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

First Quarterly Progress Report, September 14—December 31, 1979

MASTER

April 8, 1980

Work Performed Under Contract No. AC22-79ET14858

Chem Systems Research Center
Fairfield, New Jersey

U. S. DEPARTMENT OF ENERGY

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FIRST QUARTERLY PROGRESS REPORT

September 14 - December 31, 1979

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 CENTER
ONE EVANS STREET
FAIRFIELD, NJ 07006

April 8, 1980

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C.L.

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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_4 alcohols. The objectives of this contract are to: 1) develop a catalyst and reactor system for producing a mixture of C_1 - C_4 alcohols, which we call Alkanol fuel, to be used as a synthetic transportation fuel and 2) assess the technical and economic feasibility of scaling the process concept to a commercial-scale application.

This first quarterly report presents the experimental work performed for the period of September 15 - December 31, 1979. In this quarter, the contract schedule called for work to be performed on Task 1 - "Catalyst Formulation and Screening Studies" only. Some of the accomplishments made this quarter were:

1. A small (75cc) fixed-bed, plug-flow, vapor phase reaction system was set up and operated utilizing catalyst bed dilution with inert media to help limit the large exotherm associated with the synthesis gas conversion reactions.
2. A total of fifteen (15) catalysts containing varying amounts of Cu, Co, Zn, Cr and K were prepared and seven of these catalysts were tested.
3. We have identified at least one promising catalyst composition which has resulted in a 30% conversion per pass of carbon monoxide (synthesis gas had a 3.5 H_2/CO ratio) with a carbon selectivity to alcohols of about 80%.

Plans for the next quarter include studying the effect of catalyst manufacturing techniques on catalyst activity and selectivity; setting up a "Berty" reaction system to operate in parallel with the fixed-bed, plug flow reactor for the purpose of obtaining kinetic-type data, and initiating the engineering and economic assessment study.

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_4), 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 TO DATE

3.1 Task 1 - Catalyst Formulation & Screening Studies

The initial screening of catalysts was carried out in a small fixed-bed, plug-flow, vapor-phase unit. In these initial tests, special emphasis was placed on devising a method for controlling the reaction exotherm and on development of on-line analysis for monitoring the product yields and selectivities of the catalysts under study. Reaction exotherm was satisfactorily controlled by catalyst bed dilution with inert media (alumina beads).

A total of fifteen catalysts containing varying composition of Cu, Co, Zn, Cr and K were prepared by the end of this reporting period, and seven of these were tested. Single-pass carbon monoxide conversions of 30% and carbon selectivity to liquid products as high as 82.5% were obtained with the catalyst having the composition of $\text{Cu}_1\text{Cr}_{0.8}\text{Co}_{1.0}\text{K}_{0.09}$. All of the test runs were carried out at ~ 900 psig, $240\text{--}280^\circ\text{C}$, and VHSV (NTP) of $\sim 4000\text{ hr}^{-1}$ with a synthesis gas containing 66% H_2 , 19% CO, 13% CO_2 and 2% N_2 (natural gas-based steam reformer effluent gas). Later argon was used as an internal standard in the synthesis gas instead of nitrogen. The results of the other tests indicate that at least two catalyst compositions gave CO conversions of about 20% and selectivities to liquid products of up to 85%.

It is considered to be too early to attempt to correlate catalyst compositions with activity and selectivity. However, a study of the data enables us to identify some useful rudimentary relationships:

- A high level of Cr is detrimental to catalyst activity. The Cr level should be close to or less than the level of Cu or Co.
- The ratio of Cu/Co should be equal to or slightly less than 1.
- The inclusion of zinc at low levels (less than 5%) does not appear to affect the catalyst activity.

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

A gradientless, fixed-bed vapor phase reaction system ("Berty" reactor) will be installed and operated in parallel with the fixed-bed, plug flow reaction system. The latter will be used for longer duration tests in which ample quantities of alcohols product will be recovered and analyzed. The Berty reactor will be used to obtain chemical reaction rate data.

Additional catalysts containing varying compositions of Cu, Co, Zn, Cr and K will be prepared using the coprecipitation and evaporation method of catalyst production and then tested in either the plug-flow or Berty reactor (Subtask 1.1).

A study of the effect of catalyst production techniques will be initiated using the best catalyst composition determined from the screening tests of Subtask 1.1. We will investigate alternate methods such as mechanical blending of the metal oxides; impregnation of high surface area supports such as alumina; doping of commercial methanol synthesis catalysts with promoters such as cobalt and potassium. Catalyst optimization studies will be initiated. As a starting point, we will fix the composition of copper, zinc, cobalt and potassium and then add various promoters such as thorium, titanium, vanadium, indium, cerium, iron and manganese, respectively. We will then fix the composition of copper, zinc, cobalt with the best promoter determined from the above study and then add various alkali promoters such as sodium, cesium, lithium or rubidium.

Task 2: Process Variables Studies in BSU

No work will be done on this task in the next quarter.

Task 3: Engineering Studies and Economic Analyses

Initial work on this task will be to determine the feasibility of scaling up a fixed-bed, vapor-phase reactor for the C_1 - C_4 alcohols synthesis in terms of heat removal. As a starting point, we will consider the case of 60% carbon monoxide conversion per pass with 90% selectivity to C_1 - C_4 alcohols at

100 atm reactor pressure, 250-260°C reaction temperature and 4000 hourly space velocity with a synthesis gas containing 70% H₂, 35% CO, 5% CO₂. We will also begin the development of a conceptual flowsheet consisting of the major process modules. The coal gasification and shift steps must be included in the flowsheet, since there is a beneficial synergistic effect between the low level heats available in the coal gasification environment and the heat duties required for the azeotropic separation of water from the alcohol products.

Task 4: Performance Studies in PDU

No work will be done on this task in the next quarter.

5.0 DETAILED DESCRIPTION OF TECHNICAL PROGRESS

5.1 Task 1 - Catalyst Formulation and Screening Studies

5.1.1 Background & Literature Review

5.1.1.1 Review of Catalyst Development

The production of chemicals and clean fuels from synthesis gas has been known for over fifty years, and research and development efforts in this area have taken many directions. The initial foundation for the development of this chemistry began in the 1920's with the well-known work of Fischer and Tropsch ^(1,2,3,4) for producing liquid hydrocarbons from synthesis gas. The reactions between CO and H₂ were carried out at pressures between 100 and 150 atm, at temperatures of 400 to 450°C in the presence of an alkali-activated, iron oxide catalyst.

The scientific and industrial importance of this chemistry was so apparent that experimental research on the subject was initiated in laboratories throughout the world. The research centered on the development of improved catalysts for the Fischer-Tropsch synthesis as well as on other chemical routes to alcohols. The various processes for obtaining higher alcohols from CO and H₂ can be classified into three groups:

1. Synthesis by catalytic processes aimed at producing hydrocarbons from CO and H₂.
2. Synthesis with modified methanol catalysts.
3. Oxo synthesis from CO, H₂ and olefins.

The Oxo synthesis (hydroformylation) was originated in Germany during World War II as a process for the production of higher alcohols. However, its utilization was limited by the requirement for the additional olefinic reactant.

The discovery and concomitant improvements in the $\text{ZnO-Cr}_2\text{O}_3$ -based catalysts during the 1920's through 1950's represented a decisive step in the selective synthesis of higher alcohols. The first high yields of methanol in the presence of these catalysts were reported by BASF⁽⁵⁾ in 1923. Natta and Strada⁽⁶⁾ in 1930 found that the highest yields of alcohols were obtained with ZnO-based catalysts promoted by potassium, rubidium or cesium ion. A few years later, Morgan and coworkers⁽⁷⁾ studied the quantitative influence of the addition of five different alkali ions to a chromium oxide-manganese oxide catalyst. Although they found Li^+ , Na^+ , K^+ (added as hydroxides) to inhibit the overall reaction yield, they did not observe this phenomenon when Rb^+ or Cs^+ was present. Other researchers^(8,9) also found that alkaline metals can be used as promoters for the synthesis of higher alcohols. The overall conclusion from a recent review⁽¹⁰⁾ of this older work is that the catalytic synthesis of higher alcohols is not selective and the resultant alcohol mixtures have methanol as a predominant component.

The following types of catalysts have been proposed⁽¹¹⁾ for the synthesis of higher alcohols:

1. ZnO-based catalysts with alkaline promoters;
2. $\text{ZnO-Cr}_2\text{O}_3$ -based catalysts with alkaline promoters;
3. Oxides of zinc, manganese, chromium-activated with alkaline promoters;
4. Copper, ZnO, Cr_2O_3 catalysts activated with alkaline promoters;
5. Copper and oxides of zinc, chromium, manganese, calcium, lead, aluminum, thorium, etc. activated with alkaline metals and;
6. Catalysts containing cobalt.

Catalysts containing cobalt result in a fundamentally different product spectrum. The modified methanol catalysts mentioned above lead mainly to the formation of primary isobutanol among other higher alcohols. On the other hand, the catalysts containing Co lead to the formation of high amounts of ethanol. High yields of ethanol were observed by Taylor⁽¹²⁾

working with a catalyst containing Cu, Mn and Co. Operating at 40°C, 200 atm at high space velocities, the selectivity of ethanol was up to 22% wt. High selectivities of ethanol equivalent to 29% wt of the condensed product were also obtained by Klyukvin, et. al.⁽¹³⁾ using a catalyst composed of ZnO:CoO = 3:1, and operating at 320-330°C and 120 atm. In general, the higher alcohols obtained with catalysts containing cobalt are predominantly of the linear type, whereas with the modified methanol catalysts, they appear mainly as the branched type.

A marked change in product composition was noted by Rao, et. al.⁽¹⁴⁾ in their recent work on the synthesis of gasoline range hydrocarbons from synthesis gas. The incorporation of cobalt into the catalyst (Fe/ZSM-5) reduced the aromatic fraction and increased the olefinic and oxygenate fractions. They also found that the extent of the water gas shift reaction was substantially reduced with this cobalt-promoted catalyst.

The Institut Francais du Petrole (IFP) has found⁽¹⁵⁾ that when using a catalyst containing a mixture of Cu and Co oxides and alkali metal salts along with the oxides of either chromium, iron, vanadium or manganese, much higher yields of normal unbranched alcohols with two or more carbon atoms, particularly ethanol, can be obtained.

At 250°C and 60 atm, conversion is 35% per pass. The selectivity to alcohols is over 95% with CO₂ and CH₄ accounting for the major portion of the yield loss. Selectivity to normal two carbon or higher alcohols is in excess of 71% with ethanol being the major product. In contrast to the isobutanol synthesis, the branched and/or iso alcohol to normal linear alcohol ratio is quite low. The rate of alcohol formation is high compared to Fischer-Tropsch processes, and reaction temperatures and pressures are moderate.

A variety of catalyst compositions have been reported by IFP to be effective for alcohol production. A typical product distribution of alcohols is shown below:

TYPICAL ALCOHOL PRODUCT DISTRIBUTION
(weight percent)

methanol	20
ethanol	38
n-propanol	21
i-propanol	3
n-butanol	17
i-butanol	--
Total	99

High yields of methanol and iso-alcohols, in particular isobutanol, were obtained by BASF⁽¹⁶⁾ with catalysts containing oxides of zirconium, indium, titanium and potassium at 435°C, 250 atm and space velocities (NTP) of 7500 hr⁻¹.

5.1.1.2 Review of Chemical Mechanisms

The chemistry of hydrogenation of CO is extremely complex and literally hundreds of hydrocarbon and oxygenated products can result. The nature of the catalyst utilized in the synthesis is the key to product selectivity (and productivity). This has been quite effectively depicted by Klier⁽¹⁷⁾ in Figure 5.1.1.2-1 showing the variety of products that can be obtained by the use of three basic groups of catalysts: metals, organometallics, and metal oxides.

The following notable researchers have hypothesized mechanisms for the synthesis of higher alcohols which will be briefly summarized below:

1. Fischer-Tropsch⁽¹⁻⁴⁾
Homologation via an acetic acid intermediate.

2. Natta⁽⁶⁾

Homologation via formation of fatty acid salt intermediates.

3. Morgan⁽⁷⁾

Aldolic condensation of formaldehyde.

4. Wender⁽¹⁸⁾

Direct homologation of methanol.

Fischer and Tropsch⁽¹⁻⁴⁾ suggested that higher alcohols are formed from methanol through the following consecutive reactions:

and so forth for primary linear higher alcohols. Isoalcohols are formed by the transformation of acetic acid into acetone which then undergoes reduction to isopropylalcohol:

Figure 5.1.1.2-1 - Reactions of Carbon Monoxide and Hydrogen

A further addition of CO and H_2 to isopropylalcohol leads to the formation of isobutylalcohol.

Natta's hypothesis ⁽⁶⁾ implies that the catalysts play a fundamental role in the formation of intermediate fatty acid salts. A five-step consecutive sequence proceeds as follows:

1. Synthesis of methanol by ZnO catalysis:

2. Formation of potassium methylate by either reaction with alkali or alkali zincate:

3. Reaction of alkali methylate and CO with the formation of alkali acetate:

4. Hydrogenation of alkali acetate to alkali ethylate:

5. Hydrolysis of the alcoholate:

Morgan and coworkers ⁽⁷⁾ based their hypothesis upon the fact that a number of aldehydes, including unsaturated and hydroxyaldehydes, have been identified in the synthesis product stream. Presumably, these aldehydes formed through the intermediate formation of fatty acid salts, as in the Natta mechanism. Morgan's hypothesis is that higher alcohols are formed through an aldolic condensation of formaldehyde as follows:

Wender and coworkers⁽²¹⁾ suggested a direct homologation mechanism based on their synthesis of ethanol in the presence of cobalt-base catalysts:

Methanol is more reactive towards homologation than ethanol and synthesis products, therefore, should be richer in ethanol if this mechanism were correct, but this is in contrast with experimental evidence. Natta⁽⁹⁾ has also hypothesized that methanol in place of olefin may participate in oxosynthesis reactions. In other words, Wender's homologation mechanism can be considered as belonging to the oxosynthesis reaction type if the formation of free methylene radicals through dehydration of methanol is assumed:

Further homologation of ethanol by formation of ethylidene radicals can hydroformylate to form propanol and so on. However, the rate of reaction of these higher homologations becomes decreasingly lower as carbon number increases.

Several other hypotheses have been formulated by various investigators but none of them appear to be entirely satisfactory. A review of these is presented by Emmett⁽¹¹⁾ From these reviews, the following conclusions can be made:

1. Methanol is an intermediate product in the synthesis of higher alcohols;
2. Higher alcohol synthesis is a strong function of basicity of the catalyst;
3. Above 400°C with ZnO-base catalysts, isobutanol and n-propanol are formed in large proportions along with methanol;
4. Below 400°C, higher alcohols can be produced when using certain transition metal catalysts (in particular, metals of the iron group);
5. Catalysis with metals of the iron group (or with ThO₂) results in hydrocarbon formation together with higher alcohols. With ZnO-base catalysts in the absence of iron group metals and dehydrating catalysts (like alumina), the formation of hydrocarbons is almost completely prevented.

A review of more recent literature (1970 to present) will be presented in the next quarterly report.

5.1.1.3 Chem Systems Approach

Chem Systems has been heavily involved in catalyst development for conversion of synthesis gases to a variety of chemical products. In the past few years, we have been developing a liquid-phase methanol (LPMeOH) synthesis process under EPRI support. As an outgrowth of our LPMeOH experiences, we have been investigating the effectiveness of catalysts comprised of a Fischer-Tropsch element and a low pressure methanol synthesis catalyst for the production of C₁-C₄ alcohol mixtures ("alkanols"). In particular, our approach is based on improvements of the catalyst system claimed by IFP which consists of copper, cobalt, and zinc promoted by 1) an alkali element and by 2) one or more of the following elements: V, Cr, Mn, Fe, Zr, Ti, Th, In or Ce.

5.1.2 Experimental Procedures

The catalytic activity of proposed catalyst formulations for the synthesis of higher alcohols was originally to be tested in a 3" ID Berty reactor. This reactor provides a high internal recirculation of feed and product gases through the catalyst bed and minimizes the thermal and concentration gradients common in other types of reactors. Both the reaction rate and mass velocities that occur in commercial catalytic reactors can be accurately reproduced in the Berty reactor.

Due to a long delivery time of the Berty reactor, it was decided early in the program to set up a fixed-bed mini reactor unit to enable preliminary screening of catalysts. A schematic of the mini reactor unit presently being used is shown in Figure 5.1.2-1.

The mini reactor (Figure 5.1.2-2) was fabricated from 1" schedule 80 stainless steel pipe (Type 316L). One inch Swagelok connectors were welded to both ends of a 4" long pipe. The reactor volume is approximately 75 ml.

The reactor was heated and maintained at reaction temperature in a sand bath (Techne Model SBL-2D) controlled by a single ECS Model 6821 solid state controller. The temperature gradient between the top and bottom of the sand bath was less than 10°C during steady-state operation.

Two on-line chromatographs were used to analyze the reactor effluent gases. The unreacted feed gas (including H₂, CO, CO₂) and light hydrocarbons (CH₄, C₂H₆, C₂H₄, etc.) were analyzed on a Carle 311H (TCD) instrument using Porapak QS and Mol Sieve 5A columns. The organic products including alcohols, esters, aldehydes were quantified on a Hewlett-Packard 5720A (FID) instrument using a Porapak QS column. To keep the effluent in vapor-phase, the exit lines from the reactor and back pressure regulator were heat traced to about 150°C.

FIGURE 5.1.2-1

SCHEMATIC OF FIXED-BED, PLUG-FLOW REACTOR SYSTEM

FIGURE 5.1.2-1
SCHEMATIC OF FIXED-BED, PLUG-FLOW REACTOR SYSTEM

Catalyst charge to the reactor consisted of approximately 75 ml of a mixture of 25% catalyst and 75% inert support (alumina beads, Rhodia SCS-9, 2-4 mm OD). The function of the inert support was to improve heat transfer characteristics of the reactor and increase the VHSV so as to control the reaction exotherm within 10°C .

The catalyst was reduced according to established procedures for activating methanol catalysts. Initially the catalyst temperature was brought to $\sim 195^{\circ}\text{C}$ with nitrogen purge at a VHSV of $\sim 1000\text{ hr}^{-1}$ (NTP). Then the reduction gas consisting of 2% H_2 and 98% N_2 was introduced at $\sim 500\text{ hr}^{-1}$ VHSV. This condition was maintained for approximately 16-24 hrs until the effluent H_2 concentration was the same as in the feed gas. The catalyst temperature was then raised in 10° increments until a final bed temperature of $245\text{-}250^{\circ}\text{C}$ was reached. At each temperature level, the H_2 concentration in the effluent was allowed to equilibrate to that of the reduction gas before raising the temperature by another 10° increment. The catalyst was put under nitrogen blanket after the reduction was completed and maintained at $\sim 200^{\circ}\text{C}$.

In early tests, the reactor was pressurized with nitrogen to 900 psig. At this pressure, the feed gas having the composition similar to a steam reformer gas, i.e. 66% H_2 , 19% CO , 13% CO_2 and 2% N_2 , was introduced at a rate equivalent to a VHSV of $\sim 4000\text{ hr}^{-1}$. It took about 2-4 hours to purge nitrogen from the reactor to the concentration in the feed gas. Due to this delay, the feed gas was directly used to pressurize the reactor. The catalyst temperature was then adjusted to that of the first data point (usually 240°C). Argon was later substituted for nitrogen as an internal standard in the feed gas to improve the accuracy of the material balance calculations.

The effluent gas was monitored at each data point to determine the conversion and selectivity level. The temperature was raised in 10° increments up to 280°C for most runs. If the CO conversion was low, the temperature was raised even further to 320°C . At the end of the run, the reactor was depressurized, and the spent catalyst was recovered for subsequent examination.

5.1.3 Preparation of Catalysts

A total of fifteen catalysts comprising compositions of $\text{Cu}_1\text{Zn}_{0-2}\text{Cr}_{0.8-4}\text{Co}_{0.25-4}\text{K}_{0.09-0.45}$ were prepared by the end of December, 1979. Details of these catalysts are given in Table 5.1.3-1.

Two preparation methods were used. Most of the catalysts were prepared via the evaporation method. The nitrate or carbonate salts of copper, zinc, chromium and cobalt were dissolved in deionized water, then evaporated, dried and finally calcined in air to produce the metal oxides. When using this method, the relative ratios of copper, zinc, chromium and cobalt in the final catalyst are the same as in the starting solution. On the other hand, when using the precipitation method, high levels of Cu, Zn, Cr, and CO were found in the mother liquor after precipitation of the catalyst.

The following is a brief description of preparation for each catalyst:

Table 5.1.3-1

<u>Catalyst</u>	<u>Formulation</u>	<u>Preparation Method</u>	<u>Tested In</u>
197-1	$\text{Cu}_1\text{Zn}_0\text{Cr}_{0.8}\text{Co}_1\text{K}_{0.09}$	Evaporation	Run 194-39
197-2	$\text{Cu}_1\text{Zn}_{0.125}\text{Cr}_1\text{Co}_1\text{K}_{0.11}$	Evaporation	Run 194-62
197-4	$\text{Cu}_1\text{Zn}_{0.125}\text{Cr}_1\text{Co}_1\text{K}_{0.11}$	Ppt. w/ Na_2CO_3	Run 194-71
197-6	$\text{Cu}_1\text{Zn}_{0.125}\text{Cr}_1\text{Co}_1\text{K}_{0.11}$	Ppt. w/ NH_4OH	
197-8	$\text{Cu}_1\text{Zn}_{0.125}\text{Cr}_1\text{Co}_{0.5}\text{K}_{0.11}$	Evaporation	
197-9	$\text{Cu}_1\text{Zn}_{0.5}\text{Cr}_1\text{Co}_{0.5}\text{K}_{0.11}$	Evaporation	Run 194-79
197-10	$\text{Cu}_1\text{Zn}_{0.5}\text{Cr}_4\text{Co}_1\text{K}_{0.45}$	Evaporation	Run 194-87
197-11	$\text{Cu}_1\text{Zn}_{0.125}\text{Cr}_1\text{Co}_{0.25}\text{K}_{0.11}$	Evaporation	Run 194-91
197-12	$\text{Cu}_1\text{Zn}_2\text{Cr}_4\text{Co}_1\text{K}_{0.45}$	Evaporation	
197-13	$\text{Cu}_1\text{Zn}_{0.5}\text{Cr}_1\text{Co}_{0.25}\text{K}_{0.11}$	Evaporation	
197-14	$\text{Cu}_1\text{Zn}_{0.5}\text{Cr}_4\text{Co}_4\text{K}_{0.45}$	Evaporation	
197-15	$\text{Cu}_1\text{Zn}_2\text{Cr}_4\text{Co}_4\text{K}_{0.45}$	Evaporation	
197-16	$\text{Cu}_1\text{Zn}_{0.5}\text{Cr}_1\text{Co}_1\text{K}_{0.11}$	Evaporation	
197-17	$\text{Cu}_1\text{Zn}_{0.125}\text{Cr}_1\text{Co}_1\text{K}_{0.11}$	Evaporation	
197-18	$\text{Cu}_1\text{Zn}_{0.77}\text{Cr}_4\text{Co}_1\text{K}_{0.45}$	Evaporation	Run 194-83

197-1: $\text{Cu}_1\text{Zn}_0\text{Cr}_{0.8}\text{Co}_1\text{K}_{0.09}$

The first catalyst to be prepared was one described in US Patent 4,122,110 issued to IFP having an atomic ratio of $\text{Cu}_1\text{Cr}_{0.8}\text{Co}_1\text{K}_{0.09}$.

To a mixture of 80 gms of CrO_3 , 241.5 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 128.1 gms of cobalt carbonate, 225 ml deionized water was added, stirring occasionally. After gas evolution stopped, 50 gms of citric acid monohydrate were added. The resulting solution was first dried at 200°C for 2 hrs, and then calcined in air at 450°C for 3 hrs. The resulting powder was pelletized* into 3/16" x 1/8" tablets. These tablets were then impregnated with KOH solution to introduce 2% wt K as K_2O , and calcined again at 400°C for 2 hrs.

197-2: $\text{Cu}_1\text{Zn}_{0.125}\text{Cr}_1\text{Co}_1\text{K}_{0.11}$

A mixture of 120.8 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 18.6 gms of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 145.5 gms of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 200 gms of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 3.9 gms of K_2CO_3 was dissolved in 250 ml of deionized water. To this solution, 30 gms of citric acid monohydrate was added. The resulting solution was first evaporated to dryness, then further dried at 200°C for 2 hrs, and finally calcined in air at 450°C for 3 hrs. The resulting black powder was pelletized into 3/16" x 1/8" tablets, and calcined again at 400°C for 2 hrs.

197-4: $\text{Cu}_1\text{Zn}_{0.125}\text{Cr}_1\text{Co}_1\text{K}_{0.11}$

A mixture of 120.8 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 18.6 gms of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 145.5 gms of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 200 gms of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in ~1000 ml of deionized water. To this aqueous solution, approximately 500 ml of hot sodium

*The calcined metal oxides were ground in a mortar and pestle with Sterotex HM (equivalent to 2-4% wt of the oxides) to -50 mesh powder. The resulting fine black powder was pelletized using Stokes' single punch pelletizer into 3/16" x 1/8" tablets. The Sterotex HM was used as binder and lubricant for the pelletization. It was later burned off at 400°C for 2 hrs.

carbonate solution containing 230.5 gms of Na_2CO_3 was added under vigorous stirring. The resulting precipitate was filtered and washed with ~9 liters of deionized water.

The filter cake was dried at 120°C overnight, and then slurried into ~50 ml solution containing 3.9 gms of K_2CO_3 . The slurry was dried at 120°C initially for 2 hrs, then calcined at 450°C for 3 hrs. The resulting black powder was pelletized into 3/16" x 1/8" tablets.

197-6: $\text{Cu}_1\text{Zn}_{0.125}\text{Cr}_1\text{Co}_1\text{K}_{0.11}$ —

A mixture of 116.3 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 2 \frac{1}{2}\text{H}_2\text{O}$, 18.6 gms of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 145.5 gms of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 200 gms of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in ~1000 ml of deionized water. To this aqueous solution, 228 gms of NH_4OH (28.3% wt NH_3) were added dropwise under vigorous stirring. The resulting precipitate was filtered and washed with ~2 liters of deionized water.

The filter cake was dried at 120°C overnight, and then slurried into ~50 ml solution containing 3.6 gms of KOH . The slurry was dried at 120°C to dryness and calcined at 450°C for 3 hrs. The resulting black powder was then pelletized into 3/16" x 1/8" tablets.

197-8: $\text{Cu}_1\text{Zn}_{0.125}\text{Cr}_1\text{Co}_{0.5}\text{K}_{0.11}$ —

A mixture of 87.2 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 2 \frac{1}{2}\text{H}_2\text{O}$, 150 gms of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 54.6 gms of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 14 gms of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 4.2 gms of KNO_3 was dissolved in ~500 ml of deionized water.

To this solution, 19.5 gms of citric acid monohydrate were added. The resulting solution was first evaporated, then dried at 200°C for 2 hrs, and finally calcined at 450°C for 3 hrs. The resulting black powder was pelletized into 3/16" x 1/8" tablets.

197-9: $\text{Cu}_1\text{Zn}_{0.5}\text{Cr}_1\text{Co}_{0.5}\text{K}_{0.11}$ —

A mixture of 116.3 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 2 \frac{1}{2}\text{H}_2\text{O}$, 200.1 gms $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 72.5 gms $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 74.4 gms of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 5.6 gms of KNO_3 was dissolved in ~500 ml of deionized water. Then 29.4 gms of citric acid monohydrate were added.

The remaining steps are the same as those described for Prep. 197-8.

197-10: $\text{Cu}_1\text{Zn}_{0.5}\text{Cr}_4\text{Co}_1\text{K}_{0.45}$

To a mixture of 116.3 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 2 \frac{1}{2}\text{H}_2\text{O}$, 28.8 gms of ZnCO_3 (70.8% ZnO), 63.6 gms of cobalt carbonate, and 200 gms of CrO_3 , ~200 ml of deionized water were added with occasional stirring. After gas evolution stopped, 68.3 gms of citric acid monohydrate were added. The resulting solution was then dried at 200°C for 2 hrs, and calcined at 450°C for 3 hrs. The resulting powder was pelletized into 3/16" x 1/8" tablets.

The tablets were impregnated with KOH solution to introduce 4.85% wt K as K_2O , and calcined again at 400°C for 2 hrs.

197-11: $\text{Cu}_1\text{Zn}_{0.125}\text{Cr}_1\text{Co}_{0.25}\text{K}_{0.11}$

To a mixture of 232.6 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 2 \frac{1}{2}\text{H}_2\text{O}$, 14.4 gms of ZnCO_3 (70.8% ZnO), 31.8 gms of cobalt carbonate (46.25% wt Co), and 100 gms of CrO_3 , ~200 ml of deionized water were added with occasional stirring. After gas evolution stopped, 50.4 gms of citric acid monohydrate were added. The resulting solution was dried at 200°C for 2 hrs, and calcined at 450°C for 3 hrs. The resulting powder was then pelletized into 3/16" x 1/8" tablets.

The tablets were impregnated with KOH solution to introduce 3.0% wt K as K_2O , and calcined again at 400°C for 2 hrs.

197-12: $\text{Cu}_1\text{Zn}_2\text{Cr}_4\text{Co}_1\text{K}_{0.45}$

To a mixture of 58.2 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 2 \frac{1}{2}\text{H}_2\text{O}$, 57.7 gms of ZnCO_3 , 31.8 gms of cobalt carbonate and 100 gms of CrO_3 , ~200 ml of deionized water were added stirring occasionally. After gas evolution stopped, 42 gms of citric acid monohydrate were added. The resulting solution was then dried first at 200°C for 2 hrs, and calcined at 450°C for 3 hrs. The resulting powder was then pelletized into 3/16" x 1/8" tablets.

The tablets were impregnated with KOH solution to introduce 3.7% wt K as K_2O , and calcined again at 400°C for 2 hrs.

197-13: $\text{Cu}_1\text{Zn}_{0.5}\text{Cr}_1\text{Co}_{0.25}\text{K}_{0.11}$

To a mixture of 116.3 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 2 \frac{1}{2}\text{H}_2\text{O}$, 28.8 gms of ZnCO_3 , 15.9 gms of cobalt carbonate, and 50 gms CrO_3 , ~200 ml of deionized water were added with occasional stirring. After gas evolution stopped, 29.4 gms of citric acid monohydrate were added. The resulting solution was dried at 200°C , and calcined at 450°C for 3 hrs. The resulting powder was then pelletized into $3/16"$ x $1/8"$ tablets.

The finished tablets were impregnated with KOH solution to introduce 2.6% wt K as K_2O , and calcined at 400°C for 2 hrs.

197-14: $\text{Cu}_1\text{Zn}_{0.5}\text{Cr}_4\text{Co}_4\text{K}_{0.45}$

To a mixture of 58.2 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 2 \frac{1}{2}\text{H}_2\text{O}$, 14.4 gms of ZnCO_3 , 127.3 gms of cobalt carbonate, and 100 gms of CrO_3 , ~200 ml of deionized water were added with occasional stirring. After gas evolution stopped, ~50 gms of citric acid monohydrate were added. The resulting solution was then dried at 200°C for 2 hrs and calcined at 450°C for 3 hrs. The resulting powder was pelletized into $7/32"$ x $1/8"$ tablets.

The tablets were impregnated with KOH solution to introduce 3.2% wt K as K_2O , and calcined again at 400°C for 2 hrs.

197-15: $\text{Cu}_1\text{Zn}_2\text{Cr}_4\text{Co}_4\text{K}_{0.45}$

To a mixture of 58.2 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 2 \frac{1}{2}\text{H}_2\text{O}$, 57.5 gms of ZnCO_3 , 127.3 gms of cobalt carbonate, and 100 gms of CrO_3 , ~200 ml of deionized water were added with occasional stirring. The resulting solution was dried first at 200°C for 2 hrs, and calcined at 450°C for 3 hrs. The resulting powder was then pelletized into $7/32"$ x $1/8"$ tablets.

These tablets were impregnated with KOH solution to introduce 2.7% wt K as K_2O , and calcined again at 400°C for 2 hrs.

197-16: $\text{Cu}_1\text{Zn}_{0.5}\text{Cr}_1\text{Co}_1\text{K}_{0.1}$ —

To a mixture of 116.3 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 2 \frac{1}{2}\text{H}_2\text{O}$, 28.8 gms of ZnCO_3 , 63.6 gms of cobalt carbonate, and 50 gms of CrO_3 , ~200 ml of deionized water were added with occasional stirring. After gas evolution stopped, 36.7 gms of citric acid monohydrate were added. The resulting solution was then dried at 200°C for 2 hrs, and calcined at 450°C for 3 hrs. The resulting black powder was pelletized into 7/32" x 1/8" tablets.

These tablets were impregnated with KOH solution to introduce 2.0% wt K as K_2O , and calcined again at 400°C for 2 hrs.

197-17: $\text{Cu}_1\text{Zn}_{0.125}\text{Cr}_1\text{Co}_1\text{K}_{0.11}$ —

To a mixture of 116.3 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 2 \frac{1}{2}\text{H}_2\text{O}$, 7.2 gms of ZnCO_3 , 63.6 gms of cobalt carbonate, and 50 gms of CrO_3 , ~200 ml of deionized water were added with occasional stirring. After gas evolution stopped, 32.7 gms of citric acid monohydrate were added. The resulting solution was first dried at 200°C for 2 hrs, and calcined at 450°C for 3 hrs. The resulting powder was pelletized into 7/32" x 1/8" tablets.

These tablets were impregnated with KOH solution to introduce 2.3% wt K as K_2O , and calcined again at 400°C for 2 hrs.

197-18: $\text{Cu}_1\text{Zn}_{0.77}\text{Cr}_4\text{Co}_1\text{K}_{0.45}$ —

To a mixture of 116.3 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 2 \frac{1}{2}\text{H}_2\text{O}$, 44.4 gms of ZnCO_3 , 63.6 gms of cobalt carbonate, and 200 gms of CrO_3 , ~200 ml of deionized water were added with occasional stirring. After gas evolution stopped, 63.8 gms of citric acid monohydrate were added. The resulting solution was dried at 200°C for 2 hrs, and calcined at 450°C for 3 hrs. The resulting powder was pelletized into 3/16" x 1/8" tablets.

These tablets were then impregnated with KOH solutions to introduce 4.4% wt K as K_2O , and calcined again at 400°C for 2 hrs.

Catalyst Characterization

Detailed catalyst characterization will be confined to those catalyst preparations which we believe to be promising as regards activity and selectivity (initial) towards synthetic transportation fuels. To date, partial catalyst characterization data are available only on Preparations #197-1 and 197-2, which are summarized in Table 5.1.3-2 below and Table 5.1.3-3.

Table 5.1.3-2

Catalyst Characterization Data

<u>Catalyst No.</u>	<u>Formula</u>	<u>B.E.T. Area m²/gm</u>	<u>Total Pore Volume cc/gm</u>
197-2	$\text{CuZn}_{0.125}\text{CrCoK}_{0.11}$	8.13	0.065
197-1	$\text{CuCr}_{0.8}\text{CoK}_{0.09}$	24.0	0.17

The overall surface area of #197-2 catalyst is about a third that of #197-1 catalyst. This decrease appears to be associated with a sharp decrease in the amount of medium-sized pores (10-50 nm diameter). The amount of large pores (over 55 nm) and small pores (less than 10 nm) does not seem to be that much different. Both catalysts were produced by the evaporation technique, and we have no explanation at the present time for the measured differences in surface area and pore volume between these two catalysts. Atomic absorption analyses of these two catalysts confirmed the calculated atomic formulas determined during the catalyst preparation steps.

As the catalyst development phase progresses, we will be obtaining more catalyst characterization data which will be reported in future quarterly progress reports.

Table 5.1.3-3
Pore Volume Data for Fresh Catalysts

<u>Average Diameter, Å</u>	<u>Cumulative Pore Volume, cc/gm</u>	
	<u>Catalyst #197-1</u>	<u>Catalyst #197-2</u>
550.0	0.004	0.019
475.0	0.009	0.025
425.0	0.014	0.033
375.0	0.021	0.042
325.0	0.034	0.048
290.0	0.040	0.051
270.0	0.048	0.052
250.0	0.058	0.054
230.0	0.070	0.056
210.0	0.085	0.057
190.0	0.103	0.058
170.0	0.124	0.059
155.0	0.135	0.059
145.0	0.145	0.060
135.0	0.150	0.060
125.0	0.156	0.060
115.0	0.162	0.061
105.0	0.164	0.061
97.5	0.165	0.061
92.5	0.167	0.061
87.5	0.167	0.061
82.5	0.167	0.062
77.5	0.168	0.062
72.5	0.169	0.062
67.5	0.169	0.062
62.5	0.169	0.062
57.5	0.169	0.062
52.5	0.169	0.062
47.5	0.169	0.063
42.5	0.169	0.063
37.5	0.170	0.063
32.5	0.170	0.063
27.5	0.171	0.064
22.5	TOTAL = 0.172	TOTAL = 0.065

Basis: N₂ Desorption Pore Volume Distribution using a Digisorb 2500.

5.1.4 Experimental Results:

Of the fifteen catalysts prepared, seven catalysts were tested during this quarter. All the tests were made in the vapor-phase, fixed-bed, plug-flow reactor unit described earlier.

Run 194-39: Evaluation of IFP Catalyst (Prep. 197-1)

The catalyst has a composition of $\text{Cu}_1\text{Cr}_{0.8}\text{Co}_1\text{K}_{0.09}$. The initial attempt to test this catalyst was unsuccessful because the reaction temperature could not be properly controlled due to the high heat of reaction. To overcome this problem, the catalyst concentration was reduced by diluting with inerts (i.e., 25% catalyst/75% inerts by volume). Approximately 10 ml (14.9 gm) of catalyst Prep. 197-1 was randomly mixed with 30 ml of inert material (Rhodia SCS-9, 2-4 MM OD). The catalyst was then reduced following the standard procedure described previously.

After the reduction was completed, the reactor was pressurized with nitrogen to 940 psig at 130°C. Feed gas having the composition of 66% H_2 , 19% CO, 13% CO_2 and 2% N_2 was then introduced at a rate corresponding to a VHSV of 4000 hr^{-1} based on the volume of the catalyst. The effluent gas was continuously analyzed through the on-line gas chromatograph. When the nitrogen was completely displaced in the reactor system, a temperature scan covering the range of 250-280°C was carried out. At the reactor temperature of 280°C, a hot spot of 325°C was observed.

A steady state liquid product was collected at 270°C (hot spot at 275°C) in two glass cold traps in a dry ice-acetone bath. This point was designated as Run 194-39-17. The analysis of the liquid products collected from Run 194-39-17 is given in Table 5.1.4-1. The analysis indicates that the main products of this reaction are methanol, ethanol, n-propanol, n-butanol and some n-pentanol and n-hexanol. Due to the accumulation of liquids in the exit lines, it was not possible to obtain a reliable measure of the liquid yields directly. However, since an accurate analysis of the quantity of CO_2 and light hydrocarbons including CH_4 , C_2H_6 and C_2H_4 was available, the yields to liquid products could be estimated by difference calculations. The run results are given in Table 5.1.4-2.

The spent catalyst appeared to be in good shape, and weighed 13.8 gms. The recovery of the catalyst was 100% of the theoretical amount if we assume that only copper was reduced to metal, and all other components remained as oxides.

Table 5.1.4-1

Analysis of Liquid Products (Run 194-39-17)

<u>Compound</u>	<u>Weight % *</u>
Methanol	38.9
Ethanol	37.3
Methyl Acetate	0.5
1-Propanol	13.3
Ethyl Acetate	0.2
sec-Butanol	0.1
n-Hexane	0.1
1-Butanol	5.3
2&3 Pentanol	0.1
n-Heptane	0.2
1-Pentanol	2.3
n-Octane	0.1
1-Hexanol	0.7
n-Nonane	0.1
	<hr/> 99.8%

*GC analysis, normalized to an H₂O-free basis

Table 5.1.4-2

Summary For Run 194-39

Temperature: 260, 270, 280°C

Pressure: 955 psia

VHSV: 3900 hr⁻¹ (@ 20°C & 1 atm) (Based on undiluted catalyst)

Feed Rate: 39 liters/hr

Hours on Stream:		22.6	33.0	35.2
		Effluent, Mole%		
	Feed Mole%	260°C	270°C	280°C
H ₂	66.7	64.5	64.0	57.4
CO	18.5	16.3	15.2	5.9
CO ₂	12.8	15.4	16.0	23.1
N ₂	2.0	2.5	2.4	2.9
CH ₄	--	1.3	2.2	10.0
C ₂ H ₆	--	--	0.2	0.7
	100.0	100.0	100.0	100.0
Conversion of CO		30.0%	31.5%	78.0%
	H ₂	23.0%	20.0%	41.0%
	CO ₂	4.0%	-4.2%	-24.0%
Carbon Selectivity to CO ₂		--	9.1%	21.7%
	Methane	17.5%	31.4%	47.8%
	Ethane	--	5.7%	6.7%
Liquid Products		82.5%	53.8%	23.8%
(by difference)				

Run 194-62: $\text{Cu}_1\text{Zn}_{0.125}\text{Cr}_1\text{Co}_1\text{K}_{0.11}$ (Prep. 197-2)

The reactor was loaded with a mixture of 10 ml (16.8 gms) of catalyst Prep. 197-2 and 30 ml of inert material. After the reduction was completed following the standard procedure, the catalyst was tested at 945 psig, $\sim 3900 \text{ hr}^{-1}$ VHSV, and temperatures from 240°C to 290°C by 10° increment.

A steady-state liquid product was collected at 290°C (hot spot at 295°C). This point was designated as Run 194-62-7. The analysis on the liquid products collected from Run 194-62-7 is given in Table 5.1.4-3. No attempt was made to identify the unknowns in the liquid products. The run summary at each temperature level is also given in Table 5.1.4-4.

Some of the spent catalyst appeared partially broken when examined. The catalyst weighed 15.8 gms. The recovery of the catalyst was $\sim 101.2\%$ of the theoretical amount if only copper was reduced to metal.

Table 5.1.4-3

Analysis of Liquid Product (Run 194-62-7)

<u>Compound</u>	<u>Weight %*</u>
Methanol	35.8
Ethanol	37.5
1-Propanol	8.3
1-Butanol	2.8
1-Pentanol	1.4
1-Hexanol	0.6
Methyl Acetate	2.5
Ethyl Acetate	1.2
Methyl Propionate	1.2
Unknowns	<u>8.6</u>
	99.9

*GC analysis, normalized to an H_2O -free basis

Table 5.1.4-4

Summary For Run 194-62

Temperature: 240, 250, 260, 270, 280, 290°C

Pressure: 960 psia

VHSV: $\sim 3700 \text{ hr}^{-1}$ (@ 20°C & 1 atm)

Feed Rate: 37.1 liters/hr

Hours on Stream:

3.3

4.0

4.7

5.2

6.3

16.0

	Feed, Mole%	Effluent, Mole%					
		240°C	250°C	260°C	270°C	280°C	290°C
H ₂	67.01	66.89	66.66	66.31	66.27	64.65	61.36
CO	18.36	18.14	17.92	17.68	16.67	14.73	11.17
CO ₂	12.63	12.77	12.97	13.26	14.01	16.59	20.73
N ₂	2.00	2.20	2.20	2.26	2.29	2.37	2.53
CH ₄	--	--	0.25	0.49	0.76	1.60	3.81
C ₂ H ₄	--	--	--	--	--	0.06	0.16
C ₂ H ₆	--	--	--	--	--	--	0.25
	100.0						

Conversion of CO	10.2%	11.3%	14.8%	20.7%	32.3%	51.9%
H ₂	9.3%	9.6%	12.4%	13.6%	18.6%	27.6%
CO ₂	8.1%	6.7%	7.1%	3.1%	-10.8%	-29.8%
Carbon Selectivity to CO ₂	--	--	--	--	23.1%	39.4%
Methane	--	7.8%	12.0%	15.8%	22.8%	31.6%
C ₂ H ₄ + C ₂ H ₆	--	--	--	--	1.6%	6.8%
Liquid Products (by difference)	100.0	92.2%	88.0%	84.2%	52.5%	22.2%

Run 194-71: $\text{Cu}_{.1}\text{Zn}_{0.125}\text{Cr}_{.1}\text{Co}_{.1}\text{K}_{0.11}$ (Prep. 197-4)

To collect more liquid products, the entire volume of the reactor was loaded with a mixture of 18.5 ml (24.3 gms) of catalyst Prep. 197-4 and 55.5 ml of inert material. After the reduction was completed following the standard procedure, the reactor was directly pressurized with the feed gas to 940 psig. The catalyst was then tested at $\sim 4100 \text{ hr}^{-1}$ VHSV, and 250, 260, 270°C.

A steady state liquid product was collected at 270°C (hot spot at 273°C). This point was designated as Run 194-71-3. The analysis on this liquid products is given in Table 5.1.4-5. The summary for Run 194-71 is also given in Table 5.1.4-6.

The spent catalyst weighed 22.7 gms. Catalyst recovery was 100.4% of the theoretical amount.

Table 5.1.4-5

Analysis of Liquid Product (Run 194-71-3)

<u>Compound</u>	<u>Weight, % *</u>
Methanol	27.8
Ethanol	34.9
n-Propanol	17.5
n-Butanol	9.5
n-Pentanol	3.2
Other Organics**	<u>7.1</u>
	100.0

*GC analysis, normalized to an H_2O -free basis

**Including esters, aldehydes, and unknowns

Table 5.1.4-6

Summary For Run 194-71

Temperature: 250, 260, 270°C

Pressure: 955 psia

VHSV: 4130 hr⁻¹ (@ 20°C & 1 atm)

Feed Rate: 76.4 liters/hr

Hours on Stream:		3.0	4.7	7.1
		<u>Effluent, Mole%</u>		
	<u>Feed, Mole%</u>	<u>250°C</u>	<u>260°C</u>	<u>270°C</u>
H ₂	66.8	67.80	67.64	66.46
CO	18.5	17.46	16.64	15.90
CO ₂	12.7	12.37	12.91	14.12
N ₂	2.0	2.13	2.17	2.21
CH ₄	--	0.24	0.64	1.23
C ₂ H ₆	--	--	--	0.08
	100.0			
Conversion of CO		11.4%	17.1%	22.2%
	H ₂	4.6%	6.6%	9.9%
	CO ₂	8.9%	6.7%	-0.2%
Carbon Selectivity to CO ₂		--	--	0.7%
	CH ₄	6.9%	14.7%	27.1%
	C ₂ H ₆	--	--	3.5%
	Liquid Products	93.1%	85.3%	68.7%
	(by difference)			

Run 194-79: Cu₁Zn_{0.5}Cr₁Co_{0.5}K_{0.1} (Prep. 197-9)

A mixture of 10.5 ml (18.5 gms) of catalyst Prep. 197-9 and 55.4 ml of inert material was loaded into the reactor. The catalyst was reduced following the standard procedure, and then tested at 910 psig, $\sim 4000 \text{ hr}^{-1}$ VHSV and temperatures of 240, 250, 260, 270, 280°C.

In an effort to improve the accuracy of the gas analysis, argon was substituted as an internal standard in the feed gas. The new feed gas consists of 60.5% H₂, 17.5% CO, 12% CO₂ and 10% Ar. A pair of 75 ml sampling bombs was installed on the reactor exit to collect the liquid product under pressure. A cooling coil assembly was also installed to condense the product prior to the sampling bombs.

A steady state was maintained at 270°C for 2 hrs, but no liquid product was collected. The summary for Run 194-79 is given in Table 5.1.4-7.

The spent catalyst appeared in good shape, and weighed 16.8 gms. The catalyst recovery was 98.4% of the theoretical amount.

Table 5.1.4-7

Summary For Run 194-79

Temperature: 240, 250, 260, 270, 280°C

Pressure: 925 psia

VHSV: ~4000 hr⁻¹ (@ 20°C & 1 atm)

Feed Rate: 41.7 liters/hr

Hours on Stream:		2.2	3.4	4.3	5.5	6.8
		Effluent, Mole%				
	Feed, Mole%	240°C	250°C	260°C	270°C	280°C
H ₂	62.6	62.58	62.08	61.94	61.47	59.54
CO	16.7	16.46	16.40	16.11	15.59	14.83
CO ₂	11.5	11.64	11.80	11.91	12.35	14.08
Ar	9.2	9.32	9.44	9.60	9.79	10.03
CH ₄	--	--	0.28	0.44	0.80	1.39
C ₂ H ₄	--	--	--	--	--	0.03
C ₂ H ₆	--	--	--	--	--	0.10
	<u>100.0</u>					

Conversion of CO	3.1%	4.7%	7.9%	12.6%	18.9%
H ₂	1.5%	3.5%	5.3%	7.9%	12.9%
CO ₂	0.5%	0.4%	1.1%	-0.5%	-11.9%

Carbon Selectivity to CO ₂	--	--	--	2.8%	43.4%
CH ₄	--	33.0%	28.9%	35.5%	40.3%
C ₂ H ₄ + C ₂ H ₆	--	--	--	--	7.5%
Liquid Products (by difference)	100.0	67.0%	71.1%	61.7%	8.8%

Run 194-83: $\text{Cu}_1\text{Zn}_{0.77}\text{Cr}_4\text{Co}_1\text{K}_{0.45}$ (Prep. 197-18)

A mixture of 18.5 ml (23.7 gm) of catalyst Prep. 197-18 and 55.5 ml of inert material was loaded into the reactor. After the reduction was completed following the standard procedure, the catalyst was tested at 905 psig, $\sim 3900 \text{ hr}^{-1}$ VHSV, and temperatures from 250°C to 320°C by 10° increment.

This catalyst appeared quite inactive under these test conditions. No conversion of CO was observed at all temperature levels. Only a low level conversion of CO_2 was observed. This seemed to increase with temperature. At 320°C , the conversion of CO_2 reached 6.3%. The summary for this run is given in Table 5.1.4-8.

The spent catalyst weighed 23.1 gms. Catalyst recovery was 100% of the theoretical amount.

Table 5.1.4-8

Summary For Run 194-83

Temperature: 270, 290, 310, 320°C

Pressure: 920 psia

VHSV: 3916 hr^{-1} (@ 20°C & 1 atm)

Feed Rate: 72.4 liters/hr

Hours on Stream: 3.6 6.3 7.4 8.0

	Feed, Mole%	Effluent, Mole%			
		270°C	290°C	310°C	320°C
H_2	62.1	62.1	61.9	61.6	61.5
CO	16.9	17.0	17.3	17.7	17.8
CO_2	11.7	11.6	11.5	11.3	11.2
Ar	9.3	9.3	9.4	9.4	9.5
	100.0				

Conversion of CO	-0.6%	-1.5%	-3.6%	-3.1%
H_2	$\sim 0.0\%$	0.9%	1.9%	3.1%
CO_2	0.9%	2.2%	4.4%	6.3

194-87: $\text{Cu}_1\text{Zn}_{0.5}\text{Cr}_4\text{Co}_1\text{K}_{0.45}$ (Prep. 197-10)

A mixture of 18.5 ml (26.9 gms) of catalyst Prep. 197-10 and 55.5 ml of inert support was loaded into the reactor. After the reduction was completed following the standard procedure, the catalyst was tested at 920 psig, $\sim 4000 \text{ hr}^{-1}$ VHSV, and 250, 260, 270, 280°C .

This catalyst was not active at the test conditions. Only a very low conversion of CO_2 was noted. However, at the end of the run, a small amount of liquid product (~ 2 gms) was collected. The analysis of that liquid is given in Table 5.1.4-9. The run summary is given in Table 5.1.4-10.

The spent catalyst weighed 26.6 gm. This catalyst recovery corresponds to 102% of the theoretical amount.

Table 5.1.4-9
Analysis of Liquid Product (Run 194-87)

<u>Compound</u>	<u>Weight, %</u>
Methanol	93.0
Ethanol	2.6
Pentanol	1.8
Ethyl Propionate	2.6
	<u>100.0</u>

*GC analysis, normalized to an H_2O -free basis

Table 5.1.4-10

Summary For Run 194-87

Temperature: 260, 270°C

Pressure: 935 psia

VHSV: 3933 hr⁻¹ (@ 20°C & 1 atm)

Feed Rate: 72.8 liters/hr

	<u>Feed, Mole%</u>	<u>Effluent, Mole%</u>	
		<u>260°C</u>	<u>270°C</u>
H ₂	61.5	61.4	61.6
CO	17.2	17.5	17.4
CO ₂	11.9	11.6	11.6
Ar	<u>9.4</u>	9.5	9.4
	100.0		
		<u>260°C</u>	<u>270°C</u>
Conversion of CO		-0.7%	-1.2%
H ₂		1.2%	~0.0%
CO ₂		3.6%	2.5%

Run 194-91: $\text{Cu}_1\text{Zn}_{0.125}\text{Cr}_1\text{Co}_{0.25}\text{K}_{0.11}$ (Prep. 197-11)

A mixture of 18.5 ml (25.8 gm) of catalyst Prep. 197-11 and 55.5 ml of inert support was loaded into the reactor, followed by the reduction according to the standard procedure described previously. The catalyst was tested at 910 psig, $\sim 4300 \text{ hr}^{-1}$ VHSV, and four different temperatures of 250, 260, 270 and 280°C .

An additional on-line gas chromatograph (Hewlett-Packard 5720A (FID)) was installed to the reactor exit line so that all condensible products could be directly quantified. The water content could be estimated from the product material balance, and compared to that obtained by Karl-Fisher titration on the collected liquid products.

No CO conversion was observed at all levels of temperature studied. The conversion level of CO_2 was 2.8% at 250°C (See Table 5.1.4-11), and reached 5.5% at 280°C . The result of direct liquid analysis is given in Table 5.1.4-10).

The spent catalyst weighed 23.8 gm. Catalyst recovery was 100.8% of the expected amount.

Table 5.1.4-11
Analysis of Liquid Product (Run 194-91)

<u>Compound</u>	<u>Weight %*</u>			
	<u>250$^\circ\text{C}$</u>	<u>260$^\circ\text{C}$</u>	<u>270$^\circ\text{C}$</u>	<u>280$^\circ\text{C}$</u>
Methanol	64.1	100.0	100.0	83.4
Ethanol	0.0	0.0	0.0	1.6
Propanol	0.0	0.0	0.0	7.0
Butanol	12.3	0.0	0.0	0.0
Pentanol	<u>23.6</u>	<u>0.0</u>	<u>0.0</u>	<u>8.0</u>
	100.0	100.0	100.0	100.0

*GC analysis, normalized to an H_2O -free basis

Table 5.1.4-12

Summary of Run 194-91

Temperature: 250, 260, 270, 280°C					
Pressure: 925 psia					
VHSV: 4163 hr ⁻¹ (@ 20°C & 1 atm)					
Feed Rate: 77.0 liters/hr					
Hours on Stream:		1.4	2.7	4.1	5.5
		<u>Effluent, Mole%</u>			
	<u>Feed, Mole%</u>	<u>250°C</u>	<u>260°C</u>	<u>270°C</u>	<u>280°C</u>
H ₂	62.0	61.75	61.7	61.7	61.5
CO	17.0	17.35	17.5	17.5	17.7
CO ₂	11.7	11.5	11.4	11.4	11.3
Ar	<u>9.3</u>	<u>9.4</u>	<u>9.4</u>	<u>9.4</u>	<u>9.5</u>
	100.0	100.0	100.0	100.0	100.0
Conversion of CO		-1.0%	-1.9	-1.9	-1.9
H ₂		1.5%	1.5	1.5	2.9
CO ₂		2.8%	3.6	3.6	5.5

5.1.5 Analysis of Results

During the period covered by this report, one of the prime tasks was to develop proper operating techniques for generating reliable and meaningful data. A vapor-phase, fixed-bed, plug-flow reactor was set up and used as a screening tool prior to the arrival of the Berty reactor.

One of the inherent disadvantages of a plug-flow, fixed-bed reactor when used for studying a highly exothermic reaction is the difficulty in controlling the reactor temperature and the prevention of temperature runaways. One method frequently used to moderate the reaction exotherm calls for dilution of the catalyst with an inert solid thereby reducing the catalyst concentration in the reactor. It was possible to control the reaction temperature by simply diluting the catalyst with an inert support in a volumetric ratio of catalyst/inert = 1/3 at CO conversions as high as 30% per pass. The same dilution was used with all the catalysts tested so far.

Another aspect that had to be carefully studied involved the development of reliable analytical procedures. Because of the size of the reactor, very small amounts of liquid are formed so that the quantitative collection of the liquid is difficult in short duration testing. At the present operating conditions, the liquid product rate is only about 1 gm/hr, and the liquids can be easily lost in the exit lines and back pressure regulator. Several modifications were made to the reactor system to overcome this difficulty, but we were still unable to obtain quantitative collection of the liquids.

In view of this, we decided to use two on-line gas chromatographs to quantify both gas and liquid products directly from the effluent. At any set of conditions, the feed and effluent compositions can be accurately determined by using an inert component such as N_2 or argon as an internal standard. Consumption of CO, CO_2 and H_2 can thus be determined. Also production of CH_4 and lower hydrocarbons can be estimated by difference. The direct on-line analysis of the alcohol products in vapor-phase allows for the determination of the product distribution and also the weight ratio of the various alcohols. This method of analysis when fully developed will provide a fast means for screening catalysts.

The results from seven test runs are summarized in Table 5.1.5-1. A single data point condition, at which a steady-state liquid product was collected, is reported for most runs. For Run 194-91, however, all four data points are listed, since the liquid product could be directly analyzed by the on-line gas chromatograph.

The first catalyst tested (Prep. 197-1) was based on one of the examples in US Patent 4,112,110. The results from Run 194-39 indicate that higher alcohols were definitely produced although the selectivities are lower than those claimed in the patent (See Table 5.1.5-2). At present, this divergence can not be readily explained although the catalyst was prepared following steps similar to those described in the patent, and also tested under conditions similar to those specified in the patent. The use of a different reactor system or even a different reduction procedure could cause such a divergence.

Table 5.1.5-2

Comparison of Product Distribution (Weight Basis)

	<u>U.S. Patent 4,112,110</u>	<u>Run 194-39-17</u>
Methanol	100.0	100.0
Ethanol	164.5	96.0
n-Propanol	82.9	35.9
i-Propanol	7.9	Trace
n-Butanol	59.2	13.7
i-Butanol	1.3	Trace
Others	1.3	11.2

The results of the other six catalysts tested are also shown in Table 5.1.5-1. The liquid products collected from Runs 194-62 and 194-71 indicate that higher alcohols were produced in selectivities close to those of Run 194-39. The catalysts used in these two runs have identical composition, but were prepared by two different methods: one catalyst (Prep. 197-2) was prepared by evaporation while the second catalyst (Prep. 197-4) was prepared by coprecipitation with Na_2CO_3 . Thus, the different results from Runs 194-62 and 194-71 may be attributed to the preparation method.

Table 5.1.5-1
HIGHER ALCOHOLS RUN SUMMARY

RUN NO.:	194-39	194-62	194-71	194-79
CATALYST:	#197-1 Cu ₁ Cr _{0.8} Co ₁ K _{0.09}	#197-2 Cu ₁ Zn _{0.125} Cr ₁ Co ₁ K _{0.11}	#197-4 Cu ₁ Zn _{0.125} Cr ₁ Co ₁ K _{0.11}	#197-9 Cu ₁ Zn _{0.5} Cr ₁ Co _{0.5} K _{0.11}
Temperature, °C	270	270	270	270
Pressure, PSIA	955	960	955	925
VHSV, Hr ⁻¹ (NTP)	3900	3354	4130	3967
Hours on Stream	33.0	16.0	7.1	5.5
Feed Composition, Mole %				
H ₂	66.7	67.01	66.8	62.6
CO	18.5	18.36	18.5	16.7
CO ₂	12.8	12.63	12.7	11.5
N ₂	2.0	2.00	2.0	---
Ar	---	---	---	9.2
CO Conversion	31.5	51.9	22.2	12.6
H ₂ Conversion	20.0	27.6	9.9	7.9
CO ₂ Conversion	-4.2	-29.8	-0.2	-0.5
Selectivities to (Mole %)				
CO ₂ (CO)	9.1	39.4	0.7	2.8
Methane	31.4	31.6	27.1	35.5
Light Hydrocarbons	5.7	6.8	3.5	0.0
Liquid Products*	53.8	22.2	68.7	61.7
Total	100.0	100.0	100.0	100.0
Liquid Composition Relative to Methanol (Methanol = 100)				No Liquid Products Collected
Methanol	100.0	100.0	100.0	
Ethanol	96.0	104.9	125.1	
Propanol	35.9	23.3	61.3	
Butanol	14.0	8.0	33.2	
C ₅ + Alcohols	8.0	5.4	10.1	
C ₅ + Hydrocarbons	1.3	0.0	0.0	
Others**	1.9	37.9	26.1	

*By Difference

**Including Esters, Aldehydes, Unknowns

Table 5.1.5-1
HIGHER ALCOHOLS RUN SUMMARY
(Continued)

RUN NO.:	194-83	194-87	194-91	194-91
CATALYST:	#197-18 Cu ₁ Zn _{0.77} Cr ₄ Co ₁ K _{0.45}	197-10 Cu ₁ Zn _{0.5} Cr ₄ Co ₁ K _{0.45}	197-11 Cu ₁ Zn _{0.125} Cr ₁ Co _{0.25} K _{0.11}	197-11 Cu ₁ Zn _{0.125} Cr ₁ Co _{0.25} K _{0.11}
Temperature, °C	320	270	250	260
Pressure, PSIA	920	935	925	925
VHSV, Hr ⁻¹ (NTP)	3916	3827	4163	4163
Hours on Stream	8.0	5.3	1.4	2.7
Feed Composition, Mole %				
H ₂	62.1	61.5	62.0	62.0
CO	16.9	17.2	17.0	17.0
CO ₂	11.7	11.9	11.7	11.7
N ₂	---	---	---	---
Ar	9.3	9.4	9.3	9.3
CO Conversion	-3.1	-1.2	-1.0	-1.9
H ₂ Conversion	3.0	-0.2	1.5	1.5
CO ₂ Conversion	6.3	2.5	2.8	3.6
Selectivities to (Mole %)				
CO ₂ (CO)	(71.3)	(66.5)	(51.6)	(74.4)
Methane	---	---	---	---
Light Hydrocarbons	---	---	---	---
Liquid Products*	28.7	33.5	48.4	25.6
Total	100.0	100.0	100.0	100.0
Liquid Composition Relative to Methanol (Methanol = 100)	No Liquid Products Collected			
Methanol		100.0	100.0	100.0
Ethanol		0.03	---	---
Propanol		---	---	---
Butanol		0.02	0.2	---
C ₅ + Alcohols		---	0.4	---
C ₅ + Hydrocarbons		---	---	---
Others**		0.03	---	---

*By Difference

**Including Esters, Aldehydes, Unknowns

Table 5.1.5-1
HIGHER ALCOHOLS RUN SUMMARY
(Concluded)

RUN NO.:	194-91	194-91		
CATALYST:	197-11 Cu ₁ Zn _{0.125} Cr ₁ Co _{0.25} K _{0.11}	197-11 Cu ₁ Zn _{0.125} Cr ₁ Co _{0.25} K _{0.11}		
Temperature, °C	270	280		
Pressure, PSIA	925	925		
VHSV, Hr ⁻¹ (NTP)	4163	4163		
Hours on Stream	4.1	5.5		
Feed Composition, Mole %				
H ₂	62.0	62.0		
CO	17.0	17.0		
CO ₂	11.7	11.7		
N ₂	---	---		
Ar	9.3	9.3		
CO Conversion	-1.9	-1.9		
H ₂ Conversion	1.5	2.9		
CO ₂ Conversion	3.6	5.5		
Selectivities to (Mole %)				
CO ₂ (CO)	(74.6)	(51.5)		
Methane	---	---		
Light Hydrocarbons	---	---		
Liquid Products*	25.4	48.5		
Total	100.0	100.0		
Liquid Composition Relative to Methanol (Methanol = 100)				
Methanol	100.0	100.0		
Ethanol	---	0.02		
Propanol	---	0.08		
Butanol	---	---		
C ₅ + Alcohols	---	0.10		
C ₅ + Hydrocarbons	---	---		
Others**	---	---		

*By Difference

**Including Esters, Aldehydes, Unknowns

No liquid product was collected in Runs 194-79 and 194-83. A closer examination of the run data, especially for Run 194-79, indicates that the liquid product should have been formed and collected. For these runs, we presume that the liquid was trapped in the exit lines of the reactor.

Some catalysts such as Prep. 197-18, 197-10 and 197-11 exhibited no catalytic activity. A low level of CO₂ conversion was observed under the operating conditions as indicated in Table 5.1.5-1. Liquid product collected from these runs consisted primarily of water, and a small amount of methanol.

The conversion of CO₂ to CO, methanol and water can be explained by the following simultaneous reactions:

At the test conditions, both reactions are thermodynamically favorable as shown in Figure 5.1.5-1. In Figures 5.1.5-2 through 5.1.5-8, the conversion level of each feed gas component is plotted with respect to the reaction temperature for each test run. Active and inactive catalysts can be readily distinguishable from these plots. Also, higher yields to liquid products can be obtained if the reaction is operated in the region where the formation of CO₂ is minimal, below about a temperature of 270°C.

In Figures 5.1.5-9 through 5.1.5-12, both the conversion and selectivity to liquid products are plotted against the reaction temperature for those runs where some activity was observed. The conversion level of catalyst 194-39 appears higher than that of the other catalysts. As expected, the carbon selectivity to liquids of this catalyst, as well as the other catalysts, decreases rapidly with the reaction temperature.

From Figures 5.1.5-11 and 12, it appears that alcohol, predominantly methanol, is the initial observed product of the syn gas reactions, at least at 240°C and 4000 space velocity. Whether the hydrocarbon gas formation occurs from either secondary alcohol decomposition reactions or from primary syn gas conversion (methanation) reactions can not be determined from the present data. However, a residence time scan in the Berty reactor should give more information about the chemical mechanisms involved.

It is considered to be too early to attempt to correlate the catalyst composition with its activity and selectivity. However, the study of the data in Table 5.1.5-1 and the catalyst compositions (in Table 5.1.5-3) enables us to identify some rudimentary relationships:

- A high level of Cr is detrimental to the catalyst activity. The Cr level should be close to or less than the level of the Cu or Co.
- The ratio of Cu/Co should be equal to or slightly less than 1.
- The inclusion of zinc at low levels (less than 5% by weight) does not appear to affect the catalyst activity.

Table 5.1.5-3

Weight Percent of Catalyst Components

<u>Prep.</u>	<u>Weight %</u>				
	<u>Cu</u>	<u>Zn</u>	<u>Cr</u>	<u>Co</u>	<u>K</u>
197-1	37.9	0.0	24.8	35.2	2.1
197-2	34.0	4.4	27.8	31.5	2.3
197-4	34.0	4.4	27.8	31.5	2.3
197-9	34.9	18.0	28.6	16.2	2.4
197-18	15.9	12.6	52.2	14.8	4.4
197-10	16.7	8.6	54.6	15.5	4.6
197-11	44.5	5.7	36.4	10.3	3.0

FIGURE 5.1.5-1

EQUILIBRIUM CONSTANTS VS TEMPERATURE

FIGURE 5.1.5-2

FEED GAS CONVERSION VS. REACTION TEMPERATURE

RUN 194-39

CATALYST 197-1 : Cu , Cr_2O_3 , Co , K_2O

PRESSURE 955 PSIA

WHSV 3900 hr^{-1}

(Below zero indicates net make)

FIGURE 5.1.5-3

FEED GAS CONVERSION VS. REACTION TEMPERATURE

RUN 194-62

CATALYST 197-2: Cu, Zn, 0.125 Cr, Co, K 0.11

PRESSURE 960 PSIA

VHSV 3700 hr⁻¹

(Below zero indicates net make)

FIGURE 5.1.5-4

FEED GAS CONVERSION VS. REACTION TEMPERATURE

RUN 194-71

CATALYST 197-4 : Cu, Zn, 125 Cr, Co, Kd. 11

PRESSURE 955 PSIA

VHSV 4130 hr⁻¹

(Below zero indicates net make)

FIGURE 5.1.5-5

FIGURE 5.1.5-6

FEED GAS CONVERSION VS. REACTION TEMPERATURE

RUN 194-83

CATALYST : 197-18 Cu Zn 0.77 Cr 4 Co 1 K 0.45

PRESSURE 920 PSIA

VHSV 3916 hr⁻¹

(Below zero indicates net make)

FIGURE 5.1.5-7

FEED GAS CONVERSION VS. REACTION TEMPERATURE

RUN 194-87

CATALYST 197-10 : Cu, $\text{Sn}_{0.5}$, Cr_4Co , $\text{K}_{0.45}$

PRESSURE 935 PSIA

VHSV 3933 hr^{-1}

(Below zero indicates net make)

FIGURE 5.1.5-8

FEED GAS CONVERSION & REACTION TEMPERATURE

RUN 194-91

CATALYST 197-11 : Cu, Zn 0.125 Cr, Co 0.25 K 0.11

PRESSURE 925 PSIA

VHSV 4163 hr⁻¹

(Below zero indicates net make)

FIGURE 5.1.5-9

CONVERSION & SELECTIVITY VS. REACTION TEMPERATURE

RUN 194-39 CATALYST: 197-1 Cu, Zn, CrO₂, Co, K₂O
 PRESSURE 955 PSIA VHSV 3900 HR⁻¹

$$\text{CONVERSION} = \frac{\text{CO} + \text{CO}_2 \text{ CONSUMED}}{\text{CO} + \text{CO}_2 \text{ FED}} \quad \text{IF CO \& CO}_2 \text{ ARE CONSUMED}$$

$$= \frac{\text{CO CONSUMED}}{\text{CO FED}} \quad \text{IF ONLY CO IS CONSUMED}$$

$$\text{SELECTIVITY TO LIQUIDS} = \left[\frac{\text{GAS PRODUCED}^*}{\text{CO} (+ \text{CO}_2) \text{ CONSUMED}} \right] \times 100$$

*CH₄, C₂H₄, C₂H₆

FIGURE 5.1.5-10

CONVERSION & SELECTIVITY VS. REACTION TEMPERATURE

RUN 194-62 CATALYST 197-3 $\text{Cu}_1\text{Zn}_{0.125}\text{Cr}_{0.8}\text{Co}_{1.1}\text{K}_{0.11}$
 PRESSURE 960 PSIA, VHSV 3700 hr^{-1}

$$\text{CONVERSION} = \frac{\text{CO} + \text{CO}_2 \text{ CONSUMED}}{\text{CO} + \text{CO}_2 \text{ FED}} \quad \text{IF CO \& CO}_2 \text{ ARE CONSUMED}$$

$$= \frac{\text{CO CONSUMED}}{\text{CO FED}} \quad \text{IF CO IS CONSUMED}$$

$$\text{SELECTIVITY TO LIQUIDS} = \left[1 - \frac{\text{GAS PRODUCED}^*}{\text{CO} + \text{CO}_2 \text{ CONSUMED}} \right] \times 100$$

* $\text{CH}_4, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6$

FIGURE 5.1.5-11

CONVERSION & SELECTIVITY VS REACTION TEMPERATURE

RUN 194-71 CATALYST 197-4 Cu, Zn, 0.25 Cr, Co, K₂O

PRESSURE 955 PSIA, VHSV 4130 hr⁻¹

$$\text{CONVERSION} = \frac{\text{CO} + \text{CO}_2 \text{ CONSUMED}}{\text{CO} + \text{CO}_2 \text{ FED}} \quad \text{IF CO \& CO}_2 \text{ ARE CONSUMED}$$

$$= \frac{\text{CO CONSUMED}}{\text{CO FED}} \quad \text{IF ONLY CO IS CONSUMED}$$

$$\text{SELECTIVITY TO LIQUIDS} = \left[1 - \frac{\text{GAS PRODUCED}^*}{\text{CO} + \text{CO}_2 \text{ CONSUMED}} \right] \times 100$$

*CH₄, C₂H₄, C₂H₆

FIGURE 5.1.5-12

CONVERSION & SELECTIVITY VS. REACTION TEMPERATURE

RUN 194-79 CATALYST 197-9: Cu, Zn, S, Cr, Co, K₂O, H₂
 PRESSURE 925 PSIA, VHSV 4000 hr⁻¹

$$\text{CONVERSION} = \frac{\text{CO} + \text{CO}_2 \text{ CONSUMED}}{\text{CO} + \text{CO}_2 \text{ FED}} \quad \text{IF CO \& CO}_2 \text{ ARE CONSUMED}$$

$$= \frac{\text{CO CONSUMED}}{\text{CO FED}} \quad \text{IF ONLY CO IS CONSUMED}$$

$$\text{SELECTIVITY TO LIQUIDS} = \left[1 - \frac{\text{GAS PRODUCED}^*}{\text{CO} + \text{CO}_2 \text{ CONSUMED}} \right] \times 100$$

*CH₄, C₂H₄, C₂H₆

5.2 Task 2 - Process Variables Studies in BSU

The objectives of this task are to perform process variables studies utilizing a bench-scale, continuous syn gas conversion unit operated with a three-phase reaction system. This unit was operated by Chem Systems at its Fairfield, New Jersey Research Center under an EPRI contract for the development of Chem Systems' Liquid Phase Methanol Process.

No work has been performed to date on this task.

5.3 Task 3 - Engineering Studies and Economic Analyses

The objectives of this task are to: 1) assess the engineering and economic feasibility of producing synthetic, alcohol-based transportation fuels from coal-derived syn gases; 2) generate a commercially-scalable reaction system for syn gas conversion to C_1 - C_4 alcohols and 3) develop an understanding of the chemistry and engineering of syn gas conversion to alcohols utilizing kinetic correlating techniques.

No work has been performed to date on this task.

5.4 Task 4 - Performance Studies in PDU

The objectives of this task are to demonstrate the performance of the catalysts developed in Tasks 1 and 2 under commercially-feasible reaction conditions utilizing a continuous, process demonstration unit (PDU). This unit was operated by Chem Systems under a prior DOE contract for the development of Chem Systems' Liquid Phase Methanation/Shift Process.

No work has been performed to date on this task.

6.0 REFERENCES

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7.0 PATENTABLE INVENTIONS

No patentable inventions were conceived during this quarterly period.

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