixtures for Fuels from Syngas

Patent Hold

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PATENT CLEARED BY CHICAGO
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Engineering, Manufacturing and Technology Services
Division

Union Carbide Corporation
South Charleston Technical Center
South Charleston, West Virginia 25303

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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 H_2/CO-ratio syngas to alcohol fuel extenders.

II. SCHEDULE

The contract work was originally planned for the 24-month period from October 1, 1984 through September 30, 1986. We are presently continuing 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.

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 that a lower operating pressure can be realized. At the same time, studies are being directed toward increasing the C_2+ alcohol selectivity of the systems.

The effects of organic additives and related metal-containing additives on the catalyst systems of ruthenium carbonyl/KI/NMP (NMP = N-methylpyrrolidone) and ruthenium carbonyl/molten phosphonium salts have now been fuither investigated. As mentioned in the previous Quarterly Report, addition of these compounds can increase both the activity and the selectivity of higher alcohol formation with the above catalyst systems.

A particular class of organic additives has also been investigated with the catalyst system of ruthenium carbonyl in organic solvents with no additional promoters. It has been found that one member of this class has the ability to substantially increase the syngas conversion activity of the ruthenium catalyst in several types of organic solvents. The system with this modification is reasonably active even at pressures as low as 3000 (methanol is the major product), it was observed that additional additives or cocatalysts enhanced the formation of ethanol.

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.

Earlier work in this project has shown the importance of specific catalyst additives in the new homologation system. Further work has now been carried out on 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. Several more additives of this type have now been found to effectively promote the methanol homologation reaction. It appears that we have now identified the important factors leading to good A25-type additives. Our plan is to synthesize more additives that fall within this class with the goal of optimizing the desirable structural and electronic properties, and progress has been made in developing a general synthetic route to such compounds.

The rate of reaction with the homologation system has frequently been observed to decrease with time. Various factors could be responsible for this observation, including the possibility of product inhibition at high methanol conversions. It has now been found, however, that the use of additional additives of a certain type give a constant rate of gas consumption throughout the reaction. No loss in activity is observed, and in some cases the ethanol selectivity actually increases. We are currently pursuing this intriguing lead and hope to understand the chemistry behind this observation.

Experiments in these studies 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. A more complete description of these experiments and tables of data are given in Appendix D.

V. CHANGES

There were no contract changes during this quarter.

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.

Don C Best

D. C. Best

Program Manager

APPENDIXES

By T. W. Leung, K. G. Moloy, and R. W. Wegman

Appendix A. USE OF CODE SYSTEM

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, metal complexes, or salts, which apparently function as catalyst promoters.

Category C consists of catalysts or co-catalysts.

Category S includes solvents for catalytic reactions.

Use of the code system 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:

A9: A metal-containing catalyst additive
A16: A metal-containing catalyst additive
A24-25: Catalyst additives
A30-31: Catalyst additives
A37: A catalyst additive
A47: A catalyst additive
A53: A catalyst additive
A58: A catalyst additive
A81-98: Catalyst additives
A99: A metal-containing catalyst additive
A100: A catalyst additive
A101: A metal-containing catalyst additive
C4: A catalyst precursor
C7: A catalyst precursor
C4: A catalyst precursor
S3: A reaction solvent
S28: A reaction solvent

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.

PROCEDURE B(a).

Into a specially designed glass liner, the catalyst and additive(s) were charged along with 15.0 g of $P(n\text{-}Bu)_4Br$. 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 cooled to room temperature, vented and purged with nitrogen. The glass liner was taken out and the content analyzed by GC methods.

The procedure for experiments using A92 as solvent is the same as described above except that A92 is used in place of $P(n\text{-}Bu)_4Br$.

PROCEDURE B(b).

In experiments where a liquid organic solvent was used, 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 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.

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P. O. BOX 8361, SOUTH CHARLESTON, W. VA. 25303

U. S. Department of Energy
Office of Science and Technical Information
P. O. Box 62
Oak Ridge, TN 37830

Dear Sir:

Eighth Quarterly Technical Progress Report:
DOE Contract DE-AC 22-84PC70022
Optimum Higher Alcohol Mixtures for Fuels From Syngas

Enclosed is a copy of the Eighth Quarterly Technical Progress Report of the subject project covering the period June 30 to September 31, 1986. This report was cleared by the Chicago Office of Patent Counsel on February 17, 1987.

If you have any questions about the report, please contact me.

Very truly yours,

B. Duane Dombek

B. Duane Dombek

BDD/lj
0538J
Enclosure.

cc:D. C. Best
S. R. Bresch
G. E. Cinquegrane

Appendix C. PROCEDURES FOR PRODUCT ANALYSIS

PROCEDURE C(a).

The organic products were analyzed by gas chromatographic methods. The analyses were carried out using a Hewlett-Parkard Model 5840A equipped with a 30m x 0.32mm DB-1 capillary column. The initial and final temperatures used were 40 and 280°C, repectively. Analyses were also carried out with an HP-5880 instrument equipped with a 6 ft.x 1/8 in. packed Tenax column. The initial and final temperatures for this instrument were set at 40 and 200°C, respectively.

PROCEDURE C(b).

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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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 can be realized. At the same time studies are directed toward increasing the C_2+ alcohol selectivity of the systems.

We have continued investigating the effects of organic additives and related metal-containing additives on the catalyst systems of ruthenium carbonyl/KI/NMP (NMP = N-methylpyrrolidone) and ruthenium carbonyl/molten phosphonium salts. As mentioned in the previous Quarterly Report, addition of these compounds can increase both the activity and the selectivity of higher alcohol formation with the above catalyst systems.

During the last quarter we investigated a particular class of organic additives, and have studied the catalyst system of ruthenium carbonyl in organic solvents with these additives and no additional promoters. We discovered that one member of this class has the ability to substantially increase the syngas conversion activity of the ruthenium catalyst in several types of organic solvents. The system with this modification is reasonably active even at pressures as low as 3000 psi. Although this particular system does not yield C_2+ alcohols (methanol is the major product), it was observed that additional additives or cocatalysts enhanced the formation of ethanol. The addition of these latter compounds probably forms a homologation catalyst system so that some of the methanol produced is transformed to ethanol.

B. Effects of Organic Additives on the Ruthenium System

We found previously that the addition of the novel additive A58 enhances the activities of the catalyst systems of $Ru_3(CO)_{12}$/KI/NMP and $Ru_3(CO)_{12}$/molten phosphonium salt. At the same time, the selectivity to C_2+ products was also increased. We have continued our studies of these types of additives. Also, we are examining combinations of these additives with metallic additives so that a further enhancement of C_2+ alcohols can be realized. With this objective in mind, we are also screening a series additives closely related to the above class.

Three more derivatives of the organic additive A58 were tested. As shown in Table I, the total activity of the Ru/KI/NMP system did not change very much with the addition of these derivatives. However, like most other derivatives of A58 we have tested, they all enhanced the formation of ethanol. The effects of the adding the related additives A93 and A94 to the Ru/KI/NMP system were also similar. An enhancement of ethanol formation was observed while the activity was not affected. Additive A95, however, did increase the activity of the system.

Since A92 is a relatively low melting solid, we attempted to use it as a solvent for an otherwise unpromoted ruthenium catalyst system. The system of Ru/A92 is a relatively active one at the pressure of 5000 psi. Attempts to promote the catalyst activity and the formation of higher alcohols by the addition of iodide failed as neither an increase in activity nor an increase in ethanol formation were observed. Addition of HI or CoI_2 completely poisoned the system.

Interestingly, the combination of $Ru_3(CO)_{12}$ and A92 in solvent S3 forms an active catalyst system which produces mainly methanol and methyl formate. Unlike the system of ruthenium/A92 with no added solvent, the activity of this particular system was not affected much by the addition of iodide.

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.

C. Effects of Metal-Containing Additives

We are also investigating the combination of organic additives of the type described above with metal-containing additives; this combination can sometimes be added as a single complex. Table II shows the results relating to this area of research. One particular combination that deserves attention is that of Ru/A16/A92. This system is very active at 6000 psi and produces mainly methanol and methyl formate. Nevertheless, when iodide or iodine was added to the system, the formation of ethanol increased moderately and the activity of the catalyst system is not affected. We are hopeful that it will be possible to find the right combination of the amounts of catalyst and additive in this system so that higher alcohols can be produced directly from syngas. We are also examining the use of other solvents for this particular catalyst system.

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.

SGHAM-L-#	
1 Catalyst	Catalyst precursor charged
2 mmole	Amount of catalyst precursor used
3 Solvent	Solvent used
4 mL/g	Amount of solvent used, in mL or grams
5 Additive	Additive employed
6 mmole	Amount of additive used
7 Press.,psi	Reaction pressure in psig
8 Temp.,°C	Reaction temperature
9 Time,hrs.	Reaction time in hours
10 H_2/CO	Syngas molar ratio
11 MeOH,g	Amount of methanol produced, in grams
12 EtOH,g	Amount of ethanol produced, in grams
13 n-PrOH,g	Amount of n-propanol produced, grams
14 n-BuOH,g	Amount of n-butanol produced, grams
15 CH_3CHO,g	Amount of acetaldehyde produced, grams
16 Other Ox.,g	Amount of other oxygenates produced, grams
17 Total Prod.,g	Weight of total products analyzed
18 % C_2+ alcohols	Weight percent of C_2 and higher alcohols
19 C_2+/C_1 ratio	Wt. ratio of C_2 and higher products to C_1

Table I. Effects of Organic Additives in Ruthenium Systems

SGHAM-L-#	3-72	4-96	4-94
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmole	2.2	1.8	2.2
3 Solvent	NMP	NMP	NMP
4 mL/g	50.0	50.0	50.0
5 Additive	KI/A96	KI/A97	KI/A98
6 mmole	3.2/3.2	1.9/3.0	3.2/3.0
7 Press.,psi	6000	6000	6000
8 Temp.,°C	230	230	230
9 Time, hrs	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH,g	3.5	2.7	3.5
12 EtOH,g	1.5	2.3	1.4
13 n-PrOH,g	0.2	0.53	0.11
14 n-BuOH,g	0.0	0.0	0.0
15 CH_3CHO,g	0.6	0.74	0.75
16 Other Ox.,g	1.0	0.0	0.88
17 Tot.Prod.,g	6.8	6.3	6.8
18 % C_2+ alcohols	25	45	22
19 C_2+/C1 ratio	0.94	1.3	0.94

See page 19 for key

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

SGHAM-L-#	5-5	2-127	2-125
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmole	2.2	2.2	2.2
3 Solvent	NMP	NMP	NMP
4 mL/g	40.0	40.0 g	40.0 g
5 Additive	A94	KI/A95	KI/A93
6 mmole	91	19/108	19/93
7 Press.,psi	6000	6000	6000
8 Temp.,°C	230	230	230
9 Time, hrs	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH,g	3.8	6.1	4.1
12 EtOH,g	2.3	2.0	2.2
13 n-PrOH,g	0.0	0.17	trace
14 n-BuOH,g	0.0	0.0	0.0
15 CH_3CHO,g	0.0	0.0	0.0
16 Other Ox.,g	0.2	0.65	0.25
17 Tot.Prod.,g	6.3	8.8	6.6
18 % C_2+ alcohols	37	25	33
19 C_2+/C1 ratio	0.66	0.44	0.61

See page 19 for key

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

SGHAM-L-#	2-117	2-123	2-125
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmole	1.8	1.8	1.8
3 Solvent	A92	A92	A92
4 mL/g	15.0 g	20.0 g	20.0 g
5 Additive	-	KI	NaI
6 mmole	-	9.0	9.0
7 Press.,psi	5000	5000	5000
8 Temp.,°C	230	230	230
9 Time, hrs	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH,g	10.3 g	8.6	4.5
12 EtOH,g	0.0	0.11	0.17
13 n-PrOH,g	0.0	0.0	0.0
14 n-BuOH,g	0.0	0.0	0.0
15 CH_3CHO,g	0.0	0.0	0.0
16 Other Ox.,g	1.0	1.22	0.46
17 Tot.Prod.,g	11.3	9.9	5.1
18 % C_2+ alcohols	0.0	1.0	3.0
19 C_2+/C1 ratio	0.0	0.10	0.09

See page 19 for key

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

SGHAM-L-#	5-7	5-11
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmole	1.8	1.8
3 Solvent	A92	A92
4 mL/g	20.0 g	20.0 g
5 Additive	HI	CoI_2
6 mmole	22	3.2
7 Press.,psi	5000	5000
8 Temp.,°C	230	230
9 Time, hrs	3.0	3.0
10 H_2/CO	1.0	1.0
11 MeOH,g	NA[a]	NA[a]
12 EtOH,g		
13 n-PrOH,g		
14 n-BuOH,g		
15 CH_3CHO,g		
16 Other Ox.,g		
17 Tot.Prod.,g		
18 % C_2+ alcohols		
19 C_2+/C_1 ratio		

[a] Product not analyzed due to formation of a gum-like material; no liquid remained.

See page 19 for key

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

SGHAM-L-#	6-6	6-8	6-12
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmole	4.7	4.7	4.7
3 Solvent	S3	S3	S3
4 mL/g	40.0 g	40.0 g	40.0 g
5 Additive	A92	A92	A92
6 mmole	93	93	93
7 Press.,psi	6000	4000	3000
8 Temp.,°C	230	230	230
9 Time, hrs	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH,g	13.5	14.1	4.3
12 EtOH,g	0.20	0.1	0.0
13 n-PrOH,g	0.0	0.0	0.0
14 n-BuOH,g	0.0	0.0	0.0
15 CH_3CHO,g	0.0	0.0	0.0
16 Other Ox.,g	10.4	1.81	0.37
17 Tot.Prod.,g	24.1	16.0	4.7
18 % C_2+ alcohols	0.0	0.0	0.0
19 C_2+/C1 ratio	0.32	0.10	0.0

See page 19 for key

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

SGHAM-L-#	4-119	4-121
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmole	4.7	4.7
3 Solvent	S3	S28
4 mL/g	40.0 g	40.0 g
5 Additive	A92/PPNI[a]	A92/KI
6 mmole	93/7.5	93/19
7 Press.,psi	6000	6000
8 Temp.,°C	230	230
9 Time, hrs	3.0	3.0
10 H_2/CO	1.0	1.0
11 MeOH,g	6.9	9.6
12 EtOH,g	1.9	1.4
13 n-PrOH,g	trace	trace
14 n-BuOH,g	0.0	0.0
15 CH_3CHO,g	0.0	0.0
16 Other Ox.,g	2.9	3.8
17 Tot.Prod.,g	11.8	14.8
18 % C_2+ ROH	16	10
19 C_2+/C1 ratio	0.59	0.28

[a] PPNI = bis(triphenylphosphine)iminium iodide

See page 19 for key

Table II. Effects of Metal-Containing Additives

SGHAM-L-#	3-54	3-70
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmole	2.2	2.2
3 Solvent	NMP	NMP
4 mL/g	50.0 g	50.0 g
5 Additive	A16/A94	A99
6 mmole	1.5/3.7	1.0
7 Press.,psi	6000	6000
8 Temp.,°C	230	230
9 Time, hrs	3.0	3.0
10 H_2/CO	1.0	1.0
11 MeOH,g	2.2	3.5
12 EtOH,g	2.8	1.7
13 n-PrOH,g	0.2	0.26
14 n-BuOH,g	trace	0.0
15 CH_3CHO,g	1.0	0.61
16 Other Ox.,g	0.2	0.6
17 Tot.Prod.,g	6.4	6.7
18 % C_2+ alcohols	47	29
19 C_2+/C1 ratio	1.9	0.91

See page 19 for key

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

SGHAM-L-#	3-60	4-98
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmole	1.8	1.8
3 Solvent	$P(n\text{-}Bu)_4Br$	$P(n\text{-}Bu)_4Br$
4 mL/g	15.0 g	15.0 g
5 Additive	A100/A16	A94/C6
6 mmole	3.0/3.0	4.1/0.82
7 Press.,psi	5000	5000
8 Temp.,°C	230	230
9 Time, hrs	3.0	3.0
10 H_2/CO	1.0	1.0
11 MeOH,g	0.13	0.61
12 EtOH,g	0.36	1.8
13 n-PrOH,g	0.17	0.94
14 n-BuOH,g	0.74	1.3
15 CH_3CHO,g	trace	0.10
16 Other Ox.,g	6.8	12.3
17 Tot.Prod.,g	8.1	17.1
18 % C_2+ alcohols	16	24
19 C_2+/C1 ratio	61	27

See page 19 for key

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

SGHAM-L-#	4-84	4-90
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmole	1.8	1.8
3 Solvent	$P(n-Bu)_4Br$	$P(n-Bu)_4Br$
4 mL/g	15.0 g	15.0 g
5 Additive	A101	A99
6 mmole	3.0	1.0
7 Press.,psi	5000	5000
8 Temp.,°C	230	230
9 Time, hrs	3.0	3.0
10 H_2/CO	1.0	1.0
11 MeOH,g	0.60	0.77
12 EtOH,g	1.8	2.0
13 n-PrOH,g	0.69	0.54
14 n-BuOH,g	0.82	0.18
15 CH_3CHO,g	0.18	0.32
16 Other Ox.,g	8.0	0.7
17 Tot.Prod.,g	12.1	4.5
18 % C_2+ alcohols	27	60
19 C_2+/C1	11	4.8

See page 19 for key

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

SGHAM-L-#	2-129	4-117	4-119
1 Catalyst	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
2 mmole	2.2	2.2	2.2
3 Solvent	S3	S3	S3
4 mL/g	40.0 g	40.0 g	40.0 g
5 Additive	A16/A92	A16/A92/I2	A16/A92/PPNI[a]
6 mmole	93/1.5	93/1.5/2.0	93/1.5/19
7 Press.,psi	6000	6000	6000
8 Temp.,°C	230	230	230
9 Time, hrs	3.0	3.0	3.0
10 H_2/CO	1.0	1.0	1.0
11 MeOH,g	11.2	10.2	8.7
12 EtOH,g	0.20	1.4	1.6
13 n-PrOH,g	0.0	0.0	0.0
14 n-BuOH,g	0.0	0.0	0.0
15 CH_3CHO,g	0.0	0.0	0.0
16 Other Ox.,g	4.4	2.9	2.1
17 Tot.Prod.,g	15.8	14.5	12.4
18 % C_2+ alcohols	1.3	10	13
19 C_2+/C1 ratio	0.13	0.18	0.25

[a] PPNI = bis(triphenylphosphine)iminium iodide

See page 19 for key

D. Task 1 Summary

Studies have been carried out on a particular class of organic additives with the catalyst system of ruthenium carbonyl in organic solvents. It has been discovered that one member of this class has the ability to substantially increase the syngas conversion activity of the ruthenium catalyst in several types of organic solvents. The system with this modification is reasonably active even at pressures as low as 3000 psi. Although this particular system does not yield C_2+ alcohols (methanol is the major product), additional additives or cocatalysts have been found to enhance the formation of ethanol. It is presumed that the addition of these latter compounds forms a homologation catalyst system so that some of the methanol produced from syngas is transformed to ethanol in a second reaction step.

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.

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 experimental variables.

B. Methanol Homologation

Homologation of methanol yields ethanol according to equation 1.

$$CH_3OH + 2H_2 + CO \text{ ------> } CH_3CH_2OH + H_2O \qquad (1)$$

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/liter/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-Ru-A25-A28.

C. Catalyst Studies

Earlier work in this project has shown that additives A9 and A25 are critical components of the catalyst. In the absence of one or both, the homologation reaction is not observed. We have been working to expand the set of possible A25-type additives that will yield superior homologation catalysts. In the last Quarterly Report, we documented the results of homologation experiments carried out with a number of additives similar to A25. At that time we had found only three additives, A37, A47 and A53, that resulted in catalysts generating ethanol with selectivities greater than 60%. Additives A37, A47 and A53 are structurally similar to A25, but in addition possessed a common feature not found in the other A25-type additives that yielded poor homologation catalysts. Since then we have prepared other A25-type additives that possess the same characteristics of A37, A47 and A53, and we have examined them as catalyst components in the low pressure homologation reaction. The results are reported in Table III. All of the runs reported in Table III were carried out at 975 psig with H_2/CO = 2:1.

Catalysts containing additives A82 to A86 result in ethanol selectivities of 54.2% to 68.4%. These selectivities approach those obtained with A25. Additives A82 to A86, A37, A47 and A53 fall in a general class of additives with similar structural and electronic properties. Additives A81 and A87 (Table III, runs 21-48 and 21-76) fall outside the scope of this general class and result in poor homologation catalysts. Thus, it appears that the important factors leading to good A25-type additives have been identified. Our plan is to synthesize more additives that fall within this class with the goal of optimizing the desirable structural and electronic properties.

However, none of the additives which would be of interest in this regard have been reported in the literature. Thus, we have devised what we believe will be a short, general synthesis of this type of additive.

The first step in this synthesis has been reported in the literature. We have carried out this step and obtained a quantitative yield of a key intermediate; this is an improvement over the 50% yield reported in the literature. The second step of the synthesis is unknown, but enough literature precedent exists to suggest that it should be successful. So far, we have found this to be the case and have successfully applied it to the synthesis of two precursors of A25-type additives. The success of this step indicates that this synthesis will find broad applicability to the preparation of these additives. The third step in this synthesis is well known in the literature and we have been able to apply it to the synthesis of A25 and an A25-type additive, A91.

More additives of this type will be prepared during the next quarter and each will be tested for methanol homologation activity.

We have been studying the effects of adding promoters of another type to the A9-Ru-A25-A28 catalysts. The results are given in Table IV. All the runs reported in Table IV were carried out for 2.5 hours at 140°C and 975 psig. In a typical homologation experiment the activity of the A9-Ru-A25-A28 catalyst appears to diminish during the course of the reaction. It is thought that the loss in activity reflects dissociation of A25 from an A9-A25 complex that is formed under homologation reaction conditions. In runs carried out with A25:A24 = 1:0.5 to 1:1.5 (21-86, 89, 94) the catalyst activity does not appear to diminish. The rate of gas consumption is constant throughout the reaction. (In a run with the A9-Ru-A25-A28 catalyst, carried out to the same methanol conversion, the rate of gas consumption eventually decreases.) NMR analysis indicates that A25 has remained bound to A9 through the entire reaction. Similar results have been found with catalysts containing A25:A88 and A25:A89. With A25:A88 = 1:1.5, the ethanol selectivity is increased by 5% to 80%, relative to the base case without A88 (run 21-82). No loss in activity was observed. Interestingly, decreasing A88 such that A25:A88 = 1:0.5 results in a very active catalyst (run 21-120). There is no indication of catalyst deactivation; the ethanol selectivity is however reduced by 10%.

Additives C4 and A25 were charged as the complex C13 along with C7, A28 and various amounts of A88. Run 21-125 does not contain A88. In this case the ethanol selectivity is 83%. Addition of A88 (runs 21-127 and 21-130) results in slight increases in the amount of gas consumed and the ethanol selectivity. The rate of gas uptake was relatively constant during the 2.5 hr reaction time.

In a previous report (Sixth Quarterly Technical Progress Report, April 28, 1986) it was noted that at the end of a standard homologation reaction A25 is recovered as a mixture of A30 and A31. As A25 dissociates from the A25-A9 complex under reaction conditions, A25 reacts with A28 to form A30. As A30 is produced, the concentration of A25 must decrease. This means that the active catalyst concentration must fall, presumably leading to a decline in the rate of ethanol production. The significance of the results reported in Table IV for the A25:A90 mixtures is that A25 is not converted to A30 under reaction conditions. NMR of the recovered catalyst components indicates that A25 is recovered only as an A25-A9 complex. We are currently pursuing this intriguing lead and hope to understand the chemistry behind the A25:A90 interaction.

A comprehensive 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.

Table III. Effects of Catalyst Composition Changes

SGHAM-W-#	Catalysts, molar ratio	EtOH sel.%
21-48	A9:C7:A81:A28 = 1:2:2:20	19.3
21-54	A9:C7:A82:A28 = 1:2:2:20	54.2
21-56	A9:C7:A83:A28 = 1:2:2:20	58.2
21-68	A9:C7:A84:A28 = 1:2:2:20	68.4
21-71	A9:C7:A85:A28 = 1:2:2:20	59.0
21-73	A9:C7:A86:A28 = 1:2:2:20	60.1
21-76	A9:C7:A87:A28 = 1:2:2:20	12.6

Table IV. Effects of Additional Promoters on the Standard Catalyst

SGHAM-W-#	Catalysts, molar ratio	gas uptake	EtOH sel.%
21-82 (Std.)	A9:C7:A25:A28 = 1:2:1:20	3000	75.7
21-86	A9:C7:A25:A24:A28 = 1:2:1:0.5:20	2886	75.7
21-89	A9:C7:A25:A24:A28 = 1:2:1:1:20	2770	75.0
21-94	A9:C7:A25:A24:A28 = 1:2:1.5:1:20	2298	72.3
21-96	A9:C7:A25:A88:A28 = 1:2:1.5:1:20	2945	80.3
21-120	A9:C7:A25:A88:A28 = 1:2:0.5:1:20	4150	71.0
21-99	A9:C7:A25:A89:A28 = 1:2:1.5:1:20	1550	71.4
21-125	C13:C7:A28 = 1:2:20	2400	83.1
21-127	C13:C7:A88:A28 = 1:2:0.5:20	2500	85.8
21-130	C13:C7:A88:A28 = 1:2:1.5:20	2782	84.6

Key to Table V.

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_2/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.%	Molar selectivity to products:
18 EtOH	Free ethanol
19 EtOH Eq.	Ethanol equivalents
20 Total EtOH	Total ethanol
21 Other Oxy.	Other oxygenates

Table V. Comprehensive Table of Homologation Experiments

SGHAM-W-#	21-48	21-54	21-56
1 Catalyst	C4	C4	C4
2 mmole	2.00	2.00	2.00
3 Cocatalyst	C7	C7	C7
4 mmole	4.00	4.00	4.00
5 Additive	A81	A82	A83
6 mmole	4.00	4.00	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	0.0	0.0	0.0
12 Pressure,psi	975	975	975
13 H_2/CO	2:1	2:1	2:1
14 Temp.,°C	140	140	140
15 Time,hr	1.00	3.70	2.00
16 Uptake,psi	462	1338	1489
17 Product Sel.%			
18 EtOH	8.59	33.78	33.25
19 EtOH eq.	10.68	20.48	24.96
20 Total EtOH	19.28	54.26	58.21
21 Other Oxy.	80.72	45.74	41.79

See page 37 for key

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

SGHAM-W-#	21-68	21-71	21-73
1 Catalyst	C4	C4	C4
2 mmole	2.00	2.00	2.00
3 Cocatalyst	C7	C7	C7
4 mmole	4.00	4.00	4.00
5 Additive	A84	A85	A86
6 mmole	4.00	4.00	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	0.0	0.0	0.0
12 Pressure,psi	975	975	975
13 H_2/CO	2:1	2:1	2:1
14 Temp.,°C	140	140	140
15 Time,hr	2.00	2.20	2.00
16 Uptake,psi	2300	1543	1540
17 Product Sel.%			
18 EtOH	36.44	37.66	38.27
19 EtOH eq.	31.91	21.37	21.85
20 Total EtOH	68.36	59.03	60.12
21 Other Oxy.	31.64	40.97	39.88

See page 37 for key

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

SGHAM-W-#	21-76	21-82
1 Catalyst	C4	C4
2 mmole	2.00	2.00
3 Cocatalyst	C7	C7
4 mmole	4.00	4.00
5 Additive	A87	A25
6 mmole	4.00	2.00
7 Promoter	A28	A28
8 mmole	20.00	20.00
9 MeOH(mL)	40.00	40.00
10 Solvent	none	none
11 mL	0.0	0.0
12 Pressure,psi	975	975
13 H_2/CO	2:1	2:1
14 Temp.,°C	140	140
15 Time,hr	1.00	2.50
16 Uptake,psi	250	3000
17 Product Sel.%		
19 EtOH	5.63	47.11
20 EtOH eq.	6.94	28.64
21 Total EtOH	12.57	75.75
22 Other Oxy.	87.43	24.25

See page 37 for key

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

SGHAM-W-#	21-86	21-89	21-94
1 Catalyst	C4	C4	C4
2 mmole	2.00	2.00	2.00
3 Cocatalyst	C7	C7	C7
4 mmole	4.00	4.00	4.00
5 Additive	A25:A24	A25:A24	A25:A24
6 mmole	1:2	2:2	3:2
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	0.0	0.0	0.0
12 Pressure,psi	975	975	975
13 H_2/CO	2:1	2:1	2:1
14 Temp.,°C	140	140	140
15 Time,hr	2.50	2.50	2.50
16 Uptake,psi	2886	2770	2298
17 Product Sel.%			
18 EtOH	49.91	48.85	45.45
19 EtOH eq.	25.80	26.14	26.88
20 Total EtOH	75.71	74.99	72.33
21 Other Oxy.	24.29	25.01	27.67

See page 37 for key

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

SGHAM-W-#	21-96	21-99	21-120
1 Catalyst	C4	C4	C4
2 mmole	2.00	2.00	2.00
3 Cocatalyst	C7	C7	C7
4 mmole	4.00	4.00	4.00
5 Additive	A25:A88	A25:A89	A25:A88
6 mmole	3:1	3:1	1:2
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	0.0	0.0	0.0
12 Pressure,psi	975	975	975
13 H_2/CO	2:1	2:1	2:1
14 Temp.,°C	140	140	140
15 Time,hr	2.50	2.50	2.50
16 Uptake,psi	2945	1550	4150
17 Product Sel.%			
18 EtOH	53.98	42.66	44.83
19 EtOH eq.	26.34	28.78	26.02
20 Total EtOH	80.32	71.43	70.85
21 Other Oxy.	19.68	28.57	29.15

See page 37 for key

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

SGHAM-W-#	21-125	21-127	21-130
1 Catalyst	C13	C13	C13
2 mmole	2.00	2.00	2.00
3 Cocatalyst	C7	C7	C7
4 mmole	4.00	4.00	4.00
5 Additive	none	A88	A88
6 mmole	4.00	1.00	3.00
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	0.0	0.0	0.0
12 Pressure,psi	975	975	975
13 H_2/CO	2:1	2:1	2:1
14 Temp.,°C	140	140	140
15 Time,hr	2.50	2.50	2.50
16 Uptake,psi	2400	2500	2782
17 Product Sel.%			
18 EtOH	55.09	57.19	55.77
19 EtOH eq.	28.09	28.66	28.84
20 Total EtOH	83.18	85.84	84.61
21 Other Oxy.	16.82	14.16	15.39

See page 37 for key

E. 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 out, 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 carried out on 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. Several more additives of this type have now been found to effectively promote the methanol homologation reaction. It appears that we have now identified the important factors leading to good A25-type additives. Our plan is to synthesize more additives that fall within this class with the goal of optimizing the desirable structural and electronic properties, and progress has been made in developing a general synthetic route to such compounds.

Reactions with the homologation system have frequently been observed to slow during the course of the process. Various factors could be responsible for this observation, including the possibility that this is an artifact of the batch-type reaction when run to high methanol conversions. It has now been found, however, that the use of additional additives of a certain type give a constant rate of gas consumption throughout the reaction. No loss in activity is observed, and in some cases the ethanol selectivity actually increases. We are currently pursuing this intriguing lead and hope to understand the chemistry behind this observation.

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