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DOE/ET/14858-3

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

Third Quarterly Progress Report for Period April 1—June 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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THIRD QUARTERLY PROGRESS REPORT

APRIL 1 - JUNE 30, 1980

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

December 3, 1980

SUBMITTED TO:

U.S. DEPARTMENT OF ENERGY
COAL LIQUEFACTION PROJECT MANAGEMENT
PITTSBURGH ENERGY TECHNOLOGY CENTER
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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 third quarterly report presents the experimental work performed for the period of April 1 - June 30, 1980. Some of the accomplishments made this quarter during the Task 1 screening studies were:

1. A total of fourteen catalysts were prepared by either evaporation of metal nitrate-citric acid solutions or by impregnation of inert supports with metal nitrate-citric acid solutions.
2. A total of fourteen 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 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 metals such as Fe, Mn, Ti, Th, etc.
Group V: Catalysts of Groups I, II or IV supported on refractory cements such as silica or titania.

3. Although none of the catalysts tested this quarter resulted in reaching the targetted oxygenates selectivities and space time yields, the following relevant observations were made:

a) Transition metals in a catalyst having the general atomic formula $CuZn_{.125}CoK_{0.1}M$ and produced by evaporation of metal nitrate - citric acid solution affect oxygenates selectivity as indicated below (in descending order):

- b) Potassium in a catalyst having the formula $\text{Cu Zn}_{.125}\text{CoA}_{0.11}$ is a better alkali promoter than cesium;
- c) Impregnation of inert supports with metal nitrate - citric acid solutions reduced activity and oxygenates productivity in comparison to the unsupported catalyst;
- d) Mechanical blending of metal oxides for a $\text{CuZn}_{.125}\text{CoCrK}_{0.11}$ results in better selectivity-conversion characteristics than coprecipitation or evaporation of nitrate-citric acid solutions. A clue to attaining higher oxygenates selectivity may rest in the fact that discrete metal/metal oxide phases, as provided by the mechanical blending method, may be more desirable than uniformly dispersed systems;
- e) For a $\text{CuZn}_{.125}\text{CoCrK}_{0.11}$ catalyst reduced in situ in the presence of CO and CO_2 - containing syn gas, there was more than a two-fold increase in oxygenates selectivity over the 43 hour run period. Another clue to attaining higher oxygenates may rest in the fact that longer-term activation periods may be required.

Plans for the next quarter include the further study of catalyst production and finishing methods for a $\text{CuZn}_{.125}\text{CoCrK}_{.11}$ -type catalyst and a scan of atomic ratios of Fe, Co and Th in a $\text{CuZn}_{.125}\text{K}_{0.11}\text{Co}_x\text{Th}_y\text{Fe}_z$ -type catalyst.

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 fourteen catalysts were prepared, three by impregnation of catalyst supports and the remaining eleven by evaporation of metal nitrate solutions. All catalysts were calcined and pelletized.

A total of fourteen catalysts were tested including eight catalysts tested in the Berty reactor and the remaining six tested in 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 metals such as Fe, Mn, Ti, Th, etc.
- Group V: Catalysts of Groups I, II or IV supported on refractory cements such as silica or titania.

Although none of the catalysts tested this quarter resulted in reaching the targetted oxygenates selectivities and space time yields, some relevant observations were made:

Transition metal elements incorporated into a catalyst having the general atomic formula $\text{CuZn}_{0.125}\text{CoK}_{0.11}\text{M}$ and produced by evaporation of metal nitrate-citric acid solutions affect oxygenates selectivity as indicated below (in descending order):

Varying the zinc/copper ratio from 0.125/1 to 0.5/1 in the above formulation in which chromium is the transition metal promoter has little or no effect on the oxygenates selectivity.

Potassium as an alkali promoter in a Group II type catalyst ($\text{CuZn}_{.125}\text{CoA}_{0.11}$) results in about a 20-40% improvement in oxygenates selectivity over that of cesium.

Supporting a $\text{CuZn}_{.125}\text{CoCrK}_{0.11}$ catalyst produced by evaporation of metal nitrate-citric acid solutions on inert supports such as titania or silica gel results in lower CO conversion rates and lower space time yields of oxygenates than those of the unsupported catalyst. The silica-supported catalyst showed apparent high activity and higher oxygenates productivity than that of the titania-supported catalyst.

One surprising observation was that the activity and oxygenates selectivity of a $\text{CuZn}_{.125}\text{CoCrK}_{0.11}$ catalyst produced by the mechanical blending of the oxides was comparable to or even higher than that of catalysts produced by coprecipitation or by evaporation. Metal oxides produced by calcination of either coprecipitated or evaporated catalysts are dispersed better than those prepared by mechanical blending of oxides. This may suggest that discrete metal/metal oxide phases in the finished catalyst may be more desirable in promoting the production of oxygenates than uniformly dispersed systems.

3.2 Task 2 - Process Variable Studies in BSU

No work has been performed on these tasks during the present reporting period.

3.3 Task 3 - Engineering Studies & Economic Analyses

No work has been performed on these tasks during the present reporting period.

3.4 Task 4 - Performance Studies in PDU

No work has been performed on these tasks during the present reporting period.

4.0 WORK PLANNED FOR NEXT QUARTER

Task 1: Catalyst Formulation and Screening Studies

Testing will continue and consist of the study of catalyst production methods when using a catalyst formulation having the atomic composition $\text{CuZn}_{0.125}\text{CrCoK}_{0.11}$. The following parameters will be investigated:

1. Effect of pelletizing pressure.
2. Effect of coprecipitation with KOH at conditions of controlled pH followed by controlled aging of the precipitated hydroxides.
3. Testing of slurry phase reaction with coprecipitated catalyst.

A scan of atomic ratios of Fe, Co and Th in the catalyst formulation having the atomic formula $\text{CuZn}_{0.125}\text{K}_{0.11}\text{Co}_x\text{Th}_y\text{Fe}_z$ and produced by the KOH-precipitation method will be made as per the table below:

<u>x</u>	<u>y</u>	<u>z</u>
1.0	1.0	0.0
1.0	0.5	0.1
1.0	0.75	0.1
1.0	0.75	0.1
0.50	0.75	0.1
0.125	0.75	0.1
0.0	0.75	0.1

An additional test will be made to study the effect of supporting a $\text{CuZn}_{0.125}\text{CoFe}_{0.5}\text{Th}_{0.5}\text{K}_{0.11}$ (#200-27-2 tested during the 2nd quarter) catalyst on a poor hydrogen chemisorption support such as manganese oxide.

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

A meeting was held with Institut Francaise du Petrole (IFP) to discuss IFP's developments in the area of catalysts and processes for making alcohol-based, synthetic motor fuels. Since 1970, IFP has been interested in the upgrading of synthesis gas towards the development of an integrated process to produce C_1 - C_5 alcohols which can be used as motor fuel blending component.

The IFP process is described in the attached diagram (Figure 5.1.1-1). Synthesis gas is compressed to a pressure of 60-100 bars and is then sent to a higher alcohols synthesis reactor where 15-20% of the gas is transformed. The unreacted synthesis gas is not recycled but sent to the methanol synthesis unit. The reaction product (alcohols and water) is sent to the separation section, where water is removed from the mixture, so that the alcohols (C_1 - C_5) can subsequently be mixed with the methanol produced in the methanol unit. If an increased production of higher alcohols is required, at least a fraction of the methanol and the ethanol, is recycled to the heavy alcohols synthesis reactor. As a consequence of this recycling, the unwanted methanation reaction will be greatly reduced. IFP's economic evaluation shows that, due to the fact that the synthesis gas is not recycled through the higher alcohols section, this process has the potential to produce a cheap mixture of alcohols suitable for use as a gasoline blending component.

One interesting point made by IFP is that their methanol and higher alcohols catalysts are not pelletized but are made as spheroid droplets that have a certain size distribution that can be altered. They saw no problems in making a slurry catalyst in the 20 to 100 micron range. IFP also mentioned that they had applied for a patent that combined the production of methanol and higher alcohols.

FIGURE 5.1.1-1

5.1.2 Experimental Procedures

5.1.2.1 Modifications To Gas Chromatographic Analyses

Improvements were made to the existing GC system thereby resulting in much better carbon closures. The modification in the analytical system has resulted in providing more reliable values of the non-condensable components (CO , CO_2 , CH_4 , H_2 , Ar) in the effluent stream. However, it is important to mention that in the case of low CO conversion, the calculated selectivities depend on the accuracy of determination of very minor components. The amount of these components in the effluent sometimes drop below the accuracy range and much significance should not be placed on the corresponding selectivity values.

Old System:

The old system consisted of two on-line, GC analyses. A schematic of the old system is given in Figure 5.1.2.1-1. The main disadvantage of this system is that only the non-condensable gases get injected into the Carle-GC. This makes it difficult to close the carbon balance of the effluent gas, due to the removal of the condensables via a cold trap on the inlet line. The small amount of condensables is hard to account for accurately. The calculation of non-condensable gases in this case depends mainly on the use of argon as an internal standard.

Revised System:

The new on-line system consists of a branched slip effluent stream feeding the:

- a) FID GC (H.P. 5720A), for product analysis (alcohols, aldehydes, alkanes and esters) and the
- b) Carle 311-TC GC equipped with a back-flush valve to avoid contamination by higher boiling components. At the same time, the whole effluent sample is injected and a cold trap is not needed on the inlet line. A schematic for the new system is given in Figure 5.1.2.1-2 with a typical chromatogram shown in Figure 5.1.2.1-3. The new system gives more reliable and accurate results.

FIGURE 5.1.2.1-1

OLD ANALYTICAL SYSTEM

FIGURE 5.1.2.1-2 - REVISED ANALYTICAL SYSTEM

FIGURE 5.1.2.1-3

Typical Chromatogram Obtained
With Revised Analytical System

NAME	CONC	RT	AREA	KF
METHANE	6.371	38	3587545	♦ 563
ETHYLENE	.135	70	106600	F 786
ETHANE	.681	82	776976	L 1140
PROPYLENE	.476	182	338672	F 712
PROPANE	.132	195	230695	> 1742
METHANOL	.733	246	384337	S 524
ACET ALD	.019	304	11416	\ 614
BUTYLENE	.039	391	89839	F 2302
N-BUTANE	.044	417	92917	F 2110
ETHANOL	.65	451	685669	S 1054
PROP ALD	.004	573	5512	Y 1229
ME ACETAT	.026	597	17279	Y 665
PENTENE	.015	657	70049	Y 4665
N-PENTANE	.008	684	38751	Y 4630
N-PROP DL	.148	729	234912	Y 1585
ET ACETAT	.008	861	11037	Y 1370
ME PROPIO	.025	889	26192	Y 1038
HEXENE	.005	915	26041	Y 5518
N-HEXANE	.005	943	26501	Y 5701
N-BUT DL	.034	1005	79671	Y 2350
PENT ALD	.006	1102	16680	Y 2800
HEPTENE	.006	1141	38717	Y 6718
N-HEPTANE	.002	1204	15071	Z 6718
N-PENT DL	.007	1337	20589	(2800
HEX ALD	.003	1481	11224	(3187
N-OCTANE	.002	1625	17978	(8201
N-HEX DL	.002	1950	7393	(3187
N-NONANE	<.001	2125	4753	< 9280
TOTALS	9.578		6973016	

5.1.2.2 Catalyst Preparation

During the 3rd quarterly reporting period, a total of fourteen catalysts were prepared, three by impregnation of catalyst supports and the remaining eleven by evaporation of metal nitrate solutions. The calculated atomic compositions of each catalyst made are shown in Table 5.1.2.2-1. The general preparation procedure is described below:

1. Preparation of Metal Salt Solutions

Table 5.1.2.2-2 summarizes the amounts and types of metal salts used to prepare the catalyst solutions. The nitrate salt was used in most cases because of its high solubility in water. In some cases, such as with vanadium, titanium, zirconium and molybdenum, salts other than the nitrates were used primarily because of availability of the specific reagent. Alkali was added as either potassium nitrate or potassium carbonate. Citric acid monohydrate was added as a complexing agent (except for catalyst 197-61) to the well stirred, metal salt solution. The solutions were slowly evaporated until foaming and/or NO_2 evolution was observed. The resulting mixture was then transferred to a Pyrex pan and dried in an oven at 125°C .

2. Catalyst Finishing

The dried cake which resulted from the oven drying was then transferred to a calcining furnace. Calcination temperature program was arbitrarily controlled to result in a 50°C increase per half-hour, 3 hour hold time at maximum temperature, 125°C per hour cooldown. A typical profile is shown in Figure 5.1.2.2-1 in which the maximum temperature is 450°C . Calcined catalyst was removed from the oven and ground in a mortar and pestle with 3 wt% Sterotex to produce a -30 mesh powder. The powder was then pelletized into 3/16" x 1/8" pellets using a Stokes single-pellet press. The calcined and pelletized catalyst was recalcined at 350°C for 8 hours to burn off the Sterotex. Details of the catalyst finishing steps are shown in Table 5.1.2.2-3.

FIGURE 5.1.2.2-1

TABLE 5.1.2.2-1

CALCULATED ATOMIC COMPOSITIONS

<u>Catalyst No.</u>	<u>Atomic Formula</u>	<u>Prep. Method</u>
197-59	$\text{CuZn}_{0.125}\text{CoMnK}_{0.11}$	Evaporation*
197-60	$\text{CuZn}_{0.125}\text{CoVK}_{0.11}$	Evaporation
197-61	$\text{CuZn}_{0.125}\text{CoTiK}_{0.11}$	Evaporation
197-65	$\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$	Impregnation on SiO_2
197-66	$\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$	Impregnation on TiO_2
197-67	$\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$	Impregnation on TiO_2
197-68	$\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$	Evaporation
197-69	$\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$	Evaporation
197-70	$\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$	Evaporation
197-71	$\text{CuZn}_{0.125}\text{CoFe}_{0.1}\text{Th}_{0.5}\text{K}_{0.11}$	Evaporation
197-72	$\text{CuZn}_{0.125}\text{CoZrK}_{0.11}$	Evaporation
200-57-1	$\text{CuZn}_{0.125}\text{CoFe}_{0.1}\text{K}_{0.11}$	Evaporation
200-57-2	$\text{CuZn}_{0.125}\text{CoFe}_{0.5}\text{K}_{0.11}$	Evaporation
200-58-1	$\text{CuZn}_{0.125}\text{CoMoK}_{0.11}$	Evaporation

*of metal nitrate-citric acid solutions

TABLE 5.1.2.2-2

COMPOSITION OF SALTS USED DURING FIRST STEP OF CATALYST PREPARATION

Catalyst No.	197 -59	197 -60	197 -61	197 -65	197 -66	197 -67	197 -68	197 -69	197 -70	197 -71	197 -72	200- 57-1	200- 57-2	200- 58-1
Salt	Weight in Grams													
$\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	116	78	116	121	121	121	241	241	121	91	121	121	121	121
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	19	13	19	19	19	19	37	37	19	14	19	19	19	19
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	146	98	146	146	146	146	291	291	146	110	145	146	146	146
$\text{Cr}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$				200	200	200	400	400	200					
$\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$										15		20	101	
$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	126													
$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$										104				
Vanadyl Acetate		65												
Titanium dipropoxide lactate			104											
Zirconium Acetate											246			
$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$														88
KNO_3	6	4	6							4		6	6	6
$\text{K}_2\text{CO}_3 \cdot 1 \frac{1}{2} \text{H}_2\text{O}$				4	4	4	9	9	4		5			

TABLE 5.1.2.2-3

CATALYST FINISHING DATA

Catalyst No.	197 -59	197 -60	197 -61	197 -65	197 -66	197 -67	197 -68	197 -69	197 -70	197 -71	197 -72	200- 57-1	200- 57-2	200- 58-1
Citric Acid Complexing Agent Used, gm	31	31	0	30	30	30	60	60	30	11	15	31	31	31
Calcination Temp., °C	450	450	450	450	450	450	350	450	450	450	450	450	450	450
Catalyst Support (1)	No	No	No	Silica Gel	Titania	Titania	No	No	No	No	No	No	No	No
% Catalyst	--	--		30	55	25	--	--	--	--	--	--	--	--
% Support	--	--		70	45	75	--	--	--	--	--	--	--	--
Particle Size	3/16" x 1/8" → 8x12 Mesh → -30 Mesh → 3/16" x 1/8" →													

(1) Supported catalysts were prepared by impregnation of the support with the metal nitrate-citric acid solution.

5.1.3 Experimental Results

A total of fourteen catalysts were tested during the third quarter including eight catalysts tested in the Berty reactor and the remaining six tested in the plug-flow reactor. These catalysts (see Table 5.1.3-1) have been characterized 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 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 metals such as Fe, Mn, Ti, Th, etc.
- Group V: Catalysts of Groups I, II or IV supported on refractory cements such as silica or titania.

Test results for the fourteen catalysts are summarized in Tables 5.1.3-2 through 5.1.3-15. Some of those catalysts tested were prepared in the previous quarter and the respective catalyst preparations were described in the Second Quarterly Progress Report.

TABLE 5.1.3-1

SUMMARY OF CATALYSTS TESTED

<u>Run No.*</u>	<u>Catalyst Number</u>	<u>Calculated Composition</u>
<u>Group I: Catalysts Containing Cu, Zn, Cr, Co and Alkali</u>		
201-51B	197-57	$\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$
201-56B	197-48	$\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$
201-58P	197-36	$\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$
201-67B	197-2	$\text{CuCoCrZn}_{0.125}\text{K}_{0.11}$
201-62B	197-16	$\text{CuZn}_{0.5}\text{CoCrK}_{0.11}$
<u>Group II: Catalysts of Group I Without Zn or Co or Cr</u>		
201-48B	197-1	$\text{CuCoCr}_{0.8}\text{K}_{0.09}$
201-60P	200-25-1	$\text{CuZn}_{0.125}\text{CoK}_{0.11}$
201-65P	200-27-1	$\text{CuZn}_{0.125}\text{CoCs}_{0.11}$
<u>Group III: Modified Methanol Synthesis Catalysts</u>		
None tested this quarter		
<u>Group IV: Catalysts of Group I Without Cr and Containing Transition Metals</u>		
201-54P	200-32	$\text{CuZn}_{0.125}\text{CoCe}_{0.14}\text{Mn}_{0.14}\text{In}_{0.14}$ $\text{Th}_{0.14}\text{Fe}_{0.14}\text{V}_{0.14}\text{Ti}_{0.14}\text{K}_{0.11}$
201-72P	197-59	$\text{CuZn}_{0.125}\text{CoMnK}_{0.11}$
201-77P	197-60	$\text{CuCoZn}_{0.125}\text{VK}_{0.11}$
201-80B	200-57-1	$\text{CuCoZn}_{0.125}\text{Fe}_{0.1}\text{K}_{0.11}$
<u>Group V: Supported Catalysts</u>		
201-79B	197-66	55% $\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$ /45% TiO_2
201-74B	197-65	30% $\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$ /70% SiO_2

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

Table 5.1.3-2
SUMMARY FOR RUN 201-48B (4-22-80)

CATALYST NO.	197-1	ATOMIC FORMULA					CuCoCr _{0.8} K _{0.09}
PREP. METHOD	Evaporation of nitrates-citric acid; Calcined at 450°C for 3 hrs.						
SURFACE AREA ⁽¹⁾	27.0	m ² /gm	FEED H ₂ /CO	2.0	CO ₂	13.5	Vol%
BULK DENSITY ⁽¹⁾	1.46	gm/cc					
TEST NO.	-2	-3	-8	-9			
Avg. Temp., °C	258	259	257	257			
Hot Spot, °C	258	259	257	257			
Pressure, psig	920	920	1190	1485			
VHSV, L/hr/kgm cat.	2679	700	3596	4322			
Hrs. on Stream	6.5	8.6	19.0	20.8			
CONVERSION							
CO, Vol%	5.7	22.3	3.2	2.4			
CO, gm mol/hr/kgm cat.	1.72	1.76	1.30	1.17			
STY of Oxygenates ⁽²⁾							
gm mol/hr/kgm cat.	0.26	0.30	0.36	0.38			
CARBON SELECTIVITY (WT%) NORMALIZED							
CH ₃ OH	7.0	5.9	15.1	19.1			
C ₂ -C ₆ Alcohols	8.0	10.9	13.0	13.4			
C ₁ -C ₆ Aldehydes	~ 0	~ 0	~ 0	~ 0			
C ₄ -C ₉ H.C.	12.9	9.5	10.9	9.4			
CH ₄	27.9	22.7	48.8	46.2			
C ₂ H ₆ , C ₃ H ₈ (LPG)	16.2	12.9	12.2	14.0			
CO ₂	20.1	38.2	0	0			
APPROACH TO ⁽³⁾ WGS EQUILIBRIUM, °C							
CARBON ACCOUNTABILITY, %	72.8	87.3	51.1	69.6			

(1) Fresh, non-reduced catalyst

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

(3) Defined as $T = T_{\text{eq}} - T_{\text{avg}}$

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 Continued
SUMMARY FOR RUN 201-48B (4-22-80)

CATALYST NO.	197-1	ATOMIC FORMULA					Cu	Co	Cr	0.8	K	0.09
PREP. METHOD	Evaporation of nitrates - citric acid; Calcined at 450°C for 3 hrs.											
SURFACE AREA ⁽¹⁾	27.0	m ² /gm	FEED H ₂ /CO	2.0	CO ₂	9.0	Vol%					
BULK DENSITY ⁽¹⁾	1.46	gm/cc										
TEST NO.	-1	-4	-5	-6	-7							
Avg. Temp., °C	258	269	269	269	255							
Hot Spot, °C	258	269	269	269	255							
Pressure, psig	920	920	915	915	1200							
VHSV, L/hr/kgm cat.	3152	2719	677	1345	3570							
Hrs. on Stream	4.1	10.6	12.8	14.5	16.6							
CONVERSION												
CO, Vol%	8.5	6.4	29.5	14.3	3.5							
CO, gm mol/hr/kgm cat.	3.10	2.01	2.31	2.22	1.44							
STY of Oxygenates ⁽²⁾												
gm mol/hr/kgm cat.	0.43	0.38	0.47	0.50	0.30							
CARBON SELECTIVITY (WT%) NORMALIZED												
CH ₃ OH	6.9	9.5	7.3	8.9	13.6							
C ₂ -C ₆ Alcohols	6.9	9.6	12.9	13.6	7.5							
C ₁ -C ₆ Aldehydes	~ 0	~ 0	~ 0	~ 0	~ 0							
C ₄ -C ₉ H.C.	10.9	8.9	5.8	5.8	8.6							
CH ₄	31.9	27.5	24.7	25.7	36.7							
C ₂ H ₆ , C ₃ H ₈ (LPG)	15.0	12.2	11.3	12.0	16.7							
CO ₂	25.8	32.3	38.0	34.0	17.1							
APPROACH TO ⁽³⁾ WGS EQUILIBRIUM, °C												
CARBON ACCOUNTABILITY, %	84.2	91.7	91.8	93.6	59.5							

(1) Fresh, non-reduced catalyst

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

(3) Defined as $T = T_{\text{eq}} - T_{\text{avg}}$

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

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

Table 5.1.3-3
SUMMARY FOR RUN 201-51B (5/2/80)

CATALYST NO.	197-57	ATOMIC FORMULA					Cu Zn _{0.125} Co Cr K _{0.11}
PREP. METHOD	Mechanical Blending of oxides of Cu, Zn, Cr, Co and K ₂ CO ₃						
SURFACE AREA ⁽¹⁾	0.5	m ² /gm	FEED H ₂ /CO	2.0	CO ₂	5.0	Vol%
BULK DENSITY ⁽¹⁾	1.90	gm/cc					
TEST NO.	-1	-2	-3				
Avg. Temp., °C	252	263	292				
Hot Spot, °C	252	263	293				
Pressure, psig	900	900	915				
VHSV, L/hr/kgm cat.	3192	2024	2346				
Hrs. on Stream	2.8	5.5	8.4				
CONVERSION							
CO, Vol%	3.2	5.8	24.9				
CO, gm mol/hr/kgm cat.	1.26	1.46	7.22				
STY of Oxygenates ⁽²⁾							
gm mol/hr/kgm cat.	0.27	0.32	1.41				
CARBON SELECTIVITY (WT%) NORMALIZED							
CH ₃ OH	0	1.0	1.2				
C ₂ -C ₆ Alcohols	0	1.6	6.1				
C ₁ -C ₆ Aldehydes	21.3	19.3	12.2				
C ₄ -C ₉ H.C.	11.8	9.5	7.1				
CH ₄	21.5	21.6	20.8				
C ₂ H ₆ , C ₃ H ₈ (LPG)	13.3	14.7	10.6				
CO ₂	32.1	32.3	42.0				
APPROACH TO ⁽³⁾ WGS EQUILIBRIUM, °C							
CARBON ACCOUNTABILITY, %	63.1	85.0	86.9				

(1) Fresh, non-reduced catalyst

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

(3) Defined as $T = T_{\text{eq}} - T_{\text{avg}}$

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

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

Table 5.1:3-4
SUMMARY FOR RUN 201-54P (5/6/80)

CATALYST NO.	200-32	ATOMIC FORMULA					CuZn _{0.125} CoCe _{0.14} Mn _{0.14} In _{0.14} Th _{0.14} Fe _{0.14} V _{0.14} Ti _{0.14} K _{0.11}				
PREP. METHOD Evaporation of nitrates - citric acid; Calcined at 450°C for 3 hrs.											
SURFACE AREA ⁽¹⁾	36.1	m ² /gm	FEED H ₂ /CO	2.0	CO ₂	5.0	Vol%				
BULK DENSITY ⁽¹⁾	1.10	gm/cc									
TEST NO.	1	-2	-3	-4							
Avg. Temp., °C	254	273	292	316							
Hot Spot, °C	254	275	293	319							
Pressure, psig	945	935	935	930							
VHSV, L/hr/kgm cat.	3601	3720	3642	3451							
Hrs. on Stream	1.7	3.1	4.8	5.9							
CONVERSION											
CO, Vol%	2.6	4.3	8.0	16.6							
CO, gm mol/hr/kgm cat.	1.16	1.98	3.60	7.08							
STY of Oxygenates ⁽²⁾											
gm mol/hr/kgm cat.	0.184	0.52	0.83	1.00							
CARBON SELECTIVITY (WT%) NORMALIZED											
CH ₃ OH	1.2	4.9	6.9	7.2							
C ₂ -C ₆ Alcohols	14.7	21.4	16.2	7.0							
C ₁ -C ₆ Aldehydes	~0	~0	~0	~0							
C ₄ -C ₉ H.C.	16.7	11.4	9.3	6.1							
CH ₄	30.6	25.1	24.2	26.0							
C ₂ H ₆ , C ₃ H ₈ (LPG)	22.3	18.1	17.1	16.9							
CO ₂	14.5	19.0	26.4	36.9							
APPROACH TO ⁽³⁾ WGS EQUILIBRIUM, °C											
CARBON ACCOUNTABILITY, %	67.1	82.5	93.2	89.6							

(1) Fresh, non-reduced catalyst

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

(3) Defined as $T = T_{\text{eq}} - T_{\text{avg}}$

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 201-56B (5-12-80)

CATALYST NO.	197-48	ATOMIC FORMULA					Cu	Zn ^{0.125}	Co	Cr	K ^{0.11}
PREP. METHOD	Coprecipitated w/ (NH ₄) ₂ CO ₃ Calcined at 450°C for 3 hrs										
SURFACE AREA ⁽¹⁾		m ² /gm	FEED H ₂ /CO	2.0	CO ₂	5.0	Vol%				
BULK DENSITY ⁽¹⁾	1.52	gm/cc									
TEST NO.	-1	-2	-3								
Avg. Temp., °C	260	272	287								
Hot Spot, °C											
Pressure, psig	885	885	885								
VHSV, L/hr/kgm cat.	2521	2492	2633								
Hrs. on Stream	2.9	5.7	7.8								
CONVERSION											
CO, Vol%	1.2	1.5	2.9								
CO, gm mol/hr/kgm cat.	0.38	0.46	0.95								
STY of Oxygenates ⁽²⁾											
gm mol/hr/kgm cat.	0.098	0.128	0.202								
CARBON SELECTIVITY (WT %) NORMALIZED											
CH ₃ OH	~0	0.4	1.0								
C ₂ -C ₆ Alcohols	6.7	6.1	2.6								
C ₁ -C ₆ Aldehydes	19.5	21.1	17.7								
C ₄ -C ₉ H.C.	13.6	11.4	9.6								
CH ₄	22.7	21.7	29.0								
C ₂ H ₆ , C ₃ H ₈ (LPG)	12.4	12.3	12.2								
CO ₂	25.1	27.0	28.0								
APPROACH TO ⁽³⁾											
WGS EQUILIBRIUM, °C											
CARBON											
ACCOUNTABILITY, %	87.1	113.9	71.6								

(1) Fresh, non-reduced catalyst

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

(3) Defined as $T = T_{\text{eq}} - T_{\text{avg}}$

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

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

CATALYST NO.:	197-36	ATOMIC FORMULA					Cu	Zn _{0.125}	Co	Cr	K _{0.11}
PREP. METHOD	Evaporation w/oxalic Acid, Calcined at 450°C for 3 hrs										
SURFACE AREA ⁽¹⁾	7.0	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	-4							
Avg. Temp., °C	265	282	280	293							
Hot Spot, °C	267	285	287	296							
Pressure, psig	930	930	1200	1200							
VHSV, L/hr/kgm cat.	2654	2709	3616	3655							
Hrs. on Stream	2.3	3.7	5.7	6.6							
CONVERSION											
CO, Vol%	7.6	14.7	7.0	13.7							
CO, gm mol/hr/kgm cat.	2.52	4.97	3.16	6.25							
STY of Oxygenates ⁽²⁾											
gm mol/hr/kgm cat.	0.30	0.60	0.63	0.99							
CARBON SELECTIVITY (WT%) NORMALIZED											
CH ₃ OH	0.4	0.8	2.6	2.1							
C ₂ -C ₆ Alcohols	3.1	3.3	17.3	13.7							
C ₁ -C ₆ Aldehydes	8.6	8.0									
C ₄ -C ₉ H.C.	11.8	7.5	10.3	6.7							
CH ₄	54.8	33.9	33.2	28.3							
C ₂ H ₆ , C ₃ H ₈ (LPG)	10.9	12.8	13.8	11.5							
CO ₂	1.8	33.8	25.3	36.3							
APPROACH TO ⁽³⁾											
WGS EQUILIBRIUM, °C											
CARBON ACCOUNTABILITY, %	55.7	81.9	75.5	83.9							

(1) Fresh, non-reduced catalyst

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

(3) Defined as $T = T_{\text{eq}} - T_{\text{avg}}$

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

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

CATALYST NO.	197-36	ATOMIC FORMULA					Cu Zn _{0.125} Co Cr K _{0.11}
PREP. METHOD	Evaporation of nitrates - citric acid; Calcined @ 450°C for 3 hrs.						
SURFACE AREA ⁽¹⁾	99.5	m ² /gm	FEED H ₂ /CO	2.0	CO ₂	5.0	Vol%
BULK DENSITY ⁽¹⁾	1.19	gm/cc					
TEST NO.	-1	-2*	-3	-4	-5		
Avg. Temp., °C	259	270	281	295	298		
Hot Spot, °C	260	271	283	298	303		
Pressure, psig	910	910	900	900	1140		
VHSV, L/hr/kgm cat.	3267	3222	3247	3376	4278		
Hrs. on Stream	2.3	3.8	5.3	6.6	7.4		
CONVERSION							
CO, Vol%	5.8	7.5	12.7	24.1	25.7		
CO, gm mol/hr/kgm cat.	2.46	3.03	5.17	10.2	13.8		
STY of Oxygenates ⁽²⁾							
gm mol/hr/kgm cat.	0.32	0.53	0.89	1.46	2.14		
CARBON SELECTIVITY (WT%) NORMALIZED							
CH ₃ OH	1.1	2.1	2.4	2.3	2.8		
C ₂ -C ₆ Alcohols	2.0	2.7	4.8	5.4	6.4		
C ₁ -C ₆ Aldehydes	9.8	12.7	10.0	6.6	6.3		
C ₄ -C ₉ H.C.	9.9	8.1	7.2	6.9	6.2		
CH ₄	15.6	16.5	16.1	17.5	11.3		
C ₂ H ₆ , C ₃ H ₈ (LPG)	11.4	12.5	12.0	12.4	18.5		
CO ₂	50.3	45.3	47.5	48.9	48.5		
APPROACH TO ⁽³⁾ WGS EQUILIBRIUM, °C		52	73	69	70		
CARBON ACCOUNTABILITY, %	57.9	72.9	75.0	78.5	78.6		

(1) Fresh, non-reduced catalyst

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

(3) Defined as $T = T_{\text{eq}} - T_{\text{avg}}$

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

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

Table 5.1.3-8
SUMMARY FOR RUN 201-62B (16-May-80)

CATALYST NO.	197-16		ATOMIC FORMULA				Cu Zn _{0.5} Co Cr K _{0.11}		
PREP. METHOD	Evaporation of nitrates - citric acid; Calcined for 3 hrs at 450°C								
SURFACE AREA ⁽¹⁾	39.2	m ² /gm	FEED H ₂ /CO	2.0	CO ₂	5.0	Vol%		
BULK DENSITY ⁽¹⁾	1.24	gm/cc							
TEST NO.	-1	-2	-3	-4	-5	-6			
Avg. Temp., °C	273	275	298	312	297	274			
Hot Spot, °C	273	275	298	312	297	274			
Pressure, psig	895	1350	930	920	915	920			
VHSV, L/hr/kgm cat.	3375	4842	3420	6766	1284	3270			
Hrs. on Stream	4.5	5.9	8.9	10.7	11.9	13.5			
CONVERSION									
CO, Vol%	14.3	11.9	93.3	88.7	98.0	12.6			
CO, gm mol/hr/kgm cat.	6.02	7.19	39.8	74.9	15.7	5.1			
STY of Oxygenates ⁽²⁾									
gm mol/hr/kgm cat.	1.05	1.43	0.28	0.45	0.016	0.73			
CARBON SELECTIVITY (WT%) NORMALIZED									
CH ₃ OH	3.5	4.9	0.1	0.1	~	4.0			
C ₂ -C ₆ Alcohols	14.0	15.0	0.6	0.5	0.1	10.4			
C ₁ -C ₆ Aldehydes	~ 0	~ 0	~ 0	~ 0	~ 0	~ 0			
C ₄ -C ₉ H.C.	8.4	6.6	6.2	6.0	6.1	14.7			
CH ₄	30.3	25.3	50.1	49.2	54.8	22.4			
C ₂ H ₆ , C ₃ H ₈ (LPG)	16.6	13.8	8.9	9.2	10.8	16.6			
CO ₂	27.1	34.4	34.1	35.0	28.1	32.0			
APPROACH TO ⁽³⁾ WGS EQUILIBRIUM, °C	165	75	84	104	57	130			
CARBON ACCOUNTABILITY, %	94.1	100.2	93.5	92.9	98.8	91.9			

(1) Fresh, non-reduced catalyst

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

(3) Defined as $T = T_{\text{eq}} - T_{\text{avg}}$

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 201-65P (21-May-80)

CATALYST NO.	200-27-1		ATOMIC FORMULA				Cu Zn _{0.125} Co Cs _{0.11}	
PREP. METHOD	Evaporation of nitrate - citric acid; Calcined at 450°C for 8 hrs.							
SURFACE AREA ⁽¹⁾	4.1	m ² /gm	FEED H ₂ /CO	2.0	CO ₂	5.0	Vol%	
BULK DENSITY ⁽¹⁾	1.44	gm/cc						
TEST NO.	1	-2	-3					
Avg. Temp., °C	272	284	297					
Hot Spot, °C	274	287	300					
Pressure, psig	900	900	900					
VHSV, L/hr/kgm cat.	2557	2419	2579					
Hrs. on Stream	2.9	4.6	6.4					
CONVERSION								
CO, Vol%	6.5	10.1	16.2					
CO, gm mol/hr/kgm cat.	2.07	3.04	5.20					
STY of Oxygenates ⁽²⁾								
gm mol/hr/kgm cat.	0.30	0.404	0.63					
CARBON SELECTIVITY (WT%) NORMALIZED								
CH ₃ OH	1.7	2.6	2.6					
C ₂ -C ₆ Alcohols	5.7	4.9	4.9					
C ₁ -C ₆ Aldehydes	7.2	5.8	4.6					
C ₄ -C ₉ H.C.	16.0	7.9	6.3					
CH ₄	31.1	34.0	33.6					
C ₂ H ₆ , C ₃ H ₈ (LPG)	14.7	14.2	13.6					
CO ₂	23.6	30.6	34.3					
APPROACH TO ⁽³⁾								
WGS EQUILIBRIUM, °C	110	142	119					
CARBON								
ACCOUNTABILITY, %	65.9	76.3	90.1					

(1) Fresh, non-reduced catalyst

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

(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 201-67B (22May 80)

CATALYST NO.	<u>197-2 Reduction in situ</u>		ATOMIC FORMULA <u>Cu Co Cr Zn_{0.125}K_{0.11}</u>				
PREP. METHOD	<u>Evaporation of Cu,Zn,Co, & Cr nitrates & K₂CO₃ Solutions; Calcined at 450°C for 3 hr</u>						
SURFACE AREA ⁽¹⁾	<u> </u>	m ² /gm	FEED H ₂ /CO	<u>2.0</u>	CO ₂	<u>5.0</u>	Vol%
BULK DENSITY ⁽¹⁾	<u> </u>	gm/cc					
TEST NO.	-0	-1	-2	-3	-4	-5	-6
	(Insitu Reduction)						
Avg. Temp., °C	<u>240</u>	<u>270</u>	<u>271</u>	<u>293</u>	<u>294</u>	<u>292</u>	<u>266</u>
Hot Spot, °C	<u>290</u>	<u>271</u>	<u>271</u>	<u>294</u>	<u>295</u>	<u>294</u>	<u>267</u>
Pressure, psig	<u>15</u>	<u>895</u>	<u>1410</u>	<u>900</u>	<u>895</u>	<u>890</u>	<u>890</u>
VHSV, L/hr/kgm cat.	<u>500</u>	<u>646</u>	<u>636</u>	<u>2541</u>	<u>730</u>	<u>700</u>	<u>622</u>
Hrs. on Stream	<u>24</u>	<u>5.3</u>	<u>6.6</u>	<u>13.6</u>	<u>17.1</u>	<u>35.7</u>	<u>42.8</u>
CONVERSION							
CO, Vol%		<u>28.5</u>	<u>36.4</u>	<u>14.6</u>	<u>58.9</u>	<u>45.0</u>	<u>11.7</u>
CO, gm mol/hr/kgm cat.		<u>2.28</u>	<u>2.87</u>	<u>4.59</u>	<u>5.33</u>	<u>39.0</u>	<u>0.9</u>
STY of Oxygenates ⁽²⁾							
gm mol/hr/kgm cat.		<u>0.28</u>	<u>0.31</u>	<u>0.79</u>	<u>0.79</u>	<u>0.54</u>	<u>0.27</u>
CARBON SELECTIVITY (WT%) NORMALIZED							
CH ₃ OH		<u>1.0</u>	<u>1.1</u>	<u>4.7</u>	<u>2.8</u>	<u>3.7</u>	<u>8.5</u>
C ₂ -C ₆ Alcohols		<u>3.3</u>	<u>2.5</u>	<u>12.4</u>	<u>10.1</u>	<u>10.2</u>	<u>20.9</u>
C ₁ -C ₆ Aldehydes		<u>8.1</u>	<u>7.2</u>	<u>Trace</u>	<u>2.0</u>	<u>Trace</u>	<u>Trace</u>
C ₄ -C ₉ H.C.		<u>9.6</u>	<u>7.2</u>	<u>2.7</u>	<u>2.4</u>	<u>2.8</u>	<u>3.8</u>
CH ₄		<u>20.7</u>	<u>21.8</u>	<u>31.5</u>	<u>26.2</u>	<u>26.8</u>	<u>23.4</u>
C ₂ H ₆ ,C ₃ H ₈ (LPG)		<u>14.5</u>	<u>15.4</u>	<u>15.6</u>	<u>16.2</u>	<u>17.1</u>	<u>11.9</u>
CO ₂		<u>42.8</u>	<u>44.8</u>	<u>33.1</u>	<u>40.3</u>	<u>39.4</u>	<u>31.4</u>
APPROACH TO ⁽³⁾ WGS EQUILIBRIUM, °C							
CARBON ACCOUNTABILITY, %		<u>91.7</u>	<u>87.1</u>	<u>94.1</u>	<u>98.3</u>	<u>99.3</u>	<u>104.4</u>

(1) Fresh, non-reduced catalyst

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

(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 5.1.3-11
SUMMARY FOR RUN 201-72P (5- June- 80)

CATALYST NO.	197-59	ATOMIC FORMULA					Cu	Zn	0.125	Co	Mn	K	0.11
PREP. METHOD	Evaporation Calcined at 450°C for 3 Hrs.												
SURFACE AREA ⁽¹⁾	m ² /gm		FEED H ₂ /CO	2.0	CO ₂	5.0	Vol%						
BULK DENSITY ⁽¹⁾	1.46		gm/cc										
TEST NO.	-1		-2		-3								
Avg. Temp., °C	243		274		294								
Hot Spot, °C	245		275		296								
Pressure, psig	900		900		895								
VHSV, L/hr/kgm cat.	2415		2402		2382								
Hrs. on Stream	3.1		4.5		5.6								
CONVERSION													
CO, Vol%	1.5		2.6		12.9								
CO, gm mol/hr/kgm cat.	0.457		0.78		3.8								
STY of Oxygenates ⁽²⁾													
gm mol/hr/kgm cat.	0.066		0.096		0.49								
CARBON SELECTIVITY (WT%) NORMALIZED													
CH ₃ OH	2.2		1.8		2.1								
C ₂ -C ₆ Alcohols	12.2		4.0		4.6								
C ₁ -C ₆ Aldehydes			6.5		6.2								
C ₄ -C ₉ H.C.	17.5		7.5		4.0								
CH ₄	39.5		29.9		26.4								
C ₂ H ₆ ;C ₃ H ₈ (LPG)	19.6		17.7		19.3								
CO ₂	9.0		32.7		37.4								
APPROACH TO ⁽³⁾													
WGS EQUILIBRIUM, °C	73		114		82								
CARBON ACCOUNTABILITY, %	60.3		143.6		90.3								

(1) Fresh, non-reduced catalyst

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

(3) Defined as $T = T_{\text{eq}} - T_{\text{avg}}$

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

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

CATALYST NO.	197-65	ATOMIC FORMULA 30% (Cu Zn _{0.125} Co Cr K _{0.11})/70% SiO ₂				
PREP. METHOD	Impregnation on silica gel; Calcined at 450°C for 3 hrs					
SURFACE AREA ⁽¹⁾	m ² /gm	FEED H ₂ /CO	2.0	CO ₂	5.0	Vol%
BULK DENSITY ⁽¹⁾	0.50 gm/cc					
TEST NO.	-1	-2	-3			
Avg. Temp., °C	267	267	267			
Hot Spot, °C	267	267	267			
Pressure, psig	905	900	880			
VHSV, L/hr/kgm cat. (including support)	7745	1744	964			
Hrs. on Stream	0.9	2.0	19.1			
CONVERSION						
CO, Vol%	2.10	8.1	6.3			
CO, gm mol/hr/kgm cat.	2.01	1.76	0.75			
STY of Oxygenates ⁽²⁾						
gm mol/hr/kgm cat.	NA	0.522	0.177			
CARBON SELECTIVITY (WT%) NORMALIZED						
CH ₃ OH	NA	6.6	6.2			
C ₂ -C ₆ Alcohols	NA	13.1	7.8			
C ₁ -C ₆ Aldehydes	NA	10.0	9.6			
C ₄ -C ₉ H.C.	NA	5.8	2.4			
CH ₄	NA	28.8	36.4			
C ₂ H ₆ , C ₃ H ₈ (LPG)	NA	23.6	18.3			
CO ₂	89.5	12.1	19.4			
APPROACH TO ⁽³⁾ WGS EQUILIBRIUM, °C	NA	73	139			
CARBON ACCOUNTABILITY, %	NA	98.8	98.4			

(1) Fresh, non-reduced catalyst

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

(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

CATALYST NO.	197-60	ATOMIC FORMULA					Cu Co V Zn _{0.125} K _{0.11}
PREP. METHOD	Evaporation, Calcined at 450°C for 3 hrs.						
SURFACE AREA ⁽¹⁾	m ² /gm	FEED H ₂ /CO	2.0	CO ₂	5.0	Vol%	
BULK DENSITY ⁽¹⁾	1.29 gm/cc						
TEST NO.	-1	-2	-3	-4	-5		
Avg. Temp., °C	255	277	289	276	288		
Hot Spot, °C	256	279	293	278	292		
Pressure, psig	885	885	880	885	885		
VHSV, L/hr/kgm cat.	2965	3084	2993	3159	3135		
Hrs. on Stream	1.8	3.0	5.4	9.0	10.9		
CONVERSION							
CO, Vol%	3.2	9.2	12.5	7.5	17.9		
CO, gm mol/hr/kgm cat.	1.18	3.54	4.67	2.91	6.99		
STY of Oxygenates ⁽²⁾							
gm mol/hr/kgm cat.	0.21	0.90	1.01	0.67	1.45		
CARBON SELECTIVITY (WT%) NORMALIZED							
CH ₃ OH	3.7	5.1	4.3	5.1	4.2		
C ₂ -C ₆ Alcohols	8.2	16.4	12.1	5.6	7.9		
C ₁ -C ₆ Aldehydes	5.6	3.9	5.2	12.2	8.7		
C ₄ -C ₉ H.C.	10.7	6.9	8.2	8.3	6.7		
CH ₄	33.6	27.1	23.7	25.3	22.4		
C ₂ H ₆ , C ₃ H ₈ (LPG)	17.5	14.1	12.6	13.3	12.1		
CO ₂	20.7	26.5	34.0	30.2	38.0		
APPROACH TO ⁽³⁾ WGS EQUILIBRIUM, °C	83	107	-89	62	96		
CARBON ACCOUNTABILITY, %	90.8	99.4	130.2	104.7	84.7		

(1) Fresh, non-reduced catalyst

(2) Space Time Yield (STY) = $\frac{\text{VHSV}}{22.4} \times \frac{\% \text{ CO in Feed}}{100} \times \frac{\% \text{ CO Conv.}}{100} \times \frac{\% \text{ Selectivity to Oxygenates}}{100}$ (3) Defined as $T = T_{\text{eq}} - T_{\text{avg}}$ where T_{eq} = water gas shift equilibrium temperature calculated for reactor effluent composition T_{avg} = average observed bulk-phase reaction temperature

CATALYST NO.	197-66	ATOMIC FORMULA 55% (Cu Zn _{0.125} Co Cr K _{0.11}) on TiO ₂				
PREP. METHOD	Impregnation w/Ti (OH) ₄ slurry; Calcined at 450°C for 3 hrs.					
SURFACE AREA ⁽¹⁾	m ² /gm	FEED H ₂ /CO	2.0	CO ₂	5.0	Vol%
BULK DENSITY ⁽¹⁾	gm/cc					
TEST NO.	-1					
Avg. Temp., °C	272					
Hot Spot, °C	272					
Pressure, psig	895					
VHSV, L/hr/kgm cat.	594					
Hrs. on Stream	9.6					
CONVERSION						
CO, Vol%	1.27					
CO, gm mol/hr/kgm cat.	0.09					
STY of Oxygenates ⁽²⁾						
gm mol/hr/kgm cat.	0.042					
CARBON SELECTIVITY (WT%) NORMALIZED						
CH ₃ OH	0.5					
C ₂ -C ₆ Alcohols	23.8					
C ₁ -C ₆ Aldehydes	20.5					
C ₄ -C ₉ H.C.	0					
CH ₄	46.0					
C ₂ H ₆ , C ₃ H ₈ (LPG)	9.1					
CO ₂	0					
APPROACH TO ⁽³⁾						
WGS EQUILIBRIUM, °C						
CARBON ACCOUNTABILITY, %	25.8					

(1) Fresh, non-reduced catalyst

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

(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 5.1.3-15
SUMMARY FOR RUN 201-80B (2-July-80)

CATALYST NO.	200-57-1	ATOMIC FORMULA	Cu Co Fe _{0.1} Zn _{0.125} K _{0.11}			
PREP. METHOD	Evaporation, Calcined at 450°C					
SURFACE AREA ⁽¹⁾	m ² /gm	FEED H ₂ /CO	2.0	CO ₂	5.0	Vol%
BULK DENSITY ⁽¹⁾	gm/cc					
TEST NO.	-1	-2				
Avg. Temp., °C	273	288				
Hot Spot, °C	274	289				
Pressure, psig	900	900				
VHSV, L/hr/kgm cat.	2700	638				
Hrs. on Stream	5.6	12.3				
CONVERSION						
CO, Vol%	3.5	14.0				
CO, gm mol/hr/kgm cat.	1.2	1.1				
STY of Oxygenates ⁽²⁾						
gm mol/hr/kgm cat.	0.426	0.253				
CARBON SELECTIVITY (WT%) NORMALIZED						
CH ₃ OH	17.1	15.5				
C ₂ -C ₆ Alcohols	14.3	4.8				
C ₁ -C ₆ Aldehydes	5.0	2.8				
C ₄ -C ₉ H.C.	3.6	2.8				
CH ₄	15.5	12.1				
C ₂ H ₆ , C ₃ H ₈ (LPG)	17.5	12.1				
CO ₂	27.0	49.9				
APPROACH TO ⁽³⁾						
WGS EQUILIBRIUM, °C		-84				
CARBON ACCOUNTABILITY, %	50.6	83.8				

(1) Fresh, non-reduced catalyst

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

(3) Defined as $T = T_{\text{eq}} - T_{\text{avg}}$

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

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

5.1.4 Analysis of Results

Although none of the catalysts tested this quarter resulted in reaching the targetted oxygenates (alcohols and aldehydes) selectivities, some relevant correlations were observed. These are illustrated in a series of plots (Figures 5.1.4-1 through 5) which show the effect of catalyst group type (as defined in Table 5.1.3-1) on the oxygenates selectivity-CO conversion relationships. In all cases, oxygenates selectivity decreases as 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 different transition metal (M) elements in a catalyst produced by the evaporation of metal nitrate-citric acid solutions and having the general atomic formula $\text{CuZn}_{0.125}\text{CoK}_{0.11}\text{M}$. At CO conversions between about 10 to 20%, there appears to be somewhat of a trend in the selectivity-CO conversion relationship with type of transition metal. The transition metal type affects the oxygenates selectivity as shown below (in descending order):

An additional catalyst formulation was prepared in which M consisted of equal atomic fractions of seven transition metal promoters - $\text{Ce}_{0.14}\text{Mn}_{0.14}\text{In}_{0.14}\text{Th}_{0.14}\text{Fe}_{0.14}\text{V}_{0.14}\text{Ti}_{0.14}$. The purpose of this formulation was to allow the rapid screening of the effects of all promoters simultaneously. If the resultant CO conversion and oxygenates selectivity were promising, additional catalysts would have been prepared containing one less transition metal promoter in turn to determine which one was the most active. However, the results of testing in the plug-flow reactor showed low activity (less than 5% CO conversion at 275°C) and low oxygenates selectivity.

Figure 5.1.4-2 shows the effect of zinc level in a Group I type catalyst ($\text{CuZn}_x\text{CrCoK}_{0.11}$) prepared by evaporation of metal nitrate-citric acid solutions. Varying the zinc atomic fraction from 0.125 to 0.5 has little or no effect on

FIGURE 5.1.4-1

CONVERSION-SELECTIVITY CHARACTERISTICS
EFFECT OF TRANSITION METAL TYPE IN
A GROUP IV TYPE CATALYST -

$\text{CuZn}_{0.125}\text{CoK}_{0.11}\text{M}_y$

FIGURE 5.1.4-2

CONVERSION-SELECTIVITY CHARACTERISTICS

EFFECT OF ZINC LEVEL IN GROUP I

CATALYST - $\text{CuCoCrK}_{0.11}\text{Zn}_x$

x
 ○ 0.5
 △ 0.125

Run No.

201-62

201-67

the oxygenates selectivity over the whole range of CO conversion. For these two catalysts, selectivity decreases linearly with CO conversion up to 98% CO conversion, at which point the oxygenates selectivity is zero.

Figure 5.1.4-3 shows the effect of alkali metal (A) type in a Group II type catalyst ($\text{CuZn}_{0.125}\text{CoA}_{0.11}$) prepared by evaporation of metal nitrate-citric acid solutions. Potassium as an alkali promoter results in about a 20-40% (relative) improvement in oxygenates selectivity over that of cesium.

Figure 5.1.4-4 shows the effect of supporting a Group I type catalyst ($\text{CuZn}_{0.125}\text{CrCoK}_{0.11}$ produced by evaporation of metal nitrate-citric acid solutions) on inert supports such as silica gel and titania. These two supported catalysts were also crushed and screened to 8 x 12 mesh vs. the 3/16" x 1/8" pellets previously used. The supported catalysts therefore have a surface area/volume ratio of about 36 cm^{-1} , which is about 2 1/2 times that of the pelletized catalyst. However, since only 55% by weight of active catalyst was supported on the titania support and 30% on the silica support, the available active surface area for the supported and unsupported catalysts at constant VHSV was approximately the same. However, the activity and STY (space time yield of oxygenated products) was lower for the supported catalysts as shown below:

Table 5.1.4-1

<u>Support Type</u>	<u>Unsupported</u>		<u>45% Titania</u>	<u>70% Silica</u>
Temperature, °C	271	267	272	267
Pressure, psig	900	900	900	880
VHSV, L/hr/kgm	646	622	594	964
Hours on Stream	5	43	10	19
CO Conversion, gmol/hr/kgm cat.	2.28	0.9	0.09	0.75
STY of Oxygenates, gmol/hr/kgm cat.	0.28	0.27	0.04	0.18

FIGURE 5.1.4-3

CONVERSION SELECTIVITY CHARACTERISTICS

EFFECT OF ALKALI METAL TYPE

IN A GROUP I CATALYST

CuZn 0.125 CoCrA 0.11

Catalyst #	A
○	200-25-1 K
△	200-27-1 Cs

FIGURE 5.1.4-4

CONVERSION-SELECTIVITY CHARACTERISTICS

EFFECT OF SUPPORTING A GROUP I

TYPE CATALYST - $\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$

It is interesting to note from Table 5.1.4-1 that the unsupported catalyst underwent a deactivation phenomena between 5 and 43 hours on-stream time in which CO conversion decreased from 28.5% to 11.7%. However, selectivity to oxygenates increased more than twofold, from 13.4% to 29.4% with the aldehydes formation essentially nil. This suggests a possible mechanism change as a result of a catalyst compositional change occurring for longer-term on-stream times (43 hours vs. 5-20 hr for the bulk of the catalysts tested to date). With the limited data available, the trend of oxygenates selectivity vs. CO conversion (Figure 5.1.4-4) appears to be insensitive to the presence and type of support (titania or silica).

Figure 5.1.4-5 shows the effect of catalyst production method for a Group I type catalyst ($\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$) on the selectivity-CO conversion relationship. Catalyst produced by mechanical blending of the metal oxides showed little dependence of selectivity to oxygenates on CO conversion level (between 0 and 25%). One surprising observation is that the activity of the mechanically-blended oxide catalyst, which had a fresh (non-reduced) surface area of only $0.5 \text{ m}^2/\text{gm}$, was comparable to or even higher than that of catalysts produced by coprecipitation or by evaporation as seen from the following table:

Table 5.1.4-2

$\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$ Formulation

<u>Preparation</u>	<u>Mechanical Blending</u>	<u>Evaporation With Oxalic Acid</u>	<u>Coprecipitation With (NH_4)₂CO₃</u>
Temperature, °C	293	293	287
VHSV, L/hr/kgm cat.	2346	3655	2633
Pressure	915	1200	885
CO Conversion, %	24.9	13.7	2.9
STY of Oxygenates, gmol/hr/kgm	1.41	0.99	0.20
Selectivity to Oxygenates, %	19.5	15.8	21.3
Selectivity to Hydrocarbons, %	38.5	47.9	50.7
Selectivity to CO ₂ , %	42.0	36.3	28.0

FIGURE 5.1.4-5

CONVERSION-SELECTIVITY CHARACTERISTICS
EFFECT OF CATALYST PRODUCTION METHOD
FOR A $\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$ CATALYST

Sample #		
197-2	○	Evaporation of nitrates w/citric acid
197-57	⬡	Mechanical blending of oxides
197-48	□	Coprecipitation with $(\text{NH}_4)_2\text{CO}_3$
197-36	△	Evaporation of nitrates w/oxalic acid

A clue to attaining higher oxygenates selectivity may rest in the fact that discrete metal/metal oxide phases, as produced by mechanical blending, may be more desirable than uniformly dispersed systems.

Catalysts produced by coprecipitation of metal nitrates with ammonium carbonate showed the greatest dependence of CO conversion level, albeit at very low CO conversion levels. Data at high CO conversion are available only for the catalyst produced by evaporation of metal nitrate-citric acid solutions. These data indicate that selectivity decreases rapidly as conversion increases at low CO conversion levels and then tends to stabilize at higher levels. At the 5-15% CO conversion level, citric acid appears to be a better complexing agent than oxalic acid as regards oxygenates selectivity.

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.