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F.O.S.S.I.L ENERGY

DEVELOPMENT OF ALCOHOL-BASED SYNTHETIC TRANSPORTATION FUELS FROM COAL-DERIVED SYNTHESIS GASES

Fourth Quarterly Progress Report for Period July 1—September 30, 1980

December 3, 1980

Work Performed Under Contract No. AC22-79ET14858

Chem Systems Research & Development Group
Fairfield, New Jersey

U. S. DEPARTMENT OF ENERGY

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CONTRACT NO. DE-AC 22-79. ET 14858

FOURTH QUARTERLY PROGRESS REPORT

JULY 1 - SEPTEMBER 30, 1980

DEVELOPMENT OF ALCOHOL-BASED SYNTHETIC
TRANSPORTATION FUELS FROM COAL-DERIVED
SYNTHESIS GASES

SUBMITTED TO:

U.S. DEPARTMENT OF ENERGY
COAL LIQUEFACTION PROJECT MANAGEMENT
PITTSBURGH ENERGY TECHNOLOGY CENTER
PITTSBURGH, PA 15213

PREPARED BY:

CHEM SYSTEMS RESEARCH & DEVELOPMENT GROUP
ONE EVANS STREET
FAIRFIELD, NJ 07006

DOE Project Manager: Richard Diffenbach
Chem Systems Project Manager: Marvin. I. Greene

DECEMBER 3, 1980

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1.0 ABSTRACT

Chem Systems, under DOE Contract No. De-AC 22-79. ET-14858, is carrying out an experimental program for the conversion of coal-derived synthesis gases to a mixture of C_1-C_6 alcohols. The objectives of this contract are to: 1) develop a catalyst and reactor system for producing a mixture of C_1-C_6 alcohols to be used as a synthetic transportation fuel and 2) assess the technical and economic feasibility of scaling the process to a commercial-scale application.

This fourth quarterly report presents the experimental work performed for the period of July 1 - September 30, 1980. Some of the accomplishments made this quarter during the Task 1 screening studies were:

1. A total of twenty-four catalysts were prepared by either evaporation of metal nitrate-citric acid solutions; by impregnation of methanol synthesis catalysts or by coprecipitation with KOH.

2. A total of seventeen catalysts were tested in either the Berty gradientless reactor or the plug-flow reactor. These catalysts have been characterized into the following five groups:

Group I: Catalysts containing Cu, Zn, Co, Cr and alkali

Group II: Catalysts of Group I without Zn, Co, or Cr

Group III: Modified methanol synthesis catalysts of Cu-Zn-Al family

Group IV: Catalysts of Group I where Cr is substituted by transition metal(s) such as Fe, Mn, Ti, Th, etc.

Group V: Catalysts of Groups I, II or IV supported on inert oxides such as SiO_2, TiO_2 or MnO

3. A $CuCoZn_{0.125}Fe_{0.1}Th_{0.5}K_{0.11}$ catalyst produced by evaporation of metal nitrate-citric acid solutions resulted in an oxygenates selectivity of about 50% (CO_2-free basis) at total CO conversions of the order of 5 to 15% per pass. The alcohols (including about 2% aldehydes) distribution was 48.2% C_1; 33.4% C_2; 10.7% C_3; 5.3% C_4 and 2.3% C_5. The calculated heating value of this Alkanol

mixture is about 78,000 Btu/gal (20% higher than that of methanol). The estimated clear Research Octane Number (RONC) of this mixture is 109. The estimated octane quality (RONC) of a mixture of 80% unleaded gasoline having an 80 RONC and 20% of the Alkanols is about 91.

4. The following observations regarding the conversion-selectivity characteristics were made:

a) Use of the evaporation technique (metal nitrate-citric acid solutions) results in a significant improvement in oxygenates selectivity over that of the KOH coprecipitation method when processing a $CuZn_{0.125}CoTh_{0.5}Fe_{0.1}K_{0.11}$ catalyst;

b) A broad maxima in the Fe/Cu ratio vs. oxygenates selectivity relationship was observed between about 0.1 and 0.25 Fe/Cu ratio with the above catalyst formulation;

c) Catalysts having an atomic formula of $CuZn_{0.125}CoK_{0.11}M$ have oxygenates selectivity varying with transition metal type according to the following series (in order of decreasing selectivity):

$$Zr \sim Th > V \gtrsim Cr > Mn > Mo;$$
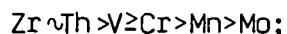
d) Recycle of methanol at 7 mol% in syn gas to a $CuZn_{0.125}CoTh_{0.5}K_{0.11}Fe_{0.1}$ catalyst resulted in no$^{/}$ improvement in oxygenates selectivity but significant conversion of the methanol was observed to primarily methane.

e) The incorporation of MnO (a poor hydrogen chemisorber) as a support for a $CuZn_{0.125}CoTh_{0.5}Fe_{0.5}K_{0.11}$ catalyst produced by evaporation did not supress hydrocarbon formation activity.

Plans for the next quarter include the preparation and testing of catalysts formulated to study a) the effect of Co/Cu ratio; b) the effects of catalyst aging on both activity and selectivity; c) less complex chemical compositions; d) calcination temperature; e) hydrogen reduction conditions and f) alternative coprecipitation methods.

2.0 OBJECTIVES AND SCOPE

This project is part of the DOE-Fossil Energy alcohol fuels research program which is directed towards developing technology for producing alcohol-based, synthetic transportation fuels from coal-derived, synthesis gases. A major on-going effort is in the area of methanol for use in methanol-gasoline blends ("methyl fuel"). Another alternative, which is the subject of this research and development project, is to produce a mixture of methanol and higher alcohols (C_2-C_6), which we call ALKANOL. This mixture has the potential for providing a synthetic transportation fuel far superior to that which would be provided by straight-run methanol. The ALKANOL fuel has improved volatility, solubility and water sensitivity characteristics over that of methyl fuel as well as having higher heats of combustion, of the order of 35-70% higher depending upon the carbon number distribution of the ALKANOL fuel.

As an outgrowth of our Liquid-Phase Methanol (LPMeOH) synthesis experience, we have been investigating the effectiveness of catalysts comprised of Fischer-Tropsch elements and low pressure methanol synthesis catalyst elements. The objectives of this contract are to: 1) develop a catalyst and reactor system for converting coal-derived synthesis gases to alcohol-based, synthetic transportation fuels and 2) assess the technical and economic feasibility of scaling the process concept to a commercial-scale application.

A multi-task program was formulated to provide the necessary information for meeting the contract objectives:

Task 1: Catalyst Formulation and Screening Studies
Task 2: Process Variables Studies in Bench-Scale Unit
Task 3: Engineering and Economic Analysis
Task 4: Catalyst Performance Studies in Process Development Unit

The experimental work is being performed at Chem Systems Research Center in Fairfield, New Jersey, and the contract will require 24 months to completion.

3.0 SUMMARY OF TECHNICAL PROGRESS

3.1 Task 1 - Catalyst Formulation & Screening Studies

During this quarterly period, a total of twenty-four catalysts were prepared by either evaporation techniques (with metal nitrates, citrates or acetates), coprecipitation techniques (with KOH) or by impregnation techniques (of potassium-promoted, methanol synthesis catalyst with a dicobalt octacarbonyl-methanol-monoethanolamine solution). All catalysts were calcined and pelletized.

A total of seventeen catalysts were tested in either the Berty gradientless reactor or the plug-flow reactor. These catalysts have been characterized into the following five groups based on their elemental composition:

Group I: Catalysts containing Cu, Zn, Co, Cr and alkali

Group II: Catalysts of Group I without Zn or Co or Cr

Group III: Modified methanol synthesis catalysts of
             Cu-Zn-Al family.

Group IV: Catalysts of Group I where Cr is substituted by
             transition metal(s) such as Fe, Mn, Th, V, etc.

Group V: Catalysts of Group I, II or IV supported on inert
             oxides such as SiO_2, TiO_2 or MnO.

The testing during this quarter was formulated to determine whether variations in the following parameters would improve oxygenates selectivity:

- Reduction temperature;
- Coprecipitation with KOH vs. evaporation of metal nitrates, citrates or acetates;
- Pelletizing pressure;
- Addition of methanol to feed gas (simulated methanol recycle) and;
- Incorporation of a MnO support having low hydrogen chemisorption capacity.

The catalyst formulation with the highest selectivity to oxygenates was $CuCoZn_{0.125}Fe_{0.1}Th_{0.5}K_{0.11}$ produced by evaporation of metal nitrate-citric acid solutions. Selectivity was about 50% (CO_2-free basis) at total CO conversions of the order to 5 to 15% per pass. The C_2+ alcohols/CH_3OH ratio was about 1/1.

Examination of the conversion-selectivity characteristics of the catalysts tested led to the following apparent correlations:

Higher temperature and lower space velocity result in higher CO conversion per pass with the higher oxygenates selectivities occurring at the lower levels of CO conversion.

For a $CuZn_{0.125}CoTh_{0.5}Fe_{0.1}K_{0.11}$ catalyst formulation, the evaporation technique results in a significant improvement in oxygenates selectivity over that of the KOH coprecipitation method, particularly at CO conversions between 5 and 20% per pass as seen from the following table:

Production Method	Evaporation		KOH Coprecipitation	
% CO Conversion	6.3	17.5	5.2	18.0
Temperature, $^{\circ}C$	270	272	245	263
VHSV, L/hr/kgm	3351	976	3262	3574
Pressure, psig	905	905	910	910
% Oxygenates Selectivity	43.1	32.8	27.9	25.1

Catalysts having an atomic formula of $CuZn_{0.125}CoK_{0.11}M$ have oxygenates selectivity varying with transition metal type according to the following series (in order of decreasing selectivity):

$$Zr \sim Th > V \gtrsim Cr > Mn > Mo;$$
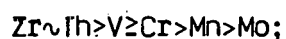
The incorporation of a poor hydrogen chemisorber in the form of MnO into a $CuZn_{0.125}CoTh_{0.5}Fe_{0.5}K_{0.11}$ catalyst produced by evaporation of metal nitrate-citric acid solutions did not suppress hydrocarbon formation activity of this catalyst. While oxygenates selectivity did not vary, selectivity to methane increased.

There appears to be a small effect of iron/copper ratio on oxygenates selectivity with a $CuZn_{0.125}CoTh_{0.5}K_{0.11}Fe_x$ catalyst produced by evaporation of metal nitrate-citric acid solutions. A broad maxima in the Fe/Cu ratio vs. oxygenates selectivity was observed between about 0.1 and 0.25 Fe/Cu ratio.

Tests with the above catalyst having a 0.1/1 Fe/Cu ratio indicated that the catalyst has little or no homologation activity when methanol is fed along with the synthesis gas. Total carbon conversion (feed methanol carbon plus CO carbon) was approximately constant but the methane/higher alcohols ratio increased from 0.8/1 to about 2.3/1 as seen below:

MeOH Content of Feed Gas, Mol %	7	0
Equivalent CO Converted, gmol/hr/kg cat.	6.4	7.6
% Selectivity To:		
CH_3OH	--	4
C_2-C_6 Oxygenates	13	21
CH_4	30	17
C_2 + H.C.	24	34
CO_2	33	24

There appears to be essentially no effect on the oxygenates selectivity-CO conversion characteristics when the chromium/copper ratio in a $CuZn_{0.125}CoK_{0.11}Cr_x$ formulation produced by evaporation of metal nitrate-citric acid solutions is varied between 0 and 1/1.

3.2 Task 2 – Process Variables Studies in BSU

No work has been performed on this task during the present reporting period.

3.3 Task 3 – Engineering Studies & Economic Analyses

No work has been performed on this task during the present reporting period.

3.4 Task 4 – Performance Studies in PDU

No work has been performed on this task during the present reporting period.

4.0   WORK PLANNED FOR NEXT QUARTER

Task 1: Catalyst Formulation and Screening Studies

Past testing has concentrated in the study and optimization of a five or six component catalyst system containing copper, cobalt, zinc, an alkali metal promoter and one or more transition metal promoters. Work concentrated on optimizing catalyst production techniques and on exploring the types and atomic ratios of the various catalyst components.

At this point, we are not convinced that five or six catalyst components are required for an effective catalyst. In the next quarter, we plan to explore less complex compositions and variables that we believe may lead to minimizing hydrocarbon selectivity and simultaneously increasing alcohols selectivity. The following discussion briefly describes the parameters that will be studied.

Aging Effects

Aging of catalysts generally results in loss of activity due to carbon laydown, metal sintering, etc. In Run 201-67B, described in the Third Quarterly Report, an increase in oxygenates selectivity was observed over the 43-hour run period even though the catalyst activity (i.e., % CO converted or the gmol/hr CO converted per kgm catalyst) declined. We plan to make an extended run (ca., 100-300 hours) with a $CuCoCr_{0.8}K_{0.09}$ catalyst and determine whether aging results in the suppression of hydrocarbon formation activity and the corresponding increase in oxygenates selectivity.

Calcination Temperature Effects

We plan to calcine future catalyst formulations at lower temperatures (ca., $350^{o}C$) then previously used. The data of Runs 201-37B and 201-34B reported in the Second Quarterly Report indicate that there is an increase in activity resulting from a reduction in calcination temperature from $550^{o}C$ to $450^{o}C$ and that further reductions in calcination temperature might improve catalyst performance.

Hydrogen Reduction Conditions

We plan to investigate the effects of modifications to the standard hydrogen reduction procedure being utilized. One change will consist of reducing a $CuCoCr_{0.8}K_{0.09}$ catalyst with a 0.2% H_2/99.8% N_2 gas vs. the standard 2% H_2/98% N_2 gas. Reduction pressure and standard hourly space velocity will be increased ten-fold, thereby maintaining contact time and hydrogen partial pressure at a constant value. The excess heat capacity of the N_2-diluent in the reducing gas should effectively absorb hydrogenation heat and prevent any localized exotherms that might possibly occur at active catalyst sites.

Another reduction procedure will consist of reducing copper-cobalt containing catalysts that do not contain zinc with a CO/CO_2 containing reducing gas. This procedure should result in maintaining the copper in its Cu^{+1} state, which has been shown in the literature to be the active species for methanol synthesis catalysts. Although methanol synthesis catalysts are reduced with reducing gases free of CO_2 content, they contain zinc which complexes the copper thereby preventing the copper from being reduced completely to its zero valence state.

Na2CO3 Coprecipitation

The bulk of the catalysts produced by coprecipitation used KOH as the coprecipitation agent. Sodium carbonate as the coprecipitation agent has been reported [a] to result in superior activity to that of KOH or NaOH coprecipitating agents, and it is the preferred material for producing methanol synthesis catalysts. Several catalysts will be produced using the Na_2CO_3 coprecipitation method.

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[a] Advances in Catalysis, Vol IV, Frankenburg, Komarewsky & Rideal (editors), New York, (1952), Pg. 276.

Catalyst Composition

The following catalysts will be tested:

Atomic Formula	Basis of Formulation
$CuCoCr_{0.8}$	3-component system; no alkali
$CuZn_{0.5}CoK_{0.11}$	Cu/Zn = 2.0; Cu/Co = 1
$Cu_{0.5}ZnCo_{0.2}$	3-component system; Cu/Zn = 0.5; Cu/Co = 5
$CuCo$	2-component system; no alkali; Cu/Co = 1
$CuCoK_{0.11}$	3-component system; Cu/Co = 1 with alkali
$CuCoTh_{0.5}$	3-component system; no alkali
$CuCo_{0.3}Cr_{0.8}K_{0.09}$	4-component system with alkali; Cu/Co = 3.33
$CuZn_{0.5}Co$	3-component system without alkali; Cu/Zn = 2
$CuZn_{0.4}Co_{0.5}Al_{0.25}K_{0.05}$	Co + K impregnated methanol synthesis catalyst; Cu/Co = 2
$CuZn_{0.4}Co_{0.5}Al_{0.25}$	Co impregnated methanol synthesis catalyst; Cu/Co = 2
$CuZn_{0.4}Co_{0.1}Al_{0.25}K_{0.05}$	Co + K impregnated methanol synthesis catalyst; Cu/Co = 10

No work is planned in the next quarter for Tasks 2, 3, and 4.

5.0 DETAILED DESCRIPTION OF TECHNICAL PROGRESS

5.1 Task 1 - Catalyst Formulation & Screening Studies

5.1.1 Recent Literature Review

IFP

Institut Francais Du Petrole (IFP) recently filed a U.K. patent application[1] for a process to manufacture alcohols from synthesis gas. The process is very similar to the West German and U.S. patents awarded to IFP and discussed in previous quarterly reports. The major difference is the enlargement of the scope of catalyst composition to include 5-40% of a rare earth metal in addition to copper, cobalt, alkali or alkaline earth metal and a transition metal of atomic Number 23 to 26 inclusive. The catalyst can also contain zinc and/or a noble metal from Group VII. The following catalyst formulations were reported to result in high space yields and selectivities of 90-98%:

1. $CuCoCr_{.8}K_{.09}$
2. $CuCoMn_{0.8}K_{0.12}$
3. $CuCoFe_{0.8}K_{0.12}$
4. $CuCoV_{0.8}K_{0.12}$
5. $CuCoCr_{0.5}La_{0.3}K_{0.09}$
6. $CuCoCr_{0.5}Ce_{0.3}K_{0.09}$
7. $CuCoMn_{0.5}Nd_{0.21}Pr_{0.09}K_{0.09}$
8. $CuCoFe_{0.5}La_{0.3}K_{0.09}$
9. $CuCoV_{0.5}La_{0.3}K_{0.09}$
10. $CuCr_{0.4}Co_{0.8}AlBa_{0.1}$
11. $CuCr_{0.2}Co_{0.8}Al_{0.4}La_{0.8}Ba_{0.1}$

Amoco

Standard Oil of Indiana (Amoco) filed for a European patent[2] for a process to produce alcohol mixtures from synthesis gases. The heart of the process is a catalyst described by the following empirical formula:

$$Cu_aThM_bA_cO_x$$

wherein   M is one or more of Ca, Mo, Rh, Mn, Pt, Ce, Cr, Zn, Al, Ti, La, V, U, Re, Ru and Pd.

A is an alkali metal and,

$a = 0.5 - 2.5$

$b = 0.01 - 1.0$

$c = 0.05 - 0.9$ and

$x =$ a number to satisfy valence requirements of other elements.

This catalyst notably is devoid of cobalt content. Methanol is the key component of the alcohol mixtures with C_1/C_2+ alcohol ratios varying from 2/1 to 16/1 and methanol content of the alcohol mixtures equivalent to 65-94% by weight. It is interesting to note that Amoco also claims a modified gasoline composition which consists of a mixture of alcohols (40% minimum methanol content) with either paraffinic hydrocarbons or paraffinic plus aromatic hydrocarbons.

Further Review of Mechanisms

There is recent evidence to suggest that for higher alcohols production, a catalyst must possess sites capable of adsorbing carbon monoxide associatively with hydrogenation to methanol or a methanol-like intermediate and also dissociatively with formation of a hydrocarbon intermediate[3-7], i.e.,

$$M + CO \xrightarrow{A} M - C\ O$$
$$M + CO \xrightarrow{B} M - C + O_{Ads}$$

$$M - C\ O + H_2 \longrightarrow M - CHOH$$

$$M - C + O_{Ads} + H_2 \longrightarrow M - CH + OH_{Ads}$$
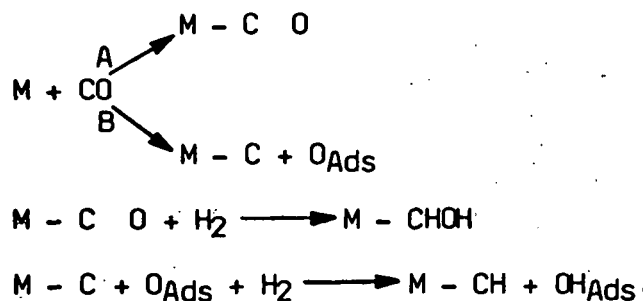
where M is an active metal or metal oxide site. M – CHOH and M – C can undergo facile hydrogenation as follows:

$$M - CHOH \xrightarrow{1/2\ H_2} M - CH_2OH \xrightarrow{1/2\ H_2} M + CH_3OH$$

$$M - C \xrightarrow{H_2} M - CH_2 \xrightarrow{1/2\ H_2} M - CH_3 \xrightarrow{1/2\ H_2} M + CH_4$$
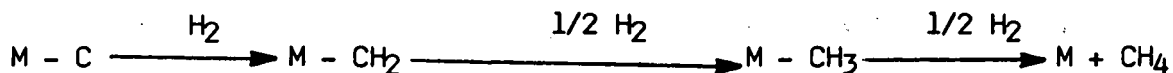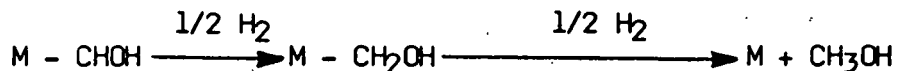
Both modes of adsorption A and B are important and in addition, the two sites which promote the two types of adsorption must be in proximity so that the methanol-like and hydrocarbon-like moieties can interact to produce higher alcohols (and higher hydrocarbons). This suggests an extremely well dispersed catalyst, i.e., a "homogeneous" heterogeneous catalyst.

$$
\begin{array}{cc}
CH & CH_2OH \\
| & | \\
M & M
\end{array}
\longrightarrow M + M - CH - CH_2OH
$$

$$M - CH - CH_2OH + CO + H_2 \longrightarrow propanol,\ butanol,\ etc.$$

$$
\begin{array}{cc}
CH & CH_3 \\
| & | \\
M & M
\end{array}
\longrightarrow M + M - CH - CH_3
$$
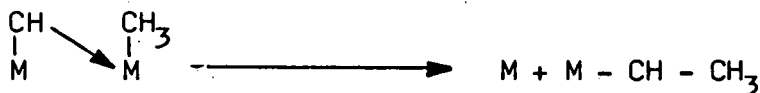
There is some evidence to say that in general, <u>associative</u> adsorption of carbon monoxide takes place on metal oxides (e.g., CO on Cu^1 in $Cu^IZn^{II}O_x$, which is the active site for methanol formation) although it can take place on metals. <u>Dissociative</u> adsorption of carbon monoxide takes place on metals (e.g., CO on Co, Ni) although it is possible that metal oxides are involved as well.

One of the problems with optimization of our present catalysts is the large number of species present on preparation and under run conditions. For example, the $CuZn_{0.125}CoCrK_{0.11}O_x$ catalyst tested is probably composed of:

Cu^o	CoO
$Cu^IZn^{II}O_x$	Cr_2O_3
Co^o	K_2O

plus any surface carbides, while a $CuZn_{0.125}CoFe_{0.5}Th_{0.5}K_{0.11}O_x$ catalyst likely has:

Cu^O Fe^O

$Cu^I Zn^{II} O_x$ Fe_3O_4

Co^O ThO_2

CoO K_2O
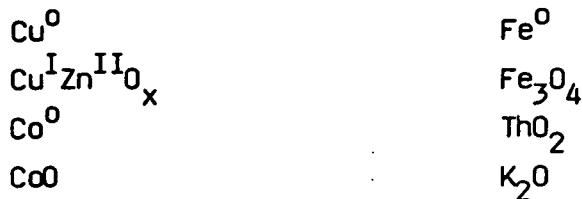
plus stable surface carbides of Fe and Co.

5.1.2 Catalyst Preparation

During the past quarter, twenty-four catalysts were prepared. The calculated atomic compositions and the respective production methods are shown in Table 5.1.2-1. The detailed composition of each of the formulations made is shown in Table 5.1.2-2. Selected catalyst formulations were analyzed by atomic absorption spectrophotometry and some differences were observed between the calculated compositions and those determined by A.A. as seen from Table 5.1.2-3.

The preparation techniques fall into three general areas:

A. Evaporation
      1) Of metal nitrate-citric acid solutions.
      2) Of metal acetate-citric acid solutions.
      3) Of metal citrates.

B. Coprecipitation
      1) With KOH
      2) With K_2CO_3

C. Detergent Dispersion
      Evaporation of a potassium-impregnated methanol
      synthesis catalyst slurried in a methanol-ethanolamine-
      dicobalt octacarbonyl solution.

TABLE 5.1.2-1

CALCULATED ATOMIC COMPOSITIONS

Catalyst Number	Atomic Formula	Preparation Method
197-72	$CuZn_{0.125}CoZrK_{0.11}$	Evaporation of metal nitrates with citric acid.
197-73	$CuZn_{0.125}CoCrK_{0.11}$	"
197-77	$CuZn_{0.125}CoTh_{0.5}K_{0.11}$	"
197-78	$CuZn_{0.125}CoCr_{0.125}K_{0.11}$	"
197-76	$CuZn_{0.125}CoCrK_{0.11}$	Evaporation of metal citrates.
197-79	$CuZn_{0.125}CoThK_{0.11}$	Coprecipitation with KOH
197-81	$CuZn_{0.125}CoTh_{0.5}Fe_{0.5}K_{0.11}/MnO$	"
197-82	$CuZn_{0.125}CoTh_{0.75}Fe_{0.10}K_{0.11}$	"
197-83	$CuZn_{0.125}CoThFe_{0.1}K_{0.11}$	"
197-84	$CuCoRu_{0.1}K_{0.11}$	"
197-85	$CuZn_{0.125}CoTh_{0.5}Fe_{0.1}K_{0.11}$	"
197-86	$CuZn_{0.125}Th_{0.5}Fe_{0.5}K_{0.11}$	Coprecipitation with K_2CO_3
197-87	$CuZn_{0.25}CoK_{0.11}$	"
197-88A	$CuZn_{0.25}CoK_{0.11}$	Coprecipitation with KOH
197-88B	$CuZn_{0.25}Co$	"
197-89	$CuZn_{0.125}Th_{0.5}Fe_{0.5}K_{0.11}$	"
200-76	$CuCoCr_{0.8}K_{0.09}$	Evaporation of metal nitrates with citric acid.
200-78-1	$CuZn_{0.4}Co_{0.5}Al_{0.25}K_{0.05}$	Detergent dispersion
200-78-2	$CuZn_{0.4}Co_{0.5}Al_{0.25}$	"
200-79	$CuZn_{0.5}CoK_{0.11}$	Evaporation of metal acetates with citric acid.
200-81-1	$CuCoTh_{0.5}CoK_{0.11}$	Coprecipitation with KOH
200-81-2	$CuCoTh_{0.5}$	"
200-83-1	$CuCoK_{0.11}$	"
200-83-2	$CuCo$	"

TABLE 5.1.2-2
DETAILED COMPOSITION OF CATALYST FORMULATIONS

CATALYST NO.	197-72	197-73	197-76	197-77	197-78	197-79	197-81	197-82	197-83	197-84	197-85	197-86	197-87	197-88-1 197-88-2	197-89-1 197-89-2	200-76	200-78-1 200-78-2	200-79	200-81-1 200-81-2	200-83-1 200-83-2
COMPONENT																				
$Cu(NO_3)_2 \cdot 2.5H_2O$	116	233	116	91	116	116	58	58	29	116	116	116	116	116	116	465	c	116[d]	116	233
$Zn(NO_3)_2 \cdot 6H_2O$	19	37	19	14	19	19	9.3	9.3	4.7		19	19	37	37	19		c	74[d]		
$Co(NO_3)_2 \cdot 6H_2O$	145[a]	291	145	110	145	145	73	73	36	145	145		145	145		582[b]		145[d]	145	291
$Mn(NO_3)_2$							145													
$Cr(NO_3)_3 \cdot 9H_2O$		400	200		25															
CrO_3																160				
$Fe(NO_3)_3 \cdot 9H_2O$							50	20	5		20	101			101					
$Th(NO_3)_4 \cdot 4H_2O$				104		321	69	103	69		138	138			138					138
$Zn(OAc)_4$	164																			
$Co_2(CO)_8$																	88			
$RuCl_3$										12										
KNO_3				4.3	5.6													10[d]		
KOH			3.2													8.6	2.4			
K_2CO_3	3.8	9.2			2.7		1.6	1.9	0.95	3.8	3.8	1.9	1.7	1.7	1.9				1.9	1.9
Citric Acid	15	60	976	11												109	47			
Calcining Temperature, °C	450	450	450	450	450	450	450	450	450	450	450	450	450	450	450	450	300	400	450	450

NOTES:
a) An equivalent amount of Cobalt Carbonate was used. ($CoCO_3$)

b) An equivalent amount of Cobalt Carbonate was used ($2CoCO_3 \; 3Co(OH)_2 \cdot H_2O$)

c) Two hundred grams of commercial methanol catalyst was used.

d) An equivalent amount of the acetate salts was used.

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TABLE 5.1.2-3
CATALYST ANALYSIS BY ATOMIC ABSORPTION

Catalyst No.	CALCULATED[1] Atomic Formula		Wt %	Wt %	MEASURED[2] Atomic Formula
197-1	$Cu_1Co_1Cr_{0.8}K_{0.09}$	Cu	28.9	32.0	$Cu_{0.8}Co_{1.0}Cr_{0.6}K_{0.11}$
		Co	26.8	34.7	
		Cr	19.0	17.4	
		K	1.6	2.5	
197-2	$Cu_1Zn_{0.125}Co_1Cr_1K_{0.11}$	Cu	25.8	28.4	$Cu_{1.05}Zn_{0.11}Co_{1.0}Cr_{0.95}K_{0.12}$
		Zn	3.3	3.0	
		Co	24.0	24.9	
		Cr	21.2	21.4	
		K	1.6	1.9	
200-76	$Cu_1Co_1Cr_{0.8}K_{0.09}$	Cu	28.9	31.0	$Cu_{1.2}Co_{1.0}Cr_{0.8}K_{0.08}$
		Co	26.8	24.4	
		Cr	19.0	16.1	
		K	1.6	1.3	
200-78-1	$Cu_1Zn_{0.5}Co_{0.5}K_{0.05}$	Cu	39.7	44.4	$Cu_1Zn_{0.3}Co_{0.5}K_{0.04}$
		Zn	20.4	14.0	
		Co	18.4	22.4	
		K	1.2	1.1	
197-79	$Cu_1Zn_{0.125}Co_1Th_1K_y$ [4]	Cu	14.8	15.0	$Cu_{1.3}Zn_{0.17}Co_1Th_{1.3}$
		Zn	1.9	2.13	
		Co	13.7	11.3	
		Th	54.1	53.1	
		K	0.0	0.0	

Notes: [1] Calculated based on materials used in preparation.
Metals % based on total metal oxide mixture.

[2] Calculated based on wt % found, Co assumed 1.00

[3] Commercial catalyst assumed to be 2 CuO: 1 ZnO

[4] Submitted before impregnation of K ($y = 0$ before impregnation)

All catalysts analyzed after calcination.

TABLE 5.1.2-3 (Continued)

CATALYST ANALYSIS BY ATOMIC ABSORPTION

Catalyst No.	CALCULATED[1] Atomic Formula	Wt %		MEASURED[2] Wt %	Atomic Formula
200-83-1	$Cu_1Co_1K_{0.11}$	Cu	39.8	39.6	$Cu_{1.0}Co_{1.0}K_{0.08}$
		Co	36.9	32.2	
		K	2.7	1.7	
197-85	$Cu_1Zn_{0.125}Co_1Th_{0.5}Fe_{0.1}K_{0.11}$	Cu	20.5	22.2	$Cu_{1.3}Zn_{0.12}Co_{1.0}Th_{0.5}Fe_{0.06}K_{0.07}$
		Zn	2.6	2.11	
		Co	19.0	16.2	
		Th	37.5	33.2	
		Fe	1.8	1.7	
		K	1.4	1.5	
197-87	$Cu_1Zn_{0.25}Co_1K_y$[4]	Cu	36.3	29.2	$Cu_{0.83}Zn_{0.21}Co_{1.0}K_{<0.01}$
		Zn	9.4	7.6	
		Co	33.7	32.4	
		K	0.0	0.15	
197-88A	$Cu_1Zn_{0.25}Co_1K_{0.11}$	Cu	35.3	45.8	$Cu_{1.5}Zn_{0.26}Co_{1.0}K_{0.095}$
		Zn	9.1	8.2	
		Co	32.7	28.7	
		K	2.4	1.8	

[1] Calculated based on materials used in preparation.

Metals % based on total metal oxide mixture.

[2] Calculated based on wt % found, Co assumed 1.00

[3] Commercial catalyst assumed to be 2 CuO: 1 ZnO

[4] Submitted before impregnation of K (y = 0 before impregnation)

All catalysts analyzed after calcination.

Evaporation Methods

The evaporation of metal nitrates in the presence of citric acid was carried out as described previously by adding citric acid (0.1 mole/mole metals) to a solution of the metal nitrates and evaporating at $100^{\circ}C$ to a viscous glass. This semi-solid is then calcined at $450^{\circ}C$ after increasing the temperature slowly. Sterotex was added, the material pelletized as above and heated slowly to $350^{\circ}C$ in order to combust the Sterotex.

The evaporation of metal acetates followed the same procedure as above except that the metal nitrates were replaced by metal acetates.

The evaporation of metal citrates differed from the above two evaporation methods in that the metal citrates were prepared separately by mixing each individual metal nitrate with excess citric acid to form a metal nitrate-citrate complex. The individual complexes were then mixed together and evaporated at $100^{\circ}C$ until a viscous, glassy paste was formed. NO_2 evolution was observed during this step. The calcining and finishing steps were the same as those of the standard evaporation method.

Coprecipitation Method

In the coprecipitation technique, the solution of metal nitrates and potassium hydroxide were prepared and charged to two burettes such that the solutions could be added sequentially or simultaneously to a well-stirred sample of deionized water ($80^{\circ}C$). With either mode of addition, the pH of the resulting solution was kept at about 9. This procedure was continued until all the metal hydroxides were precipitated from the nitrates with the KOH solution. The precipitated hydroxides were then allowed to age for about 18-24 hours at $40^{\circ}C$. The hydroxide slurry was filtered, reslurried in 5% KOH solution for one hour, filtered and slurried twice with deionized water. The filtrate had a pH of 7. The catalyst cake was dried at $120^{\circ}C$ and then calcined at $450^{\circ}C$ for 3 hours (temperature brought to $450^{\circ}C$ slowly). The calcined catalyst was

added to a potassium carbonate solution for impregnation of the potassium component of the catalyst. The water was then evaporated using a rotovap unit. The catalyst was pelletized, using Sterotex, to a 1 1/4" x 1/8" wafer which was recalcined at $350^\circ C$ for three hours (temperature brought up very slowly). The recalcined catalyst was broken apart and screened to 8 x 12 mesh particles.

When potassium carbonate, instead of potassium hydroxide was the precipitating agent (nitrates to carbonates), the above procedure also was used.

Detergent Dispersion

This method was based on a procedure developed by Shirokov[8] and consisted of dispersing and mixing oxide-base catalysts in the presence of surfactants. The atomic formulation tested with this method was $CuZn_{0.4}Co_{0.5}Al_{0.25}K_x$ where x was either 0 or 0.05. This method also allowed for the incorporation of cobalt into the catalyst in a form not previously used. A commercial methanol synthesis catalyst of the Cu-Zn-Al type was crushed and sieved through a 106 micron screen. For the formulation in which x = 0.05, some of the powdered methanol catalyst was impregnated with KOH solution to add the proper amount of K onto the catalyst. The powders were then slurried in a dry methanol-ethanolamine solution containing dicobalt octacarbonyl. The slurry was agitated in an ultrasonic bath for two hours. The mixture was removed from the ultrasonic bath and allowed to age for a period of time. The mixture was then heated to evaporate the methanol followed by heating at $200^\circ C$ for a period of 8 hours. The dried solids were broken and mixed with 3-5% Sterotex and pelletized to produce 1 1/4" x 1/8" wafers. Final finishing was accomplished by burning off the Sterotex at $300^\circ C$.

5.1.3 Experimental Results

A total of seventeen catalyst screening runs were completed during the fourth quarter including eleven tests in the Berty reactor and the

remaining six in the plug-flow reactor. These catalysts (see Table 5.1.3-1A) can be classified into the following five groups based on their elemental composition:

Group I: Catalysts containing Cu, Zn, Cr, Co, and Alkali

Group II: Catalysts of Group I without Zn, Co, or Cr

Group III: Modified methanol synthesis catalysts of the Cu-Zn-Al family.

Group IV: Catalysts of Group I where Cr is substituted by a transition metal (or metals) such as Fe, Th, Ti, V, etc.

Group V: Catalysts of Group I, II, or IV supported on inert oxides.

Runs 201-100P and 213-2B were made with catalysts that do not directly fit into any of these groups. In 201-100P, the plug-flow reactor was loaded with the first zone containing a commercial methanol synthesis catalyst followed by a second zone containing a Group IV catalyst. In 213-2B, the Berty reactor was loaded with a random and equal mixture of these same two catalysts.

The following parameters were tested this quarter:

1. Effect of incorporating a support having low hydrogen chemisorption capacity.

2. Effect of reduction conditions.

3. Effect of catalyst preparation methods.
    ● Evaporation of metal nitrate-citric acid solutions.
    ● Evaporation of metal citrate solutions.
    ● Coprecipitation of metal nitrates with KOH.

4. Effect of pelletizing pressure.

5. Effect of methanol addition to syn gas (simulation of methanol recycle).

Detailed summary of results for each of the seventeen tests is presented in Tables 5.1.3-1 through 5.1.3-17.

TABLE 5.1.3-1A

SUMMARY OF CATALYSTS TESTED

Run No.	Catalyst Number	Calculated Composition
	Group I:	**Catalysts Containing Cu, Zn, Cr, Co, and Alkali**
201-82B	197-70	$CuZn_{0.125}CoCrK_{0.11}$
201-87B	197-73	$CuZn_{0.125}CoCrK_{0.11}$
201-90B	197-76	$CuZn_{0.125}CoCrK_{0.11}$
201-91B	197-73	$CuZn_{0.125}CoCrK_{0.11}$
201-92P	197-78	$CuZn_{0.125}CoCr_{0.125}K_{0.11}$
201-97P	197-73	$CuZn_{0.125}CoCrK_{0.11}$
	Group IV:	**Catalysts of Group I Without Cr & Containing Transition Metals**
201-81P	200-58-1	$CuZn_{0.125}CoMoK_{0.11}$
201-83B	197-71	$CuZn_{0.125}CoTh_{0.5}Fe_{0.1}K_{0.11}$
201-85B	197-71	$CuZn_{0.125}CoTh_{0.5}Fe_{0.5}K_{0.11}$
201-89P	197-72	$CuZn_{0.125}CoZrK_{0.11}$
201-93B	197-77	$CuZn_{0.125}CoTh_{0.5}K_{0.11}$
201-95B	197-79	$CuZn_{0.125}CoThK_{0.11}$
213-4B	197-85	$CuZn_{0.125}CoTh_{0.5}Fe_{0.1}K_{0.11}$
	Group V:	**Supported Catalysts**
201-84P	197-67	$CuZn_{0.125}CoCrK_{0.11}$ on TiO_2
201-98B	197-81	$CuZn_{0.125}CoTh_{0.5}Fe_{0.5}K_{0.11}$ on MnO
	Catalysts	**Not Fitting Into Groups I Through V**
201-100P	MeOH cat/ 200-27-1	$CuZn_{.49}Al_{.21}\backslash CuZn_{.125}CoTh_{.5}Fe_{.5}K_{.11}$
213-2B	MeOH cat/ 200-27-1	$CuZn_{0.49}Al_{0.21}\backslash CuZn_{0.125}CoTh_{0.5}Fe_{0.5}K_{0.11}$

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* Suffix P devotes testing in the plug-flow reactor and Suffix B denotes testing in the Berty gradientless reactor.

**No catalysts were tested in Group II (Catalysts of Group I without Zn or Co or Cr) and Group III (Modified methanol synthesis catalysts).

TABLE __5.1.3-1__ SUMMARY FOR RUN __201-81 P (10-July-80)__

CATALYST NO. __200-58-1__   ATOMIC FORMULA __$CuCoMoZn_{0.125}K_{0.11}$__

PREP. METHOD __Evaporation of nitrates & $(NH_4)_6Mo_74H_2O$ w/citric acid__

SURFACE AREA[1] _____ m^2/gm   FEED H_2/CO __2.0__ CO_2 __5.0__ Vol%

BULK DENSITY[1] __1.41_____ gm/cc

TEST NO.	-1	-2	-3			
Avg. Temp., °C	265	275	283			
Hot Spot, °C	267	277	287			
Pressure, psig	885	885	885			
VHSV, L/hr/kgm cat.	3151	2972	2967			
Hrs. on Stream	3.3	5.2	6.3			

CONVERSION

	-1	-2	-3			
CO, Vol%	8.54	11.1	15.4			
CO, gm mol/hr/kgm cat.	3.38	4.16	5.73			
STY of Oxygenates[2] gm mol/hr/kgm cat.	0.277	0.258	0.276			

NORMALIZED CARBON SELECTIVITY, vol %

	-1	-2	-3			
CH_3OH	5.0	3.7	2.9			
C_2-C_6 Alcohols	2.0	1.5	1.1			
C_1-C_6 Aldehydes	0.3	0.2	0.1			
C_4-C_9 H.C.	4.9	7.6	6.9			
CH_4	28.4	27.5	28.5			
C_2+C_3 H.C.	28.4	24.3	24.3			
CO_2	30.8	35.2	36.2			
APPROACH TO[3] WGS EQUILIBRIUM, °C						
CARBON ACCOUNTABILITY, %	78.8	97.2	102.8			

---

[1] Fresh, non-reduced catalyst

[2] Space Time Yield (STY) = $\frac{VHSV}{22.4}$ x $\frac{\% \ CO \ in \ Feed}{100}$ x $\frac{\% \ CO \ Conv.}{100}$ x $\frac{\% \ Selectivity \ to \ Oxygenates}{100}$

[3] Defined as $T = T_{eq} - T_{avg}$

   where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

   T_{avg} = average observed bulk-phase reaction temperature

TABLE ___5.1.3.-2___ SUMMARY FOR RUN ___201-82B (9-July-80)___

CATALYST NO. ___197-70 Reduced in situ___ ATOMIC FORMULA $CuCrCoZn_{0.125}K_{0.11}$

PREP. METHOD ___Evaporation of metal nitrates - citric acid___

SURFACE AREA[1] _____ m^2/gm   FEED H_2/CO ___2.0___ CO_2 ___5.0___ Vol%

BULK DENSITY[1] ___1.45___ gm/cc

TEST NO.	-1	-2	-3			
Avg. Temp., °C	274	282	290			
Hot Spot, °C	275	283	292			
Pressure, psig	895	895	895			
VHSV, L/hr/kgm cat.	814	849	756			
Hrs. on Stream	48.0	50.8	70.8			

CONVERSION

CO, Vol%	0.85	2.5	0.43			
CO, gm mol/hr/kgm cat.	8.55×10^{-2}	0.026	4.12×10^{-2}			

STY of Oxygenates[2]
gm mol/hr/kgm cat.

THIS BATCH OF CATALYST WAS FOUND TO HAVE BEEN POISONED BY FOREIGN MATERIAL DURING PREPARATION.

NORMALIZED CARBON SELECTIVITY, vol %

CH_3OH						
C_2-C_6 Alcohols						
C_1-C_6 Aldehydes						
C_4-C_9 H.C.						
CH_4						
C_2+C_3 H.C.						
CO_2						
APPROACH TO[3] WGS EQUILIBRIUM, °C						
CARBON ACCOUNTABILITY, %						

[1]Fresh, non-reduced catalyst

[2]Space Time Yield (STY) = $\frac{VHSV}{22.4}$ x $\frac{\text{\% CO in Feed}}{100}$ x $\frac{\text{\% CO Conv.}}{100}$ x $\frac{\text{\% Selectivity to Oxygenates}}{100}$

[3]Defined as $T = T_{eq} - T_{avg}$

where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

T_{avg} = average observed bulk-phase reaction temperature

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TABLE 5.1.3-3 SUMMARY FOR RUN 201-83B (14-July 80)

CATALYST NO. 197-71 Reduced in situ   ATOMIC FORMULA $CuZn_{0.125}CoFe_{0.1}Th_{0.5}K_{0.11}$

PREP. METHOD Evaporation of Nitrates w/citric acid; Calcined at $450^{\circ}C$ for 3 hrs.

SURFACE AREA[1] _____ m^2/gm FEED H_2/CO __2.0__ CO_2 __5.0__ Vol%

BULK DENSITY[1] __1.80__ gm/cc

TEST NO.	-1	-2	-3			
Avg. Temp., $^{\circ}C$	246	274	275			
Hot Spot, $^{\circ}C$	247	275	276			
Pressure, psig	900	900	900			
VHSV, L/hr/kgm cat.	2063	2314	533			
Hrs. on Stream	5.2	9.2	11.4			

CONVERSION

	-1	-2	-3			
CO, Vol%	3.39	5.90	18.9			
CO, gm mol/hr/kgm cat.	0.80	1.56	1.16			
STY of Oxygenates[2] gm mol/hr/kgm cat.	0.42	0.85	0.45			

NORMALIZED CARBON SELECTIVITY, vol %

	-1	-2	-3			
CH_3OH	21.0	19.6	13.9			
C_2-C_6 Alcohols	26.5	30.3	21.3			
C_1-C_6 Aldehydes	0.8	0.6	1.0			
C_4-C_9 H.C.	8.9	6.4	5.0			
CH_4	27.1	27.7	22.5			
C_2+C_3H.C.	15.7	15.4	12.5			
CO_2	Trace	Trace	23.8			
APPROACH TO[3] WGS EQUILIBRIUM, $^{\circ}C$						
CARBON ACCOUNTABILITY, %	31.7	50.8	76.7			

[1] Fresh, non-reduced catalyst

[2] Space Time Yield (STY) = $\frac{VHSV}{22.4}$ x $\frac{\% \text{ CO in Feed}}{100}$ x $\frac{\% \text{ CO Conv.}}{100}$ x $\frac{\% \text{ Selectivity to Oxygenates}}{100}$

[3] Defined as $T = T_{eq} - T_{avg}$

where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

T_{avg} = average observed bulk-phase reaction temperature

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TABLE __5.1.3-4__ SUMMARY FOR RUN __201-84 P (18-July-80)__

CATALYST NO. __197-67__   ATOMIC FORMULA __30% (CuZn$_{0.125}$CoCrK$_{0.11}$) on TiO$_2$__

PREP. METHOD __Impregrnation of Titania with metal nitrate solution; Calcined at 450°C for 3 hrs.__

SURFACE AREA[1] _____ m^2/gm   FEED H$_2$/CO __2.0__   CO$_2$ __5.1__ Vol%

BULK DENSITY[1] __1.27__ _____ gm/cc

TEST NO.	-1	-2				
Avg. Temp., ^{o}C	261	262				
Hot Spot, ^{o}C	262	262				
Pressure, psig	890	880				
VHSV, L/hr/kgm cat.	3374	1000				
Hrs. on Stream	4.0	6.0				

CONVERSION

CO, Vol%	1.0	3.7				
CO, gm mol/hr/kgm cat.	0.42	0.45				
STY of Oxygenates[2] gm mol/hr/kgm cat.	0.025	0.048				

NORMALIZED CARBON SELECTIVITY, vol %

CH$_3$OH	0.2	0.1				
C$_2$-C$_6$ Alcohols	0.5	0.3				
C$_1$-C$_6$ Aldehydes	5.1	10.1				
C$_4$-C$_9$ H.C.	1.9	2.3				
CH$_4$	42.8	25.8				
C$_2$+C$_3$ H.C.	5.7	5.9				
CO$_2$	43.8	55.5				

APPROACH TO[3] WGS EQUILIBRIUM, ^{o}C						
CARBON ACCOUNTABILITY, %	69.3	89.2				

---

[1] Fresh, non-reduced catalyst

[2] Space Time Yield (STY) = $\frac{VHSV}{22.4}$ x $\frac{\text{% CO in Feed}}{100}$ x $\frac{\text{% CO Conv.}}{100}$ x $\frac{\text{% Selectivity to Oxygenates}}{100}$

[3] Defined as T = T_{eq} - T_{avg}

where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

T_{avg} = average observed bulk-phase reaction temperature

TABLE 5.1.3-5   SUMMARY FOR RUN   201-85B (22-July-80)

CATALYST NO. 197-71   ATOMIC FORMULA $CuZn_{0.125}CoTh_{0.5}Fe_{0.1}K_{0.11}$

PREP. METHOD Evaporation of Nitrate Solution w/citric acid; Calcined at 450°C for 3 hrs.

SURFACE AREA[1] _____ m^2/gm   FEED H_2/CO ___ 2.0 ___ CO_2 ___ 5.1 ___ Vol%

BULK DENSITY[1] 1.73 _____ gm/cc

TEST NO.	-1	-2	-3	-4	-5	-6
Avg. Temp., °C	257	258	270	271	279	280
Hot Spot, °C	258	259	271	272	280	281
Pressure, psig	905	900	905	905	905	905
VHSV, L/hr/kgm cat.	3597	882	3351	976	3258	1005
Hrs. on Stream	4.2	5.9	10.3	12.8	16.1	19.1
CONVERSION						
CO, Vol%	3.9	13.1	6.3	17.5	6.4	20.4
CO, gm mol/hr/kgm cat.	1.70	1.39	2.60	2.13	2.61	2.57
STY of Oxygenates[2] gm mol/hr/kgm cat.	0.85	0.54	1.12	0.70	0.942	0.752
NORMALIZED CARBON SELECTIVITY, vol %						
CH_3OH	14.8	10.7	15.2	10.2	13.7	9.8
C_2-C_6 Alcohols	32.0	26.4	25.8	21.0	20.8	17.5
C_1-C_6 Aldehydes	3.3	1.8	2.1	1.6	1.7	2.1
C_4-C_9 H.C.	9.4	5.5	4.9	3.4	3.1	3.6
CH_4	24.4	21.4	25.1	24.7	25.0	25.7
C_2+C_3 H.C.	16.1	13.8	14.2	13.6	12.6	12.9
CO_2	Trace	20.4	12.7	25.5	23.1	28.4
APPROACH TO[3] WGS EQUILIBRIUM, °C	147	176	134	169	67	148
CARBON ACCOUNTABILITY, %	73.3	91.1	80.3	91.5	97.5	98.0

---

[1]Fresh, non-reduced catalyst

[2]Space Time Yield (STY) = $\frac{VHSV}{22.4}$ x $\frac{\% \text{ CO in Feed}}{100}$ x $\frac{\% \text{ CO Conv.}}{100}$ x $\frac{\% \text{ Selectivity to Oxygenates}}{100}$

[3]Defined as $T = T_{eq} - T_{avg}$

where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

T_{avg} = average observed bulk-phase reaction temperature

TABLE 5.1.3-6   SUMMARY FOR RUN 201-87B (31-July-80)

CATALYST NO. 197-73   ATOMIC FORMULA $CuZn_{0.125}CrCoK_{0.11}$

PREP. METHOD Evaporation of metal nitrate-citric acid solution

SURFACE AREA[1] _____ m^2/gm FEED H_2/CO 2.0 CO_2 5.1 Vol%

BULK DENSITY[1] 1.28 gm/cc

TEST NO.	-1	-2	-3				
Avg. Temp., °C	260	260	272				
Hot Spot, °C	260	261	273				
Pressure, psig	935	930	935				
VHSV, L/hr/kgm cat.	3406	892	877				
Hrs. on Stream	4.0	6.0	9.3				

CONVERSION

	-1	-2	-3				
CO, Vol%	5.6	15.9	29.1				
CO, gm mol/hr/kgm cat.	2.41	1.79	3.22				
STY of Oxygenates[2] gm mol/hr/kgm cat.	0.48	0.276	0.558				

NORMALIZED CARBON SELECTIVITY, vol %

	-1	-2	-3				
CH_3OH	2.6	2.1	4.0				
C_2-C_6 Alcohols	7.9	6.8	12.1				
C_1-C_6 Aldehydes	9.5	6.5	1.2				
C_4-C_9 H.C.	-5.8	5.5	4.7				
CH_4	29.2	24.8	29.7				
C_2+C_3 H.C.	13.0	11.8	12.5				
CO_2	32.0	42.5	35.8				
APPROACH TO[3] WGS EQUILIBRIUM, °C							
CARBON ACCOUNTABILITY, %	68.2	99.8	93.4				

---

[1] Fresh, non-reduced catalyst

[2] Space Time Yield (STY) = $\frac{VHSV}{22.4} \times \frac{\% \ CO \ in \ Feed}{100} \times \frac{\% \ CO \ Conv.}{100} \times \frac{\% \ Selectivity \ to \ Oxygenates}{100}$

[3] Defined as $T = T_{eq} - T_{avg}$

   where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

     T_{avg} = average observed bulk-phase reaction temperature

TABLE. 5.1.3-7   SUMMARY FOR RUN 201-89 P (6-Aug.-80)

CATALYST NO. _____197-72_____ ATOMIC FORMULA $CuZn_{0.125}CoZrK_{0.11}$

PREP. METHOD Evaporation of nitrates & Zr acetate, Calcined at 450°C for 3 hrs.

SURFACE AREA[1] _____ m^2/gm   FEED H_2/CO ___2.0___ CO_2 ___5.1___ Vol%

BULK DENSITY[1] ___1.3___ gm/cc

TEST NO.	-1	-2	-3	-4		
Avg. Temp., °C	264	264	273	273		
Hot Spot, °C	265	265	273	273		
Pressure, psig	880	875	910	910		
VHSV, L/hr/kgm cat.	3548	857	2791	932		
Hrs. on Stream	4.1	6.9	10.0	14.9		

CONVERSION

	-1	-2	-3	-4		
CO, Vol%	1.0	3.9	1.4	7.2		
CO, gm mol/hr/kgm cat.	0.449	0.42	0.491	0.828		
STY of Oxygenates[2] gm mol/hr/kgm cat.	0.111	0.119	0.200	0.355		

NORMALIZED CARBON SELECTIVITY, vol %

	-1	-2	-3	-4		
CH_3OH	16.1	15.6	24.1	21.9		
C_2-C_6 Alcohols	6.7	9.0	11.3	16.9		
C_1-C_6 Aldehydes	1.8	3.6	5.3	4.0		
C_4-C_9 H.C.	3.2	4.1	3.2	5.1		
CH_4	34.8	28.7	35.5	30.7		
C_2+C_3 H.C.	9.2	8.2	14.0	13.5		
CO_2	28.2	30.8	6.6	7.9*		
APPROACH TO[3] WGS EQUILIBRIUM, °C	96.6	106.1	95.8	55.8		
CARBON ACCOUNTABILITY, %						

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[1]Fresh, non-reduced catalyst

[2]Space Time Yield (STY) = $\frac{VHSV}{22.4}$ x $\frac{\text{% CO in Feed}}{100}$ x $\frac{\text{% CO Conv.}}{100}$ x $\frac{\text{% Selectivity to Oxygenates}}{100}$

[3]Defined as T = T_{eq} - T_{avg}

where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

   T_{avg} = average observed bulk-phase reaction temperature

   * CO_2 selectivity value was not normalized

TABLE __5.1.3-8__ SUMMARY FOR RUN __201-90B (4-Aug-80)__

CATALYST NO. __197-76__ ATOMIC FORMULA $CuZn_{0.125}CoCrK_{0.11}$

PREP. METHOD Evaporation of citrates; Calcined at $450^\circ C$ for 3hrs.

SURFACE AREA[1] _____ m^2/gm FEED H_2/CO __2.0__ CO_2 __4.9__ Vol%

BULK DENSITY[1] __1.35__ gm/cc

TEST NO.	-1	-2	-3	-4		
Avg. Temp., $^\circ C$	271	273	238	246		
Hot Spot, $^\circ C$	272	273	238	246		
Pressure, psig	935	930	1600	1600		
VHSV, L/hr/kgm cat.	3509	854	322	309		
Hrs. on Stream	3.0	6.0	8.5	12.1		

CONVERSION

CO, Vol%	4.8	24.6	8.6	17.1		
CO, gm mol/hr/kgm cat.	2.07	2.61	0.339	0.647		
STY of Oxygenates[2] gm mol/hr/kgm cat.	0.364	0.355	0.070	0.104		

NORMALIZED CARBON SELECTIVITY, vol %

CH_3OH	3.4	2.7	5.9	3.7		
C_2-C_6 Alcohols	5.1	4.6	6.2	5.1		
C_1-C_6 Aldehydes	9.1	6.3	8.5	7.3		
C_4-C_9 H.C.	5.2	5.6	7.2	7.3		
CH_4	29.2	27.1	32.1	27.9		
C_2+C_3 H.C.	11.9	12.2	14.4	12.7		
CO_2	36.1	41.5	25.7	36.0		

APPROACH TO[3] WGS EQUILIBRIUM, $^\circ C$						
CARBON ACCOUNTABILITY, %	112.9	100.0	98.3	101.7		

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[1] Fresh, non-reduced catalyst

[2] Space Time Yield (STY) = $\frac{VHSV}{22.4}$ x $\frac{\% \text{ CO in Feed}}{100}$ x $\frac{\% \text{ CO Conv.}}{100}$ x $\frac{\% \text{ Selectivity to Oxygenates}}{100}$

[3] Defined as $T = T_{eq} - T_{avg}$

where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

T_{avg} = average observed bulk-phase reaction temperature

TABLE 5.1.3-9 SUMMARY FOR RUN 201-91 B (11-Aug.-80)

CATALYST NO. 197-73   ATOMIC FORMULA $CuCrCoZn_{0.125}K_{0.11}$

PREP. METHOD Evaporation of metal nitrate-citric acid; 20,000 psi pelletizing pressure

SURFACE AREA[1] _____ m^2/gm FEED H_2/CO 2.1 CO_2 5.2 Vol%

BULK DENSITY[1] _____ gm/cc

TEST NO.	-1					
Avg. Temp., $^\circ$C	271					
Hot Spot, $^\circ$C	272					
Pressure, psig	915					
VHSV, L/hr/kgm cat.	918					
Hrs. on Stream	9.2					

CONVERSION

CO, Vol%	21.2					
CO, gm mol/hr/kgm cat.	2.40					
STY of Oxygenates[2] gm mol/hr/kgm cat.	0.46					

NORMALIZED CARBON SELECTIVITY, vol %

CH_3OH	5.6					
C_2-C_6 Alcohols	12.9					
C_1-C_6 Aldehydes	0.6					
C_4-C_9 H.C.	5.3					
CH_4	29.0					
C_2+C_3 H.C.	11.8					
CO_2	34.8					
APPROACH TO[3] WGS EQUILIBRIUM, $^\circ$C	91					
CARBON ACCOUNTABILITY, %	103.5					

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[1] Fresh, non-reduced catalyst

[2] Space Time Yield (STY) = $\frac{VHSV}{22.4} \times \frac{\% \text{ CO in Feed}}{100} \times \frac{\% \text{ CO Conv.}}{100} \times \frac{\% \text{ Selectivity to Oxygenates}}{100}$

[3] Defined as $T = T_{eq} - T_{avg}$

where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

T_{avg} = average observed bulk-phase reaction temperature

TABLE 5.1.3-10 SUMMARY FOR RUN 201-92 P (15-Aug-80)

CATALYST NO. 197-78   ATOMIC FORMULA $CuZn_{0.125}CoCr_{0.125}K_{0.11}$

PREP. METHOD Evaporation of metal nitrate-citric acid solutions

SURFACE AREA[1] _____ m^2/gm FEED H_2/CO 2.0 CO_2 5.1 Vol%

BULK DENSITY[1] 1.41 gm/cc

TEST NO.	-1	-2	-3			
Avg. Temp., °C	262	276	279			
Hot Spot, °C	263	279	284			
Pressure, psig	905	920	910			
VHSV, L/hr/kgm cat.	3677	3361	969			
Hrs. on Stream	3.6	6.1	9.0			
CONVERSION						
CO, Vol%	4.0	7.9	50.9			
CO, gm mol/hr/kgm cat.	1.82	3.20	5.94			
STY of Oxygenates[2] gm mol/hr/kgm cat.	0.48	0.83	0.93			
NORMALIZED CARBON SELECTIVITY, vol %						
CH_3OH	3.6	3.5	2.4			
C_2-C_6 Alcohols	6.1	6.5	9.3			
C_1-C_6 Aldehydes	16.8	16.0	3.9			
C_4-C_9 H.C.	10.3	7.4	6.0			
CH_4	30.1	24.6	23.3			
C_2+C_3 H.C.	18.7	16.6	14.1			
CO_2	14.4	25.4	41.0			
APPROACH TO[3] WGS EQUILIBRIUM, °C	142	72	19			
CARBON ACCOUNTABILITY, %	83.9	112.8	104.6			

[1] Fresh, non-reduced catalyst

[2] Space Time Yield (STY) = $\frac{VHSV}{22.4} \times \frac{\% \ CO \ in \ Feed}{100} \times \frac{\% \ CO \ Conv.}{100} \times \frac{\% \ Selectivity \ to \ Oxygenates}{100}$

[3] Defined as $T = T_{eq} - T_{avg}$

where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

T_{avg} = average observed bulk-phase reaction temperature

TABLE __5.1.3-11__ SUMMARY FOR RUN __201-93 B (19-Aug-80)__

CATALYST NO. ____197-77____ ATOMIC FORMULA __$CuZn_{0.125}CoTh_{0.5}K_{0.11}$__

PREP. METHOD Evaporation of metal nitrates, Calcined at $450^{\circ}c$ for 3 hrs. pelletized at 10,000ps$^{\downarrow}$

SURFACE AREA[1] _____ m^2/gm   FEED H_2/CO __2.1__ CO_2 __5.0__   Vol%

BULK DENSITY[1] _____ gm/cc

TEST NO.	-1	-2	-3	-4	-5	-6
Avg. Temp., $^{\circ}C$	262	268	270	270	282	284
Hot Spot, $^{\circ}C$	262	268	270	270	283	284
Pressure, psig	920	915	920	920	920	915
VHSV, L/hr/kgm cat.	3607	900	3239	931	3431	984
Hrs. on Stream	4.0	7.0	10.2	13.1	18.1	20.2

CONVERSION

	-1	-2	-3	-4	-5	-6
CO, Vol%	4.3	30.5	7.5	29.8	13.6	63.8
CO, gm mol/hr/kgm cat.	1.90	3.37	2.98	3.41	5.73	7.71
STY of Oxygenates[2] gm mol/hr/kgm cat.	0.59	0.87	0.75	0.72	1.67	1.33

NORMALIZED CARBON SELECTIVITY, vol %

	-1	-2	-3	-4	-5	-6
CH_3OH	8.1	5.5	7.7	5.3	7.3	4.2
C_2-C_6 Alcohols	16.3	17.9	15.0	13.9	17.7	11.6
C_1-C_6 Aldehydes	6.7	2.3	2.3	1.8	4.1	1.4
C_4-C_9 H.C.	4.7	4.9	2.6	3.0	3.0	2.7
CH_4	33.5	19.8	27.8	27.4	30.2	30.6
C_2+C_3 H.C.	14.7	12.1	18.3	17.4	19.4	16.3
CO_2	16.0	37.5	26.3	31.2	18.3	33.2
APPROACH TO[3] WGS EQUILIBRIUM, $^{\circ}C$	88	70	72	142	170	122
CARBON ACCOUNTABILITY, %	106.2	100.8	109.0	105.3	100.2	103.1

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[1] Fresh, non-reduced catalyst

[2] Space Time Yield (STY) = $\dfrac{VHSV}{22.4}$ x $\dfrac{\% \text{ CO in Feed}}{100}$ x $\dfrac{\% \text{ CO Conv.}}{100}$ x $\dfrac{\% \text{ Selectivity to Oxygenates}}{100}$

[3] Defined as $T = T_{eq} - T_{avg}$

where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

T_{avg} = average observed bulk-phase reaction temperature

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TABLE __5.1.3-11__ SUMMARY FOR RUN 201-93 B (19-Aug-80) Continued

CATALYST NO. _____197-77_____ ATOMIC FORMULA $CuZn_{0.125}CoTh_{0.5}K_{0.11}$

PREP. METHOD Evaporation of Nitrates. Calcined at $450^{\circ}C$ for 3 hrs;pelletized at 10000psi

SURFACE AREA[1] _____ m^2/gm   FEED H_2/CO ____2.1____ CO_2 ____5.0____ Vol%

BULK DENSITY[1] _____ gm/cc

TEST NO.	-7					
Avg. Temp., $^{\circ}C$	257					
Hot Spot, $^{\circ}C$	257					
Pressure, psig	925					
VHSV, L/hr/kgm cat.	3248					
Hrs. on Stream	22.7					

CONVERSION

CO, Vol%	2.7					
CO, gm mol/hr/kgm cat.	1.08					
STY of Oxygenates[2] gm mol/hr/kgm cat.	0.35					

NORMALIZED CARBON SELECTIVITY,vol %

CH_3OH	13.1					
C_2-C_6 Alcohols	16.8					
C_1-C_6 Aldehydes	3.0					
C_4-C_9 H.C.	2.7					
CH_4	39.2					
C_2+C_3 H.C.	23.2					
CO_2	2.0					
APPROACH TO[3] WGS EQUILIBRIUM, $^{\circ}C$	93					
CARBON ACCOUNTABILITY, %	101.7					

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[1] Fresh, non-reduced catalyst

[2] Space Time Yield (STY) = $\frac{VHSV}{22.4}$ x $\frac{\% \ CO \ in \ Feed}{100}$ x $\frac{\% \ CO \ Conv.}{100}$ x $\frac{\% \ Selectivity \ to \ Oxygenates}{100}$

[3] Defined as $T = T_{eq} - T_{avg}$

where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

T_{avg} = average observed bulk-phase reaction temperature

TABLE __5.1.3-12__ SUMMARY FOR RUN __201-95 B (28-Aug-80)__

CATALYST NO. _____197-79_____ ATOMIC FORMULA $CuZn_{0.125}CoThK_{0.11}$

PREP. METHOD __Coprecipitation of Metal Nitrates w/KOH. Calcined at 460__ ^{o}C for 3 hrs _____

SURFACE AREA[1] _____ m^2/gm · FEED H_2/CO __2.0__ CO_2 __5.2__ Vol%

BULK DENSITY[1] __1.52__ gm/cc

TEST NO.	-1	-2	-3			
Avg. Temp., ^{o}C	260	261	273			
Hot Spot, ^{o}C	260	261	273			
Pressure, psig	920	1530	910			
VHSV, L/hr/kgm cat.	3202	3237	3364			
Hrs. on Stream	4.6	7.3	12.2			

CONVERSION

	-1	-2	-3			
CO, Vol%	3.5	7.3	4.7			
CO, gm mol/hr/kgm cat.	1.39	2.93	1.96			
STY of Oxygenates[2] gm mol/hr/kgm cat.	0.52	0.77	0.70			

NORMALIZED CARBON SELECTIVITY, vol %

	-1	-2	-3			
CH_3OH	12.6	9.0	14.3			
C_2-C_6 Alcohols	23.6	16.1	20.3			
C_1-C_6 Aldehydes	1.3	1.1	0.9			
C_4-C_9 H.C.	5.8	4.0	2.8			
CH_4	31.9	19.8	34.1			
C_2+C_3 H.C.	24.2	14.3	18.4			
CO_2	0.6	35.7	9.2			
APPROACH TO[3] WGS EQUILIBRIUM, ^{o}C						
CARBON ACCOUNTABILITY, %	90.3	89.0	104.9			

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[1]Fresh, non-reduced catalyst

[2]Space Time Yield (STY) = $\frac{VHSV}{22.4}$ x $\frac{\text{% CO in Feed}}{100}$ x $\frac{\text{% CO Conv.}}{100}$ x $\frac{\text{% Selectivity to Oxygenates}}{100}$

[3]Defined as $T = T_{eq} - T_{avg}$

where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

T_{avg} = average observed bulk-phase reaction temperature

TABLE **5.1.3-13** SUMMARY FOR RUN **201-97 P (5-Sept-80)**

CATALYST NO. **197-73** ATOMIC FORMULA $CuZn_{0.125}CoCrK_{0.11}$

PREP. METHOD **Evaporation of metal nitrates**

SURFACE AREA[1] _____ m^2/gm · FEED H_2/CO **2.1** CO_2 **5.1** Vol%

BULK DENSITY[1] **1.38** gm/cc

TEST NO.	-1					
Avg. Temp., ^oC	273					
Hot Spot, ^oC	273					
Pressure, psig	910					
VHSV, L/hr/kgm cat.	1030					
Hrs. on Stream	35.6					

CONVERSION

CO, Vol%	7.2					
CO, gm mol/hr/kgm cat.	0.92					
STY of Oxygenates[2] gm mol/hr/kgm cat.	0.19					

NORMALIZED CARBON SELECTIVITY, vol %

CH_3OH	4.8					
C_2-C_6 Alcohols	6.2					
C_1-C_6 Aldehydes	10.0					
C_4-C_9 H.C.	6.1					
CH_4	29.1					
C_2+C_3 H.C.	18.9					
CO_2	25.0					
APPROACH TO[3] WGS EQUILIBRIUM, ^oC						
CARBON ACCOUNTABILITY, %	99.1					

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[1] Fresh, non-reduced catalyst

[2] Space Time Yield (STY) = $\frac{VHSV}{22.4}$ x $\frac{\% \text{ CO in Feed}}{100}$ x $\frac{\% \text{ CO Conv.}}{100}$ x $\frac{\% \text{ Selectivity to Oxygenates}}{100}$

[3] Defined as $T = T_{eq} - T_{avg}$

where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

T_{avg} = average observed bulk-phase reaction temperature

TABLE 5.1.3-14 SUMMARY FOR RUN 201-98 B (8-Sept-80)

CATALYST NO. 197-81   ATOMIC FORMULA $CuZn_{0.125}Th_{0.5}Fe_{0.5}K_{0.11}$ on MnO

PREP. METHOD Coprecipitation of Nitrates w/KOH

SURFACE AREA[1] _____ m^2/gm   FEED H_2/CO 2.0 CO_2 5.0 Vol%

BULK DENSITY[1] 1.02 gm/cc

TEST NO.	-1	-2	-3	-4		
Avg. Temp., ^oC	267	262	262	239		
Hot Spot, ^oC	268	262	263	242		
Pressure, psig	920	920	1500	900		
VHSV, L/hr/kgm cat.	1619	4487	5162	1797		
Hrs. on Stream	3.8	8.2	11.1	15.1		

CONVERSION

	-1	-2	-3	-4		
CO, Vol%	49.6	11.9	12.3	9.1		
CO, gm mol/hr/kgm cat.	10.1	6.71	7.78	2.06		
STY of Oxygenates[2] gm mol/hr/kgm cat.	1.27	1.14	1.70	0.44		

NORMALIZED CARBON SELECTIVITY, vol %

	-1	-2	-3	-4		
CH_3OH	1.3	4.1	4.6	5.0		
C_2-C_6 Alcohols	10.8	12.1	14.7	14.3		
C_1-C_6 Aldehydes	0.5	0.8	2.6	2.3		
C_4-C_9 H.C.	15.7	12.5	12.0	10.8		
CH_4	20.3	24.2	22.5	24.9		
C_2+C_3 H.C.	27.7	32.1	28.2	29.6		
CO_2	23.7	14.2	15.4	13.1		
APPROACH TO[3] WGS EQUILIBRIUM, ^oC						
CARBON ACCOUNTABILITY, %	101.2	95.3	114.4	90.1		

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[1] Fresh, non-reduced catalyst

[2] Space Time Yield (STY) = $\frac{VHSV}{22.4}$ x $\frac{\% \text{ CO in Feed}}{100}$ x $\frac{\% \text{ CO Conv.}}{100}$ x $\frac{\% \text{ Selectivity to Oxygenates}}{100}$

[3] Defined as $T = T_{eq} - T_{avg}$

    where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

      T_{avg} = average observed bulk-phase reaction temperature

TABLE ___5.1.3-15___ SUMMARY FOR RUN ___201-100 P (12-Sept-80)___

Methanol Synthesis Catalyst (First Stage);

CATALYST NO. ___200-27-1 (second stage)___ ATOMIC FORMULA $\frac{CuZn_{.49}Al_{.21}}{Cu\ Zn_{0.125}\ Th_{0.5}\ Fe_{0.5}\ K_{0.11}\ Co}$

PREP. METHOD Evaporation of metal nitrate-citric acid solution

SURFACE AREA[1] _____ m^2/gm   FEED H_2/CO __2.1__ CO_2 __4.9__ Vol%

BULK DENSITY[1] _____ gm/cc

TEST NO.	-1	-2	-3			
Avg. Temp., °C	182	193	209			
Hot Spot, °C	183	193	219			
Pressure, psig	920	920	920			
VHSV, L/hr/kgm cat.	3402	3388	3669			
Hrs. on Stream	4.0	5.8	10.4			

CONVERSION

	-1	-2	-3			
CO, Vol%	1.4	1.8	27.9			
CO, gm mol/hr/kgm cat.	0.58	0.75	12.5			
STY of Oxygenates[2] gm mol/hr/kgm cat.	0.40	0.58	11.6			

NORMALIZED CARBON SELECTIVITY, vol %

	-1	-2	-3			
CH_3OH	68.9	71.9	90.9			
C_2-C_6 Alcohols	2.1	1.7	1.4			
C_1-C_6 Aldehydes	6.7	3.5	0.3			
C_4-C_9 H.C.	3.8	3.1	1.7			
CH_4	10.6	9.9	1.6			
C_2+C_3 H.C.	7.9	9.9	2.5			
CO_2	Trace	Trace	1.6			
APPROACH TO[3] WGS EQUILIBRIUM, °C						
CARBON ACCOUNTABILITY, %	87.2	121.3	88.5			

[1]Fresh, non-reduced catalyst

[2]Space Time Yield (STY) = $\frac{VHSV}{22.4} \times \frac{\%\ CO\ in\ Feed}{100} \times \frac{\%\ CO\ Conv.}{100} \times \frac{\%\ Selectivity\ to\ Oxygenates}{100}$

[3]Defined as $T = T_{eq} - T_{avg}$

where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

T_{avg} = average observed bulk-phase reaction temperature

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TABLE 5.1.3-16   SUMMARY FOR RUN 213-2 B (17-Sept-80)

CATALYST NO. Random Mixture of Methanol Synthesis Catalyst and 200-27-2   ATOMIC FORMULA $CuZn_{.49}Al_{.21}/CuZn_{0.125}CoTh_{0.5}Fe_{0.5}K_{0.}$

PREP. METHOD Evaporation of metal nitrates/citric acid

SURFACE AREA[1] _____ m^2/gm FEED H_2/CO ___2.1___ CO_2 ___5.0___ Vol%

BULK DENSITY[1] 1.23 _____ gm/cc

TEST NO.	-1	-2	-3	-4	-5	
Avg. Temp., ^oC	225	225	208	208	250	
Hot Spot, ^oC	225	225	208	208	250	
Pressure, psig	910	905	905	905	910	
VHSV, L/hr/kgm cat.	3632	1251	673	3521	3972	
Hrs. on Stream	3.8	7.7	11.3	14.1	19.4	

CONVERSION

	-1	-2	-3	-4	-5	
CO, Vol%	34.3	65.6	52.5	17.3	36.2	
CO, gm mol/hr/kgm cat.	14.8	9.81	4.30	7.41	17.4	
STY of Oxygenates[2] gm mol/hr/kgm cat.	10.1	5.71	2.45	6.50	8.31	

NORMALIZED CARBON SELECTIVITY, vol %

	-1	-2	-3	-4	-5	
CH_3OH	63.9	49.8	53.8	84.1	39.2	
C_2-C_6 Alcohols	4.3	8.1	3.2	3.6	7.8	
C_1-C_6 Aldehydes	~ 0	0.3	~ 0	~ 0	0.5	
C_4-C_9 H.C.	5.1	5.6	5.0	2.2	5.3	
CH_4	4.1	6.2	4.7	2.7	10.8	
$C_2 + C_3$ H.C.	5.4	7.3	6.7	3.1	10.2	
CO_2	17.3	22.7	26.5	4.3	26.2	

APPROACH TO[3] WGS EQUILIBRIUM, ^oC						
CARBON ACCOUNTABILITY, %	100.6	90.6	95.1	95.5	103.0	

[1] Fresh, non-reduced catalyst

[2] Space Time Yield (STY) = $\dfrac{VHSV}{22.4}$ x $\dfrac{\text{% CO in Feed}}{100}$ x $\dfrac{\text{% CO Conv.}}{100}$ x $\dfrac{\text{% Selectivity to Oxygenates}}{100}$

[3] Defined as $T = T_{eq} - T_{avg}$

where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

T_{avg} = average observed bulk-phase reaction temperature

TABLE 5.1.3-17 SUMMARY FOR RUN 213- 4 B (24- Sept-80)

CATALYST NO. 197-85   ATOMIC FORMULA $CuZn_{0.125}CoTh_{0.5}Fe_{0.1}K_{0.11}$

PREP. METHOD Coprecipitaion of Metal nitrates w/KOH, Calcined at 450°C for 3 hrs.

SURFACE AREA[1] _____ m^2/gm FEED H_2/CO 2.1 CO_2 4.8 Vol%

BULK DENSITY[1] 1.04 _____ gm/cc

TEST NO.	-1	-2	-3	-4*		
Avg. Temp., °C	263	263	245	267		
Hot Spot, °C	263	263	245	267		
Pressure, psig	910	905	910	920		
VHSV, L/hr/kgm cat.	3574	1092	3262	3763		
Hrs. on Stream	3.7	6.3	11.6	18.1		

CONVERSION

	-1	-2	-3	-4*		
CO, Vol%	18.0	55.9	5.2	13.5	(11.1 MeOH Conv.)	
CO, gm mol/hr/kgm cat.	7.60	7.21	2.09	5.06	(1.36 MeOH Conv.)	
STY of Oxygenates[2] gm mol/hr/kgm cat.	1.91	1.28	0.59	0.866		

NORMALIZED CARBON SELECTIVITY, vol %

	-1	-2	-3	-4*		
CH_3OH	3.9	3.0	6.4	--		
C_2-C_6 Alcohols	17.0	13.0	17.3	12.4		
C_1-C_6 Aldehydes	4.2	1.8	4.2	1.1		
C_4-C_9 H.C.	11.3	7.4	6.7	5.9		
CH_4	17.4	22.1	22.4	30.3		
C_2+C_3 H.C.	22.2	16.6	21.2	17.8		
CO_2	24.0	36.1	21.8	32.5		

APPROACH TO[3] WGS EQUILIBRIUM, °C						
CARBON ACCOUNTABILITY, %	103.0	102.9	105.9	97.9		

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[1] Fresh, non-reduced catalyst

[2] Space Time Yield (STY) = $\frac{VHSV}{22.4}$ x $\frac{\% \text{ CO in Feed}}{100}$ x $\frac{\% \text{ CO Conv.}}{100}$ x $\frac{\% \text{ Selectivity to Oxygenates}}{100}$

[3] Defined as $T = T_{eq} - T_{avg}$

where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition

T_{avg} = average observed bulk-phase reaction temperature

* 7 mol % MeOH added to feed gas   -40-

5.1.4 Analysis of Results

The maximum selectivity to alcohol-fuel component observed during the tests made this quarter was obtained with a $CuCoZn_{0.125}Fe_{0.1}Th_{0.5}K_{0.11}$ catalyst produced by evaporation of metal nitrate-citric acid solutions. Selectivity to C_1-C_6 oxygenates was about 50% (CO_2-free, carbon basis) at total CO conversions of the order of 5 to 15% per pass. The distribution of oxygenates by carbon number was as follows:

	Alcohols	Aldehydes	Total
C_1	48.2	0	48.2
C_2	33.0	0.43	33.4
C_3	10.6	0.07	10.7
C_4	5.0	0.34	5.3
C_5	1.3	1.04	2.3
C_6	0	0	0
Total	98.1	1.88	100.0

Some relevant correlations were observed for this and other catalysts tested. These correlations are illustrated in plots of the conversion vs. selectivity characteristics shown on Figures 5.1.4-1 through 5.1.4-6. In all cases, oxygenates selectivity notably decreases as total CO conversion per pass increases. The rate of the selectivity decrease does however vary with catalyst composition and catalyst production methods.

Figure 5.1.4-1 shows the effect of catalyst preparation method on the conversion-selectivity relationship. At the lower CO conversion levels, the evaporation method results in a significant increase in oxygenates selectivity over that of the KOH coprecipitation method. We plan to also test this formulation produced by a Na_2CO_3 coprecipitation method. The latter is the preferred method for the preparation of both present-day commercial methanol synthesis catalysts and of the cobalt/thoria-based F-T catalysts produced prior to WW II.

FIGURE 5.1.4-1

CONVERSION SELECTIVITY CHARACTERISTICS

EFFECT OF PREPARATION METHOD
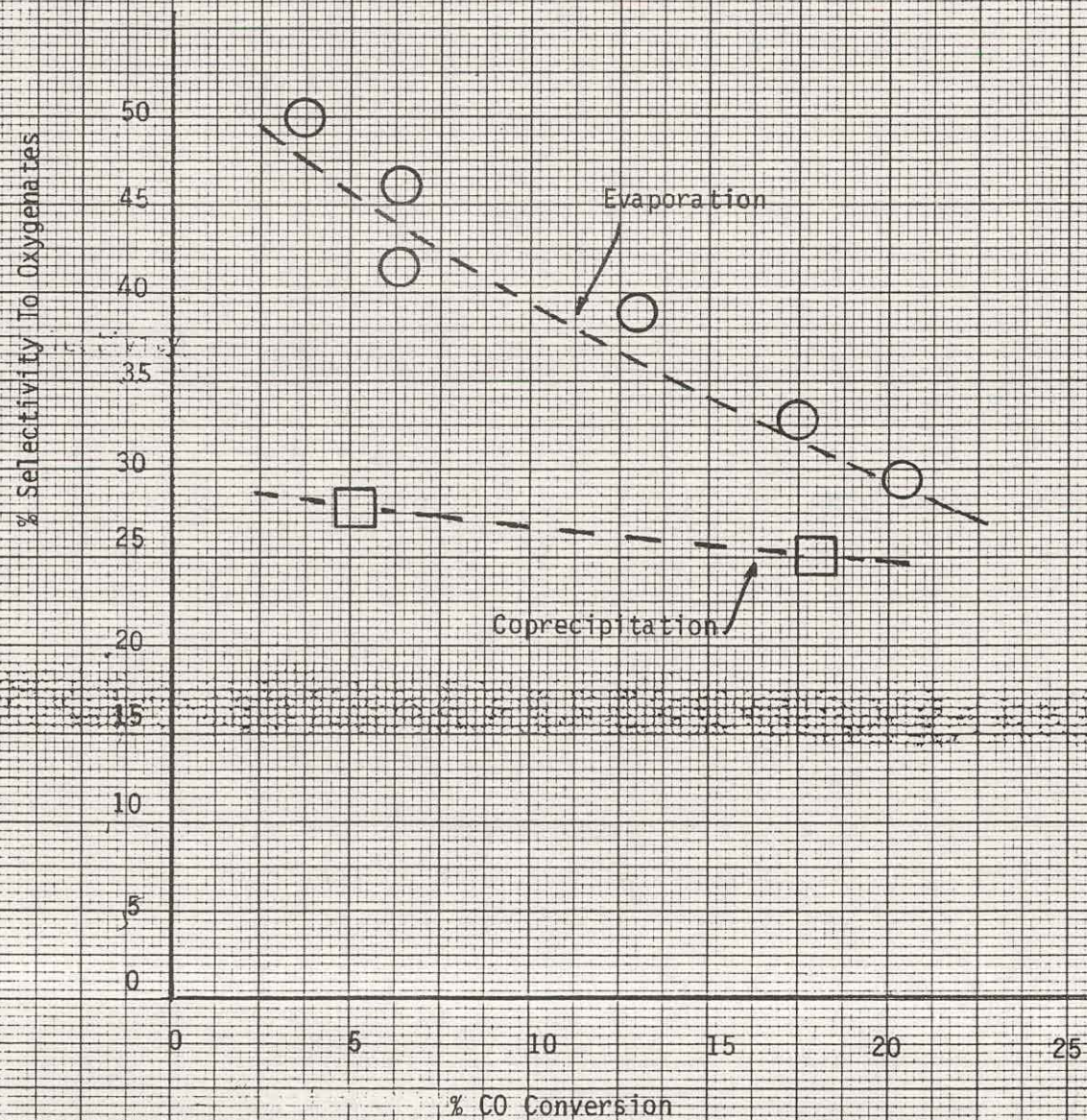
ON THE CATALYST FORMULATION $CuZn_{0.125}CoTh_{0.5}Fe_{0.1}K_{0.11}$

Figure 5.1.4-2 shows the effect of different transition metal types in a $CuZn_{0.125}CoK_{0.11}M$ formulation. Catalysts having an atomic formula of $CuZn_{0.125}CoK_{0.11}M$ have oxygenates selectivity varying with transition metal type according to the following series (in order of decreasing selectivity):
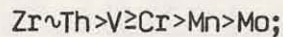
$$Zr \sim Th > V \gtrsim Cr > Mn > Mo;$$

Figure 5.1.4-3 shows the effect of supporting a $CuZn_{0.125}CoTh_{0.5}Fe_{0.5}K_{0.11}$ formulation on a manganese oxide (MnO) support. MnO as a support results in a strong metal-support interaction (SMSI) and one of the characteristics of SMSI catalysts is their poor ability to chemisorb hydrogen[9]. This means that SMSI catalysts have a lower activity for hydrogenation. Although the unsupported $CuZn_{0.125}CoTh_{0.5}Fe_{0.5}K_{0.11}$ formulation was very active as regards CO reactivity and space time yield of oxygenates, a high selectivity to C_2+ hydrocarbons was observed. It is believed that this was a result of the high hydrogenation activity of the thorium/iron constituents of the catalyst which might be reduced by incorporating a poor hydrogen chemisorber into the catalyst system. However, as can be seen from the figure, oxygenates selectivity is essentially independent of the incorporation of MnO into the catalyst. However, MnO did appear to accelerate the activity of the methanation reaction as observed by the 100% increase in methane selectivity over the range of 35-50% CO conversion.

Figure 5.1.4-4 shows the effect of iron/copper ratio in a $CuZn_{0.125}CoTh_{0.5}K_{0.11}Fe_x$ catalyst over the range 0 to 0.5/1. There appears to be a small effect of iron/copper ratio on oxygenates selectivity with an observed maxima in the relationship between Fe/Cu ratio and oxygenates selectivity. A cross-plot of Fe/Cu ratio vs. oxygenates selectivity at about 25% CO conversion per pass (see Figure 5.1.4-5) shows the broad maxima occurring between about 0.1 and 0.25 Fe/Cu ratio. At higher CO conversions, increasing the Fe/Cu ratio to a value as high as 0.5/1 appears to reduce the oxygenates selectivity relative to that of a catalyst with lower iron content.

FIGURE 5.1.4.2
CONVERSION/SELECTIVITY CHARACTERISTICS

EFFECT OF DIFFERENT TRANSITION METALS IN THE FORMULATION CuZnO.125CoMK0.11
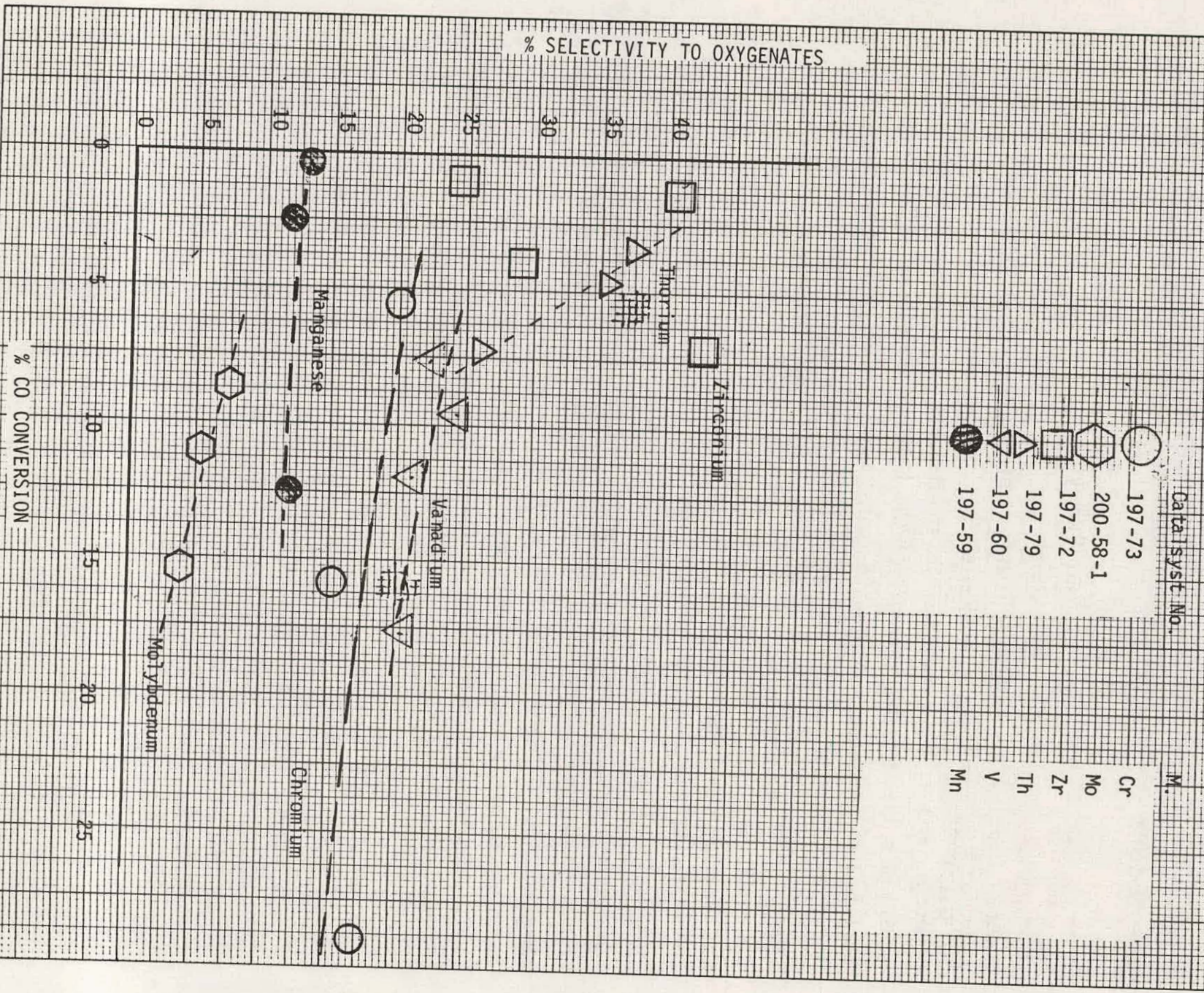
FIGURE 5.1.4-3
CONVERSION-SELECTIVITY CHARACTERISTICS
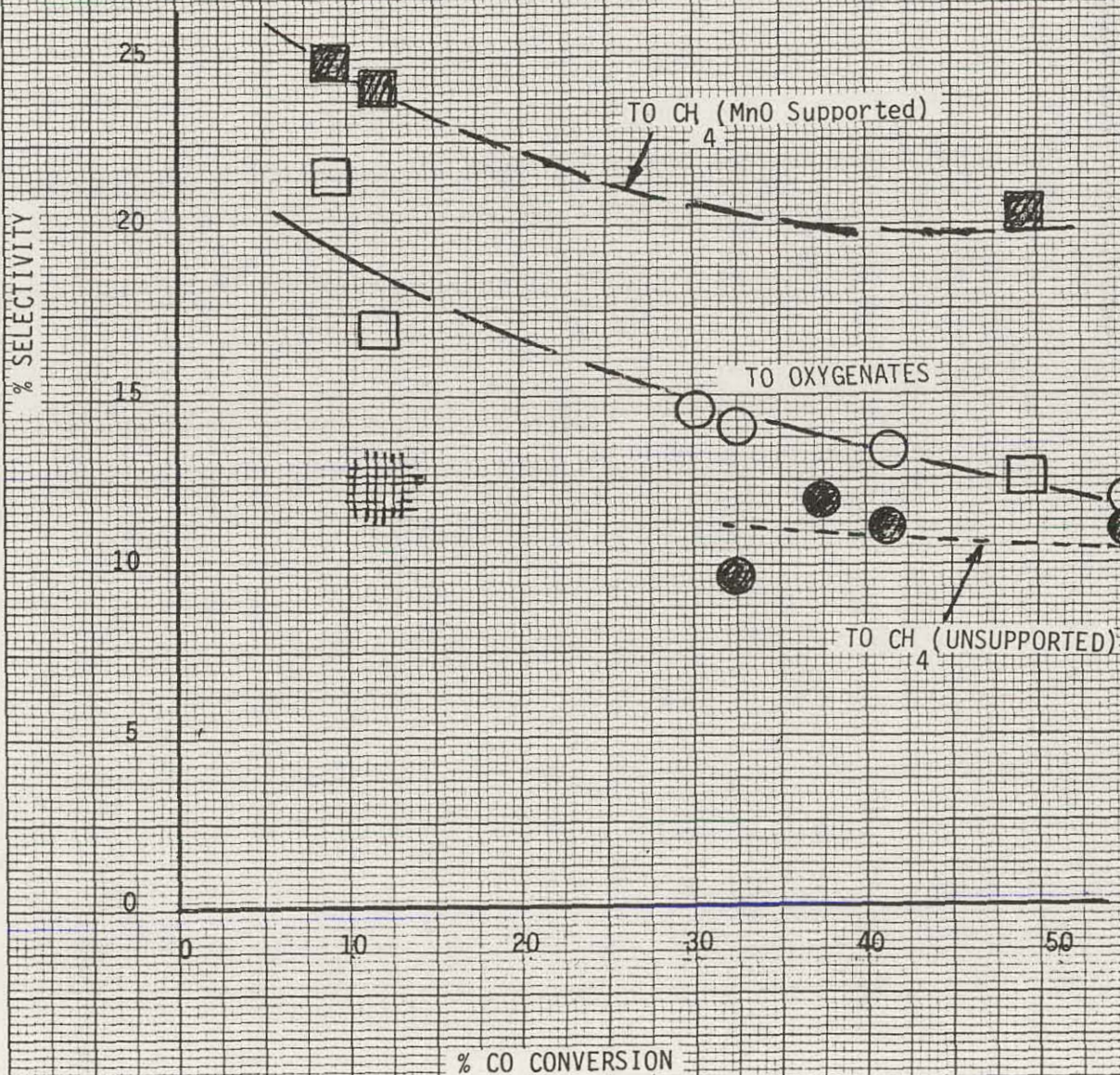EFFECT OF MnO SUPPORT ON THE CATALYST FORMULATION $CuZn_{0.125}CoTh_{0.5}CeFe_{0.5}K_{0.11}$

FIGURE 5.1.4-4

CONVERSION - SELECTIVITY CHARACTERISTICS

EFFECT OF Fe LEVEL ON THE CATALYST FORMULATION $CuZn_{0.125}CoTh_{0.5}Fe_xK_{0.11}$
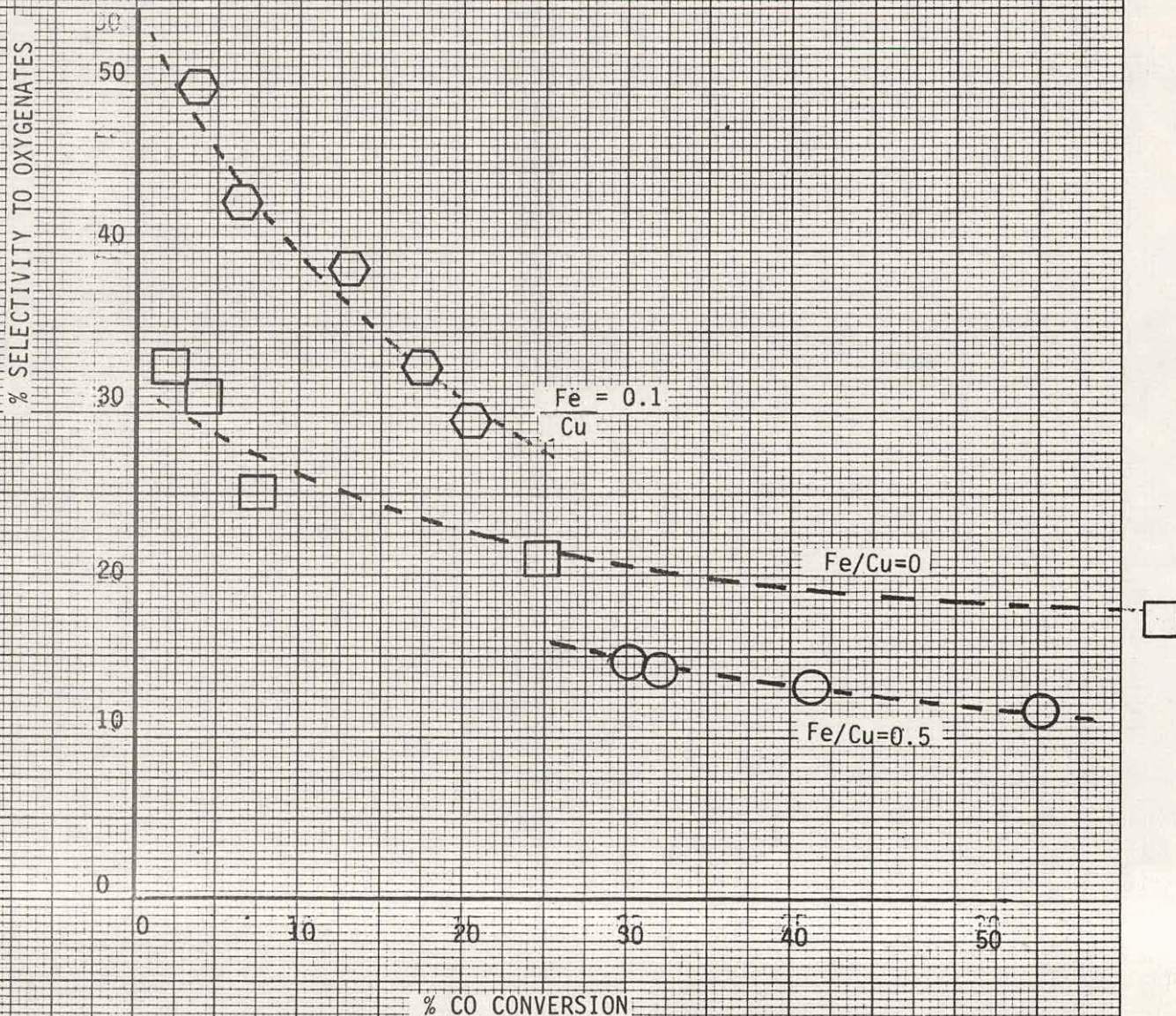
FIGURE 5.1.4-5
CONVERSION-SELECTIVITY CHARACTERISTICS
Effect of Fe/Cu Ratio in a $CuZn_{0.125}CoTh_{0.5}K_{0.11}Fe_x$ Catalyst

BASIS: 25% CO Conversion Per Pass
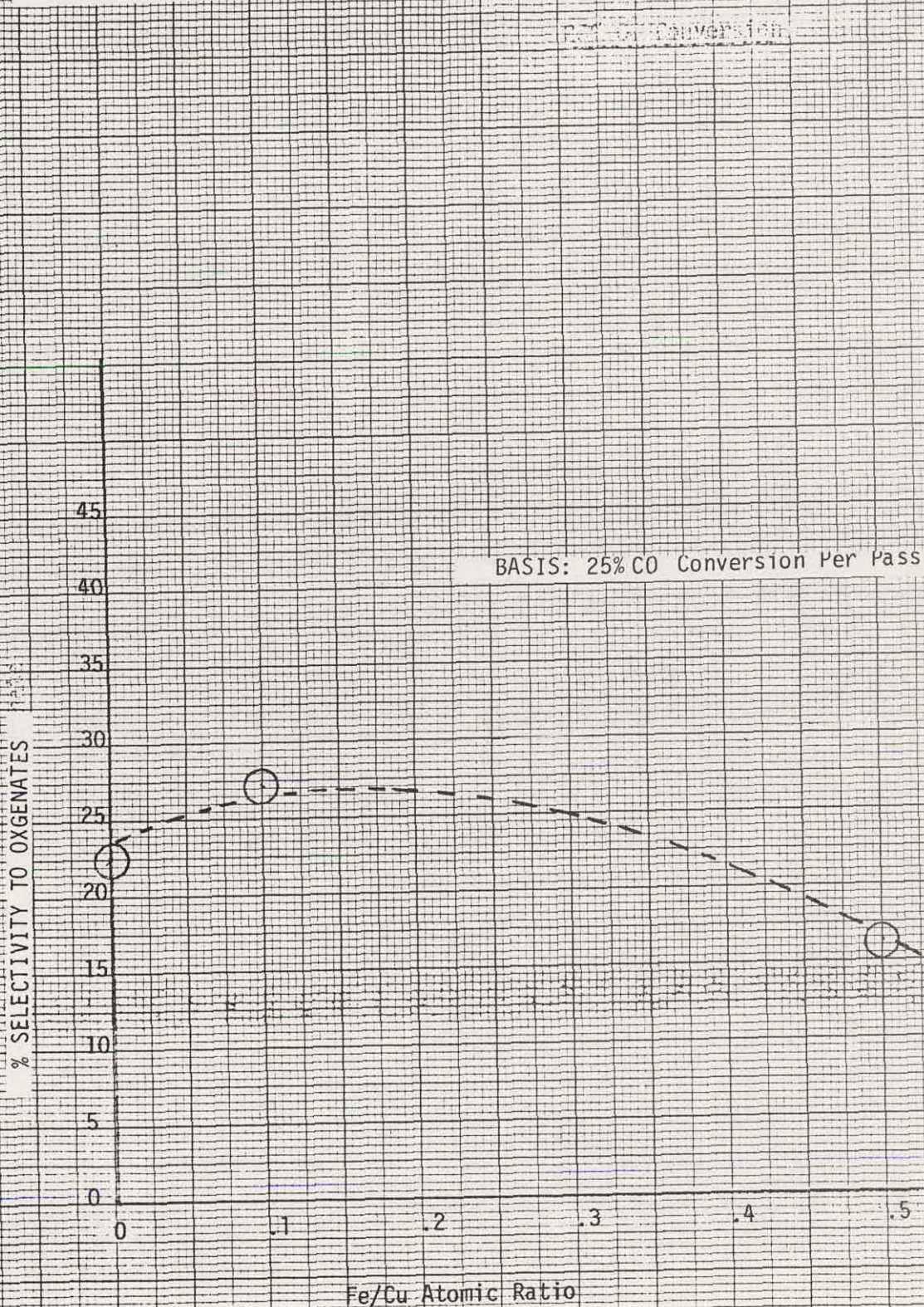
% SELECTIVITY TO OXGENATES

Fe/Cu Atomic Ratio

Figure 5.1.4-6 shows the effect of chromium/copper ratio in a $CuZn_{0.125}CoK_{0.11}Cr_x$ type catalyst over the range of 0 to 1/1. There appears to be essentially no effect of the chromium/copper ratio on oxygenates selectivity over the range investigated.

During the course of the Task 1 studies, it was hypothesized that higher alcohols (C_2+) formation might be accelerated if a sufficient quantity of methanol was allowed to chemisorb on a catalyst formulation that shows some homologation activity. Therefore, an equal mixture by weight of commercial methanol synthesis catalyst and $CuZn_{0.125}CoTh_{0.5}Fe_{0.5}K_{0.11}$ catalyst produced by KOH coprecipitation was tested in both the plug-flow and Berty reactors. The first-stage zone of the plug-flow reactor contained the methanol synthesis catalyst followed by the higher alcohols catalyst in the second-stage. In the Berty reactor, a random mixture of the two catalysts was used. The objective of these tests was to determine the effect of methanol generated in situ by the methanol synthesis catalyst. The plug-flow reactor operation was limited by exothermic heat removal resulting from the high activity of the methanol synthesis catalyst and therefore could not be operated beyond 210^OC. At this low temperature, the second-stage higher alcohols catalyst was essentially inactive. In the Berty reactor, reactor operation was not temperature-limited and high conversions to methanol were observed. However, little homologation activity was observed. Any water of hydrogenation produced by the higher alcohols catalyst reacted with CO to yield CO_2 via the water-gas shift reaction, the latter being catalyzed by both the methanol synthesis catalyst as well as the higher alcohols catalyst.

During one test condition with a $CuZn_{0.125}CoFe_{0.1}Th_{0.5}K_{0.11}$ catalyst prepared by KOH coprecipitation, methanol was co-fed with the syn gas (at 7 mol%) to simulate methanol recycle and measure the homologation activity of this formulation. Total carbon (methanol carbon plus   CO   carbon)   conversion

FIGURE 5.1.4-6

CONVERSION-SELECTIVITY CHARACTERISTICS

Effect of Cr level in catalyst formulation: $CuZn_{0.125}COCr_xK_{0.1}$

KEY

Cat No.	X
197-73	1
197-78	0.125
200-25-1	0
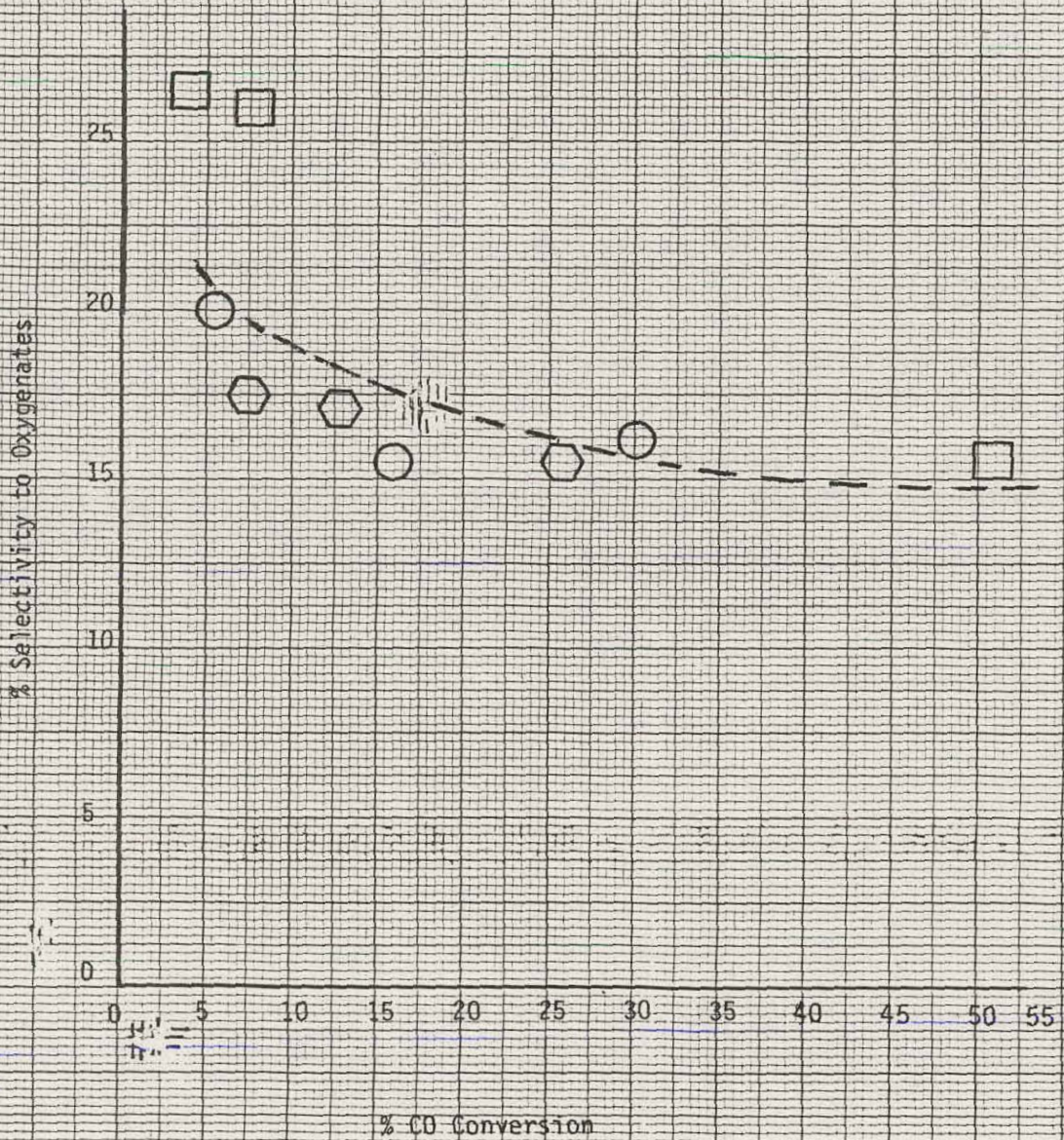
was approximately constant but the methane/higher alcohols ratio increased from 0.8/1 to about 2.3/1 as seen below:

MeOH Content of Feed Gas, Mol %	7	0
Equivalent CO Converted, gmol/hr/kg cat.	6.4	7.6
% Selectivity to CH_3OH	--	4
% Selectivity to C_2-C_6 Oxygenates	13	21
% Selectivity to CH_4	30	17
% Selectivity to C_2 + HC	24	34
% Selectivity to CO_2	33	24

5.2 Task 2: Process Variable Studies in BSU

No work was performed on this task during the reporting period.

5.3 Task 3: Engineering Studies & Economic Analyses

No work was performed on this task during the reporting period.

5.4 Task 4: Performance Studies in PDU

No work was performed on this task during the reporting period.

6.0 PATENTABLE INVENTIONS

No patentable inventions were conceived during this quarterly period.

7.0 REFERENCES

(1)   G.B. Patent 2,037,179, July 9, 1980

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(4)   Joyner, J. Catal. 50, 176 (1977)

(5)   Ponec, Catal. Rev. - Sc. Eng. 18, 151 (1978)

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(7)   Herman, Klier et al. J. Catal. 56, 407 (1979)

(8)   Sherokov, V.G. Kirillov, I.P. & S.P. Kochethov, Proceedings of First Intl. Symposium on the Preparation of Heterogeneous Catalysts, Brussels, (Oct. 14-17, 1975)

(9)   Kugler, E.L., "Synthesis of Light Olefins from CO and H_2", ACS Div. Pet. Chem. Symposium, San Francisco (Aug. 24-29, 1980)