

first thirty-six catalysts shown in Table V-3 were pelletized into 3/16" x 1/8" tablets using a Stokes pelletizer. All other catalysts were formed into 1" x 1/8" disks using a Carver Model 3 Laboratory Press operated at a controlled tableting pressure, usually 20,000 psig. The pellets or tablets were then heated slowly to 350°C in order to combust the Sterotex. Those tablets produced in the Carver press were then broken up into 3/16" x 1/8" particles.

The evaporaton of metal acetates followed the same procedure as above except that the metal acetates replaced the metal nitrates. The evaporation of metal citrates differed from the above two evaporation procedures in that the metal citrates were each prepared separately by mixing individual metal nitrates with excess citric acid to form a metal nitrate-citrate complex. The individual complexes were then mixed together and evaporated at 100°C until a viscous, glassy paste was formed. Nitrogen dioxide evolution was observed during this step. The calcining and finishing steps were the same as those of the evaporation method utilizing metal nitrates.

b. Coprecipitation

Coprecipitation of oxides from metal nitrates was carried out by using either potassium hydroxide or sodium carbonate as the coprecipitating agent (four catalyst samples were produced by a different coprecipitation technique which is discussed later in this section).

KOH Coprecipitation

In this technique, solutions of metal nitrates and potassium hydroxide were prepared and charged to two burettes such that the solutions could be added sequentially or simultaneously to a well stirred sample of deionized water. With either mode of addition, the pH of the resulting solution was kept at about 9. This procedure was continued until all metal hydroxides were precipitated by the KOH solution. The precipitate was then allowed to age for 18-24 hours while cooling. The resulting slurry was filtered in a pressure filter and washed 6-10 times with one liter of deionized

TABLE V-3

SUMMARY OF CATALYSTS PREPARED BY EVAPORATION

<u>Catalyst No.</u>	<u>Formulation (Atomic Ratio)</u>	<u>Tested In Run Number</u>
197-1	CuCoCr _{0.8} K _{0.09}	194-39P 201-22B 201-48B
197-2	CuZn _{0.125} CoCrK _{0.11}	194-62P 201-34B 201-40P 201-67B
197-8	CuZn _{0.125} Co _{0.5} CrK _{0.11}	(6)
197-9	CuZn _{0.5} Co _{0.5} CrK _{0.11}	194-79P
197-10	CuZn _{0.5} CoCr ₄ K _{0.45}	194-87P
197-11	CuZn _{0.125} Co _{0.25} CrK _{0.11}	194-91P
197-12	CuZn ₂ CoCr ₄ K _{0.45}	(6)
197-13	CuZn _{0.5} Co _{0.25} CrK _{0.11}	(6)
197-14	CuZn _{0.5} Co ₄ Cr ₄ K _{0.45}	(6)
197-15	CuZn ₂ Co ₄ Cr ₄ K _{0.45}	(6)
197-16	CuZn _{0.5} CoCrK _{0.11}	194-95P 201-62B
197-17	CuZn _{0.125} CoCrK _{0.11}	201-1P
197-18	CuZn _{0.77} CoCr ₄ K _{0.45}	194-83P
197-19	CuZn _{0.49} Co _{0.18} K _{0.07}	201-9P
197-20	CuZn _{0.49} Co _{0.5} Cr _{0.18} K _{0.09}	201-6P
197-21	CuZn _{0.49} CoCr _{0.18} K _{0.11}	(6)
197-32	CuZn _{0.125} CoCrK _{0.11} (1)	201-37B

Continued...

TABLE V-3 (CONTINUED)SUMMARY OF CATALYSTS PREPARED BY EVAPORATION

<u>Catalyst No.</u>	<u>Formulation (Atomic Ratio)</u>	<u>Tested In Run Number</u>
197-36	CuZn _{0.125} CoCrK _{0.11} (1,2)	201-58P
197-38	CuZn _{0.125} CoCrK _{0.11} (2)	(6)
197-42	CuZn _{0.125} CoCrK _{0.11} (3)	(6)
200-25-1	CuZn _{0.125} CoK _{0.11}	201-60P
200-27-1	CuZn _{0.125} CoCs _{0.11}	201-65P
200-27-2	CuZn _{0.125} CoFe _{0.5} Th _{0.5} K _{0.11}	201-45B 201-100P 213-2B
200-32	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}	201-54P
197-59	CuZn _{0.125} CoMnK _{0.11}	201-72P
197-60	CuZn _{0.125} CoVK _{0.11}	201-77P
197-61	CuZn _{0.125} CoTiK _{0.11}	(6)
197-68	CuZn _{0.125} CoCrK _{0.11}	(6)
197-69	CuZn _{0.125} CoCrK _{0.11}	(6)
197-70	CuZn _{0.125} CoCrK _{0.11}	201-82B
197-71	CuZn _{0.125} CoFe _{0.1} Th _{0.5} K _{0.11}	201-83B 201-85B
200-57-1	CuZn _{0.125} CoFe _{0.1} K _{0.11}	201-80B
200-57-2	CuZn _{0.125} CoFe _{0.5} K _{0.11}	(6)
200-58-1	CuZn _{0.125} CoMoK _{0.11}	201-81P

TABLE V-3 (CONTINUED)SUMMARY OF CATALYSTS PREPARED BY EVAPORATION

<u>Catalyst No.</u>	<u>Formulation (Atomic Ratio)</u>	<u>Tested In Run Number</u>
197-72	CuZn _{0.125} CoZrK _{0.11}	201-89P
197-73	CuZn _{0.125} CoCrK _{0.11}	201-87B 201-91B 201-97P
197-77	CuZn _{0.125} CoTh _{0.5} K _{0.11}	201-93B
197-78	CuZn _{0.125} CoCr _{0.125} K _{0.11}	201-92P
197-76	CuZn _{0.125} CoCrK _{0.11} (4)	201-90B
200-76	CuCoCr _{0.8} K _{0.09}	213-13B 213-14P
200-79	CuZn _{0.5} CoK _{0.11} (5)	213-25P
200-85-1	CuCoCr _{0.8} K _{0.09}	(6)
200-85-2	CuCoCr _{0.8}	(6)

(1) Calcined at 550°C.

(2) Oxalic acid used instead of citric acid as a complexing agent.

(3) No complexing agent added.

(4) Evaporation of metal citrates.

(5) Evaporation of metal acetates with citric acid.

(6) Not tested.

water. It was then reslurried with deionized water under vigorous agitation, then filtered and washed twice with deionized water until the pH of the washwater was equal to seven. The catalyst cake was dried at 120°C and calcined at 450°C (temperature increased from 150 to 450°C at 50°/hr) for three hours. The resultant catalyst was powdered and potassium carbonate solution was added to the powder to bring the potassium value in the final catalyst to the desired level. After the solution was evaporated, 3 percent sterotex was added and the catalyst pelletized at 20,000 psig. The resultant catalyst was then reheated to 350°C very slowly to combust the sterotex.

Na₂CO₃ Coprecipitation

In this technique, a sodium carbonate solution was added dropwise from a burette to a solution of the metal nitrates maintained at 80°C under vigorous agitation. The time of addition was one hour with a final pH of seven. The precipitated carbonates were then allowed to age for 18-24 hours while cooling slowly. The precipitate was filtered in a pressure filter and washed six to ten times with deionized water. The catalyst cake was removed from the filter and slurried vigorously with deionized water. The slurry was filtered and washed twice with deionized water and dried at 120°C. The dried catalyst was slowly heated to 350°C and calcined at 350°C for three hours. The resultant catalyst was powdered and enough potassium carbonate solution added to bring the potassium content to the desired level. The catalyst was dried and pelletized (usually without sterotex) at 20,000 psig.

Other Coprecipitation Procedures

Four catalysts were prepared by coprecipitation techniques other than by use of KOH or Na₂CO₃. These preparations are described below:

Catalyst 197-6 was coprecipitated with ammonium hydroxide by the following procedure:

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 percent 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 for 12 hours and then slurried into 50 ml solution containing 3.6 gms of KOH. The slurry was dried at 120°C and calcined at 450°C for 3 hrs. The resulting black powder was then pelletized into $3/16" \times 1/8"$ tablets.

Ammonium carbonate was used as a precipitating agent for Catalyst 197-48. The catalyst was prepared by the following procedure:

In a 2-liter beaker, 58.2 gms of $\text{Cu}(\text{NO}_3)_2 \cdot 2 \frac{1}{2} \text{H}_2\text{O}$, 9.3 gms of $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, 100.1 gms of $\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ and 72.6 gms of cobalt carbonate were dissolved in 1 liter of deionized water while stirring vigorously. The aqueous solution was then precipitated by adding dropwise concentrated $(\text{NH}_4)_2\text{CO}_3$ until the final solution pH was 6.5. The resulting precipitate was filtered, washed and then dried in the oven at 125°C for 12 hours. The dried filter cake was slurried in 100 ml solution containing 3.8 gms of $\text{K}_2\text{CO}_3 \cdot 1\text{-}1/2 \text{H}_2\text{O}$ followed by drying at 125°C for 12 hours and calcination at 550°C for 3 hrs.

Two catalysts were prepared using potassium carbonate instead of potassium hydroxide as a coprecipitation agent. None of these alternative procedures, however, were successful, as the precipitations never went to completion. The potassium hydroxide and sodium carbonate procedures described were the only coprecipitation procedures tried which produced acceptable results. A summary of catalysts prepared by coprecipitation is given in Table V-4. Several catalysts prepared by coprecipitation were analyzed by atomic absorption to determine the accuracy of the preparation. The results of these analyses are shown in Table V-5 and indicate that the precipitation is reasonably reliable.

TABLE V-4

SUMMARY OF CATALYSTS PREPARED BY COPRECIPITATION

<u>Catalyst No.</u>	<u>Formulation (Atomic Ratio)</u>	<u>Precipitation Agent</u>	<u>Tested In Run No.</u>
197-4	CuZn _{0.125} CoCrK _{0.11}	Na ₂ CO ₃	194-71P
197-6	CuZn _{0.125} CoCrK _{0.11}	NH ₄ OH	(1)
197-22	CuZn _{0.49} Cr _{0.18} K _{0.07}	Na ₂ CO ₃	201-11P
197-29	CuZn _{0.5} Co _{0.75} Cr _{0.14} K _{0.12}	Na ₂ CO ₃	201-17P
197-48	CuZn _{0.125} CoCrK _{0.11}	(NH ₄) ₂ CO ₃	201-56B
197-79	CuZn _{0.125} CoThK _{0.11}	KOH	201-95B
197-82	CuZn _{0.125} CoTh _{0.75} Fe _{0.1} K _{0.11}	KOH	(1)
197-83	CuZn _{0.125} CoThFe _{0.1} K _{0.11}	KOH	(1)
197-84	CuCoRu _{0.1} K _{0.11}	KOH	213-9B
197-85	CuZn _{0.125} CoTh _{0.5} Fe _{0.1} K _{0.11}	KOH	213-4B
197-86	CuZn _{0.125} Th _{0.5} Fe _{0.5} K _{0.11}	K ₂ CO ₃	(1)
197-87	CuZn _{0.25} CoK _{0.11}	K ₂ CO ₃	(1)
197-88A	CuZn _{0.25} CoK _{0.11}	KOH	(1)
197-88B	CuZn _{0.25} Co	KOH	(1)
197-89	CuZn _{0.125} Th _{0.5} Fe _{0.5} K _{0.11}	KOH	(1)
200-81-1	CuCoTh _{0.5} K _{0.11}	KOH	213-40P
200-81-2	CuCoTh _{0.5}	KOH	(1)
200-83-1	CuCoK _{0.11}	KOH	(1)
200-83-2	CuCo	KOH	213-36B
200-86	CuZn _{0.5} CoK _{0.11}	Na ₂ CO ₃	213-28P
200-88	Cu _{0.5} ZnCo _{0.2} K _{0.05}	Na ₂ CO ₃	(1)

Continued...

TABLE V-4 (CONTINUED)SUMMARY OF CATALYSTS PREPARED BY COPRECIPITATION

<u>Catalyst No.</u>	<u>Formulation (Atomic Ratio)</u>	<u>Precipitation Agent</u>	<u>Tested In Run No.</u>
200-89-1	CuCo _{0.3} Cr _{0.8} K _{0.09}	Na ₂ CO ₃	213-19B
200-89-2	CuCo _{0.3} Cr _{0.8}	NaCO ₃	(1)
197-90-1	CuZn _{0.5} CoK _{0.11}	KOH	(1)
197-90-2	CuZn _{0.5} Co	KOH	(1)
200-91	CuZn _{0.125} CoTh _{0.5} Fe _{0.1} K _{0.11}	Na ₂ CO ₃	213-29B
217-2	CuZn _{0.33} Al _{0.18}	Na ₂ CO ₃	213-43P
217-3	CuCo _{0.3} K _{0.11}	KOH	213-26B
217-5	CuCo _{0.3} K _{0.077}	KOH	213-31B
217-7-1	CuCoK _{0.05}	KOH	213-34B
217-10	Cu _{0.05} Zn	Na ₂ CO ₃	213-44P
217-22	CuCoK _{0.22}	Na ₂ CO ₃	213-54B 213-64P
217-25	CuZn _{0.33} Al _{0.18}	Na ₂ CO ₃	(1)
217-29-1	CuCoK _{0.33}	Na ₂ CO ₃	213-59B

(1) Not tested.

TABLE V-5

COMPARISON OF CALCULATED VS. MEASURED COMPOSITIONS
OF COPRECIPITATED CATALYSTS

Catalyst No.	CALCULATED ⁽¹⁾		MEASURED ⁽²⁾	
	Atomic Formula	Wt %	Wt %	Atomic Formula
200-83-1	$Cu_1Co_1K_{0.11}$	Cu 39.8	39.6	$Cu_{1.0}Co_{1.0}K_{0.08}$
		Co 36.9	32.2	
		K 2.7	1.7	
197-85	$Cu_1Zn_{0.125}Co_1Th_{0.5}Fe_{0.1}K_{0.11}$	Cu 20.5	22.2	$Cu_{1.3}Zn_{0.12}Co_{1.0}Th_{0.5}Fe_{0.06}K_{0.07}$
		Zn 2.6	2.11	
		Co 19.0	16.2	
		Th 37.5	33.2	
		Fe 1.8	1.7	
197-87	$Cu_1Zn_{0.25}Co_1K_y$ ⁽³⁾	Cu 36.3	29.2	$Cu_{0.83}Zn_{0.21}Co_{1.0}K_{<0.01}$
		Zn 9.4	7.6	
		Co 33.7	32.4	
		K 0.0	0.15	
197-88A	$Cu_1Zn_{0.25}Co_1K_{0.11}$	Cu 35.3	45.8	$Cu_{1.5}Zn_{0.26}Co_{1.0}K_{0.095}$
		Zn 9.1	8.2	
		Co 32.7	28.7	
		K 2.4	1.8	

(1) Calculated based on materials used in preparation.
Metals % based on total metal oxide mixture.

(2) Calculated based on wt% found, Co assumed 1.00.

(3) Submitted before impregnation of K (y = 0 before impregnation).

All catalysts analyzed after calcination.

c. Impregnation

This catalyst preparation procedure involved either evaporating a metal nitrate/citric acid solution in the presence of an inert support (e.g., alpha-Al₂O₃, gamma-Al₂O₃, SiO₂, etc.) or coprecipitating a metal nitrate solution using either KOH or Na₂CO₃ as a coprecipitating agent in the presence of the support. When using the evaporation technique, a rotary evaporator was used for bulk water removal prior to oven drying. Other aspects of these preparations are identical to those described in the preceding sections. A summary of catalysts prepared by this method is given in Table V-6.

Impregnated catalysts were also prepared using a commercial methanol catalyst and one of the ALKANOL catalysts as the base material. The modifying elements included cobalt, potassium, palladium (added as the nitrate) and ruthenium (added as the chloride). A summary of the catalysts prepared by this method is given in Table V-7.

d. Detergent Dispersion

This method was based on a procedure developed by Shirokov⁽⁴²⁾ and consisted of dispersing and mixing oxide-base catalysts in the presence of surfactants. The atomic formulation tested with this method was CuZn_{0.4}Co_{0.5}Al_{0.25}K_x where x was either 0 or 0.05. This method also allowed for the incorporation of cobalt into the catalyst in a form not previously used. A commercial methanol synthesis catalyst of the Cu-Zn-Al type was crushed and sieved through a 106 micron screen. For the formulation in which x = 0.05, some of the powdered methanol catalyst was impregnated with KOH solution to add the proper amount of potassium onto the catalyst. The powders were then slurried in a dry methanol-ethanolamine solution containing dicobalt octacarbonyl. The slurry was agitated in an ultrasonic bath for two hours. The mixture was removed from the ultrasonic bath and allowed to age for a period of time. The mixture was then heated to evaporate the methanol followed by heating at 200°C for a period of 8 hours. The dried solids were broken and mixed with 3-5 percent Sterotex and pelletized to produce 1 1/4" x 1/8" wafers. Final finishing was accomplished by burning off the Sterotex at 300°C.

TABLE V-6

SUMMARY OF CATALYSTS PREPARED BY
IMPREGNATION ON TO INERT SUPPORTS

<u>Catalyst</u> <u>No.</u>	<u>Formulation (Atomic Ratio)</u>	<u>Preparation</u> <u>Method</u>	<u>Tested In</u> <u>Run No.</u>
197-65	$\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$ (70% SiO_2)	Evaporation	201-74B
197-66	$\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$ (45% TiO_2)	Evaporation	201-79B
197-67	$\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$ (75% TiO_2)	Evaporation	201-84P
197-81	$\text{CuZn}_{0.125}\text{CoTh}_{0.5}\text{Fe}_{0.5}\text{K}_{0.11}$ (45% MnO)	Coprecipitation with KOH	201-98B
217-9	Co (50% $\alpha\text{-Al}_2\text{O}_3$)	Coprecipitation with Na_2CO_3	213-42B
217-15	$\text{CoK}_{0.11}$ (50% $\alpha\text{-Al}_2\text{O}_3$)	Coprecipitation with Na_2CO_3	213-38B
217-16	$\text{CoK}_{0.34}$ (50% $\alpha\text{-Al}_2\text{O}_3$)	Coprecipitation with Na_2CO_3	213-41B
217-17	$\text{CoK}_{0.05}$ (50% $\alpha\text{-Al}_2\text{O}_3$)	Coprecipitation with Na_2CO_3	213-46B 213-49B
217-24	$\text{CuCoK}_{0.11}$ (88% $\gamma\text{-Al}_2\text{O}_3$)	Evaporation	213-52P
217-29-3	$\text{CuCoK}_{0.22}$ (88% SiO_2)	Evaporation	213-61B
217-30	$\text{CuCoK}_{0.22}$ (88% Na-Y Zeolite)	Evaporation	213-65B

TABLE V-7

SUMMARY OF CATALYSTS PREPARED BY
IMPREGNATION OF METAL SALTS ONTO EXISTING CATALYSTS

<u>Catalyst No.</u>	<u>Formulation (Atomic Ratio)</u>	<u>Base Catalyst</u>	<u>Tested In Run No.</u>
197-27	$\text{CuZn}_{0.36}\text{Al}_{0.21}\text{K}_{0.07}$	197-26	201-13P
197-28	$\text{CuZn}_{0.36}\text{Al}_{0.21}\text{Co}_{0.32}\text{K}_{0.09}$	197-26	201-15P
197-30	$\text{CuZn}_{0.36}\text{Al}_{0.21}\text{Co}_{0.65}\text{K}_{0.10}$	197-26	201-32P
217-1-1	$\text{CuZn}_{0.33}\text{K}_{0.05}\text{Al}_{0.18}$	197-26	213-33P
217-23	$\text{CoK}_{0.11}\text{Pd}_{0.015}$ (50% alpha- Al_2O_3)	217-15	213-50B
217-27	$\text{CuK}_{0.11}\text{Ru}_{0.016}$ (50% alpha- Al_2O_3)	217-15	213-56B

The following two catalysts were prepared by this method:

<u>Catalyst No.</u>	<u>Formulation (Atomic Ratio)</u>	<u>Tested in Run No.</u>
200-78-1	$\text{CuZn}_{0.4}\text{Co}_{0.5}\text{Al}_{0.25}\text{K}_{0.05}$	213-11P
200-78-2	$\text{CuZn}_{0.4}\text{Co}_{0.5}\text{Al}_{0.25}$	213-16B

e. Cobalt Carbonyl Impregnation

This method aided in the dispersion of cobalt (from dicobalt octacarbonyl) onto methanol synthesis catalysts. The procedure consisted of dissolving dicobalt octacarbonyl in acetone and slurring the solution with the methanol synthesis catalyst (the methanol catalyst was either a commercial material or prepared in-house by Na_2CO_3 coprecipitation). The slurry was then placed in an ultrasonic bath for 1-2 hours, and then quickly evaporated to remove the acetone. The dried catalyst was heated to 200°C for 12 hours in order to decompose the cobalt carbonyl. A potassium carbonate solution was then added to the catalyst to bring the potassium content in the final material to the proper level. The slurry was evaporated on a rotovap and then dried and pelletized without sterotex at 20,000 psi tableting pressure. A summary of catalysts prepared by this method is given in Table V-8.

f. Mechanical Blending

This technique involved grinding the required metal nitrates or oxides in a mortar and pestle until a fine, homogeneous powder was produced. The catalysts prepared by the use of nitrates were calcined and pelletized in the same fashion as that of the catalysts produced by evaporation of nitrates. The catalysts prepared from the oxides were not calcined. Two catalysts were prepared in this way. They are:

<u>Catalyst No.</u>	<u>Formulation (Atomic Ratio)</u>	<u>Prepared From</u>
197-56	$\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$	Nitrates
197-57	$\text{CuZn}_{0.125}\text{CoCrK}_{0.11}$	Oxides

TABLE V-8

SUMMARY OF CATALYSTS PREPARED BY
COBALT CARBONYL IMPREGNATION

<u>Catalyst No.</u>	<u>Formulation (Atomic Ratio)</u>	<u>Tested in</u> <u>Run No.</u>
200-93	$\text{CuZn}_{0.33}\text{Co}_{0.13}\text{K}_{0.05}\text{Al}_{0.18}$	213-20P
200-96	$\text{CuZn}_{0.33}\text{Co}_{0.01}\text{K}_{0.05}\text{Al}_{0.18}$	213-21B
200-99	$\text{CuZn}_{0.33}\text{Co}_{0.17}\text{K}_{0.05}\text{Al}_{0.18}$	213-24B
217-6	$\text{CuZn}_{0.33}\text{Co}_{0.07}\text{K}_{0.05}\text{Al}_{0.18}$	213-32B
217-8	$\text{CuZn}_{0.33}\text{Co}_{0.13}\text{K}_{0.05}\text{Al}_{0.18}$	213-39P
217-18	$\text{Cu}_{0.5}\text{ZnCo}_{0.25}$	213-45B
217-19	$\text{Cu}_{0.5}\text{ZnCo}_{0.25}\text{K}_{0.05}$	213-47P
217-28	$\text{CuZn}_{0.33}\text{Co}_{0.4}\text{K}_{0.05}\text{Al}_{0.18}$	213-55P

g. Proprietary Catalysts

The following proprietary catalysts supplied by United Catalysts, Inc. (UCI) were tested in this program:

<u>Catalyst Designation</u>	<u>Tested in Run No.</u>
L-1122	213-57B 213-74B 226-28S 226-42S
L-1123	213-60P 213-66P
L-1124	213-82B

C. Experimental Results

1. Calculation Procedures

The methods for calculating the molar concentrations of the various feed and effluent components have been covered in Section IV-D. This section will explain the calculation procedures used to arrive at the results that have been reported in the computerized summary sheets contained in the Appendix.

Flow Rate Calculations

All synthesis feed gases that were used during this program contained an inert gas (usually argon) at a concentration of approximately 10 mole percent. The argon allowed direct comparisons between the feed and effluent gases. An example of its use is in the calculation of the synthesis gas feed rate and the vapor hourly space velocity (VHSV). The volumetric gas effluent rate (V_e in ml/min) was measured by use of a bubble meter or dry test meter. The pressure at the point of measurement was approximately 14.7 psia. The calculation for the volumetric synthesis gas feed rate (V_f in l/hr at STP) is:

$$V_f \text{ (l/hr)} = V_e \text{ (ml/min)} \times \frac{Ar_e}{Ar_f} \times \frac{273^{\circ}K}{273+T_e} \times \frac{60 \text{ min/hr}}{1000 \text{ ml/l}} \quad (36)$$

where: Ar_f = The concentration of argon in the feed gas, mole percent;

Ar_e = The concentration of argon in the effluent gas, mole percent;

T_e = Temperature of the effluent gas, °C

The value of the VHSV (1/hr/kg cat at STP) is determined by:

$$\text{VHSV (1/hr/kg cat)} = \frac{V_f \text{ (1/hr)} \times 1000 \text{ g/kg}}{\text{Weight Cat. Charged (g)}} \quad (37)$$

Conversion Calculations

The percent conversions of feed gas components (hydrogen, carbon monoxide, and carbon dioxide) were calculated from the following equation:

$$X_i = \frac{\left[I_f - \left(I_e \times \frac{Ar_f}{Ar_e} \right) \right] \times 100}{I_f} \quad (38)$$

Where I represents the reactant components: hydrogen (H), carbon monoxide (CO) or carbon dioxide (CO₂), respectively;

I_f = mole percent of I in feed gas;

I_e = mole percent of I in effluent gas; and

X_i = total percent of I converted.

The conversion of carbon monoxide to carbon dioxide is given by:

$$X_{\text{CO} \rightarrow \text{CO}_2} = X_{\text{CO}} \left[\frac{\left(\text{CO}_2_e \times \frac{Ar_f}{Ar_e} \right) - \text{CO}_2_f}{\text{CO}_f - \left(\text{CO}_e \times \frac{Ar_f}{Ar_e} \right)} \right] \quad (39)$$

where: $X_{\text{CO} \rightarrow \text{CO}_2}$ = Conversion of carbon monoxide to carbon dioxide only;

X_{CO} = Total carbon monoxide conversion.

The conversion of carbon monoxide to ALKANOLS and light gases on a carbon dioxide free basis is determined from:

$$X_{\text{CO} \rightarrow \text{ALKANOLS}} = X_{\text{CO}} - X_{\text{CO} \rightarrow \text{CO}_2} \quad (40)$$

or

$$X_{\text{CO} \rightarrow \text{ALKANOLS}} = \frac{\left[\text{CO}_f + \text{CO}_2_f - (\text{CO}_e + \text{CO}_2_e) \times \frac{\text{Ar}_f}{\text{Ar}_e} \right] \times 100}{\text{CO}_f} \quad (41)$$

The molar conversion of carbon monoxide per unit weight of catalyst (gmol/hr/kg) is calculated by the equation:

$$\text{gmol CO converted/hr/kg cat} = \frac{\text{VHSV}}{22.4} \times \frac{\text{CO}_f}{100} \times \frac{X_{\text{CO}}}{100} \quad (42)$$

Selectivity Calculations

The carbon selectivities to the various products (methane, methanol, ethanol, etc.) were calculated by the following equation:

$$S_i = n_i \times I_e \times K \quad (43)$$

where S_i = percent of carbon converted from carbon monoxide to i ;
 n_i = number of carbons in i ;
 I_e = mole percent I in effluent gas

and

$$K = \frac{\frac{\text{Ar}_f}{\text{Ar}_e} \times 100}{\text{CO}_f - \left(\text{CO}_e \times \frac{\text{Ar}_f}{\text{Ar}_e} \right)} \quad (44)$$

Carbon Accountability

The carbon accountability is defined as the ratio of carbon in the products (including any carbon dioxide produced) to carbon monoxide converted or, the carbon accountability can be:

$$\text{Carbon Accountability} = \sum_i S_i \quad (45)$$

where S_i = carbon selectivity to component i.

Carbon accountability varied usually between 90 and 110 percent. Deviations from these levels were indicative of calibration drifts between the thermal conductivity analyzer used to determine carbon monoxide conversion and the flame ionization analyzer used to detect carbon-containing synthesis products.

Space Time Yield to Oxygenates

The space time yield (STY expressed as atoms carbon/hr/kg cat) to oxygenates is calculated as follows:

$$\text{STY} = \frac{\text{VHSV}}{22.4} \times \frac{\text{CO}_f}{100} \times \frac{X_{\text{CO}}}{100} \times \frac{S_{\text{Oxygenates}}}{100} \quad (46)$$

Approach to Water Gas Shift Equilibrium Temperature

In order to calculate the approach to the water gas shift equilibrium temperature, the concentration of water in the effluent gas was first determined. This was done by assuming that all oxygen in the synthesis feed gas that is not accounted for in the effluent components has been converted to water.

The concentration of water (W_e) in the effluent gas is calculated from the following equation:

$$W_e = (CO_f + 2 \times CO2_f) - \left[Ar_f / Ar_e \sum_i N_i I_e \right] \quad (47)$$

where I_e represents reactor effluent components and

N_i = number of oxygen atoms in component i
 ($N_i = 0$ for hydrocarbons, hydrogen and argon;
 $N_i = 1$ for alcohols, aldehydes and carbon monoxide; and
 $N_i = 2$ for carbon dioxide)

If the system were at equilibrium conditions, then the equilibrium constant (K_{eq}) for the water-gas shift reaction would be:

$$K_{eq} = \frac{CO2_e \times H_e}{CO_e \times W_e} \quad (48)$$

The equilibrium temperature (T_{eq} , °C) can be calculated as follows:

$$T_{eq} (°C) = \frac{4827}{\ln K_{eq} + 4.7618} - 273^0K \quad (49)$$

The approach to water gas shift equilibrium temperature is then defined as:

$$T = T_{eq} - T_{hs} \quad (50)$$

where T_{hs} = reactor hot spot temperature (°C).

Stoichiometric H₂/CO Ratio Converted

The stoichiometric H₂/CO ratio converted, which is sometimes called the H₂/CO usage ratio, is an indication of the particular synthesis products made. It is a useful parameter to observe particularly when it is compared to the H₂/CO ratio of the synthesis feed gas. The theoretical

value of the usage ratio is 2.0 for alcohols and asymptotically approaches 2.0 from the low side for aldehydes (usage ratio for C₁ aldehyde is 1.0). The usage ratio for paraffins asymptotically approaches 2.0 from the high side for paraffins (usage ratio for methane is 3.0). The usage ratio for mono-olefins is 2.0 for all carbon numbers (In all four stoichiometries, it was assumed that water and not carbon dioxide was the byproduct of the synthesis reactions). Thus, the carbon number distribution and synthetic fuel product type will control the ultimate H₂/CO usage ratio observed in a given test.

The water-gas shift reaction has a H₂/CO usage ratio of -1. Thus, when a synthesis catalyst exhibits shift activity, the net observed usage ratio will be lower than that for the total alcohol and hydrocarbons produced.

Schulz-Flory Distribution

The Schulz-Flory distribution calculations have been covered in Section V-A.

ALKANOL Fuel Weight Distribution Calculations

The ALKANOL fuel weight distribution is determined by calculating the weight percentages of all components boiling above that of C₃ hydrocarbons and expressed on a water-free basis as follows:

$$M_i = \frac{I_e \times MW_i}{\sum_j J_e MW_j} \quad (51)$$

- where M_i = Wt percent of component i in ALKANOL fuel mixture;
- MW_i = Molecular weight of component i;
- i = ALKANOL component of interest;
- j = All ALKANOL components (except water);
- I_e = Concentration of component i in the effluent gas; and
- J_e = Concentration of component j in the effluent gas.

Higher Heating Value Calculations

The calculated higher heating value of the product (HV_T , Btu/gal) is determined by:

$$HV_T = \sum_i \frac{M_i \times HV_i \times \rho_i}{100} \quad (52)$$

- Where HV_i = Higher heating value for component i in Btu/lb_m;
- ρ_i = Density of component i in lb_m/gal.
- M_i = Weight percent of i in the ALKANOL mixture.

2. Detailed Run Summaries

The detailed computer run summaries for the 83 catalyst formulations screened in the vapor-phase test systems are included in the Appendix of this report. In total, 335 material balance tests were reported with each test representing the average of at least two product gas analyses.

D. Analysis of Results (Task 1)

1. Overview

A Newtonian approach has been utilized to guide the catalyst formulation criteria during the Task 1 screening studies. Feedback of results from the ALKANOLS synthesis tests to the catalyst formulation program helped to minimize the testing of potentially innocuous catalyst candidates. The effectiveness of a catalyst candidate was monitored by observation of the ALKANOLS selectivity vs. carbon monoxide conversion relationships at several synthesis severities. Due to the large number of potentially key reaction parameters, it was not possible to systematically explore all reaction variables for each catalyst formulation. Thus, any possible beneficial synergisms between catalyst composition (chemical as well as physical) and synthesis reaction conditions might have been overlooked.

In-house formulations were classified into five group types as described in more detail in the next section. Table V-9 summarizes the screening results for the highest ALKANOLS selectivities observed in each catalyst

group. Although the original objective of this program was to develop a catalyst system for maximizing selectivities to alcohol fuels, the product slates shown on Table V-9 for the ternary catalyst and the binary catalyst systems might be attractive for a coal conversion complex aimed at producing SNG, LPG and light (C_4-C_{10}) liquid hydrocarbons in addition to alcohol fuels.

Under the terms of the contract work statement, Chem Systems was to maintain surveillance of the state-of-the-art in alcohols synthesis technology. In this vein, we obtained samples of three proprietary catalysts from United Catalysts, Inc. for screening of initial catalyst activity and selectivity to ALKANOL fuels. These catalysts differed from the in-house formulations in that they operated under higher synthesis severity, namely, 350°C reaction temperatures and 100 atm reaction pressures as compared to $250-300^{\circ}\text{C}$ and 35-70 atm for the in-house formulations. The initial catalyst performance of these catalysts, as summarized in Table V-10, indicated improved selectivity to ALKANOLS with decreased light hydrocarbon gas selectivities as compared to the best of the in-house formulations. Thus, it was concluded that the UCI catalysts should be further evaluated under the longer-term testing in the process variables studies of Task 2.

2. Screening Studies Using Proprietary Catalysts

Screening of catalyst activity was performed on three proprietary catalysts supplied by United Catalysts, Inc. (UCI). Three screening test series were performed during this task. Catalysts L-1122 and L-1124 were screened in the Bertly reactor while L-1123 catalyst was screened in the plug-flow, diluted-bed reactor. Further in-depth process variables scans were performed for these three catalysts over extended periods of on-stream time. The results of these tests are presented in Section VI.

UCI L-1122 Catalyst (Run 213-57B)

UCI-L1122 catalyst was screened for initial catalyst performance in the Bertly reactor at four synthesis conditions as illustrated in Table V-11 (A detailed computerized summary sheet for this test is presented in the

TABLE V-9
 SCREENING RESULTS WITH HIGHEST ALKANOLS SELECTIVITIES OBSERVED FOR EACH GROUP OF IN-HOUSE CATALYST FORMULATIONS

Catalyst Group Identification	5 or 6 Component Catalyst Systems	Quaternary Catalyst Systems	Ternary Catalyst Systems	Binary Catalyst Systems	Modified Low Pressure Methanol Synthesis Catalysts
Run No.	I	II	III	IV	V
Catalyst No.	201-858-2	213-25P-4	213-508-2	213-468-1	213-328-4
Catalyst Formulation	197-71 CuCoFe _{0.1} Th _{0.5} Zn _{0.125} K _{0.11}	200-79 CuCoZn _{0.5} K _{0.11}	217-23 CoPd _{0.05} K _{0.11} (50% Al ₂ O ₃)	217-17 CoK _{0.05} (50% Al ₂ O ₃)	217-6 CuCo _{0.07} A ₁ _{0.16} Zn _{0.33} K _{0.05}
Catalyst Preparation Method	Evaporation of nitrates	Evaporation of acetates	Impregnation of Pd(NO ₂) ₂ onto 217-15(2)	Coprecipitation onto support	Cobalt carbonyl impregnation
Run Conditions	258	287	273	263	300
Average Temperature, °C	900	950	910	910	950
Pressure, psig	882	3100	4370	3870	3605
Space Velocity (1/hr/kg cat) hours On-Stream	5.9	9.2	2.3	1.7	13.4
Results	10.43	11.13	19.82	8.13	8.34
CO Conversion (CO ₂ -free basis), Vol %	64.4	56.7	54.4	63.6	73.9
Product Selectivity, Mt % ALKANOLS	35.6	43.3	45.6	36.4	26.1
Gas (C ₁ -C ₃ H.C.)	34.6	26.3	1.1	1.0	81.9
Alkano] Methano]	57.2	56.0	78.6	68.0	13.9
C ₂ -C ₆ Oxygenates	8.2	17.7	20.3	31.0	4.2
C ₄ -C ₉ Hydrocarbons					

(1) Synthesis gas feed had a 2/1 H₂/CO ratio with 11.12% CO₂ content except for Group I catalyst which was tested with a synthesis gas having 5% CO₂ content.
 All tests were performed in the Berty reactor with the exception of the Group II catalyst which was tested in the diluted-bed, plug-flow reactor.

(2) CoK_{0.11} coprecipitated onto 50% Al₂O₃ support.

TABLE V-10

COMPARISON OF INITIAL CATALYST PERFORMANCE
OF UCI CATALYSTS L-1122, L-1123, AND L-1124

Run No. (1)	213-57B	213-60P	213-63B
Catalyst Identification	UCI L-1122	UCI L-1123	UCI L-1124
Maximum Reduction Temperature, °C (2)	240	240	450
Synthesis Temperature, °C	348	351	359
Synthesis VHSV, 1/hr/kg cat	2400	2800	2500
Synthesis Pressure, psig	1480	1470	1505
Hours on Stream	2.3	6.1	1.3
Reactor Type	Berty	Plug-Flow	Berty
<u>Results</u>			
CO Conversion, (3), Vol %	18.6	12.1	9.0
ALKANOL Selectivity, Wt %	96.7	90.2	96.3
C ₁ -C ₃ H.C. Selectivity, Wt %	3.3	9.8	3.7

(1) Tests made with 2/1 H₂/CO synthesis gas having 5% CO₂ content.

(2) Reduction using 2% H₂/98% N₂, 1 atm., 500 VHSV.

(3) CO₂-free basis.

TABLE V-11

INITIAL CATALYST PERFORMANCE OF UCI L-1122
CATALYST SCREENED IN THE BERTY REACTOR

<u>Test No. (213-57)</u>	1	2	3	4
(1) <u>Test Conditions</u>				
Temperature, °C	299	348	301	350
VHSV, l/hr/kg cat	2480	2425	5680	6240
Hours on Stream	0.5	2.3	4.6	5.3
<u>Run Results</u>				
CO Conversion, Vol%(2)	25.85	18.62	9.57	17.16
ALKANOLS Selectivity, Wt%	99.2	96.7	99.3	96.7
C ₁ -C ₃ H.C. Selectivity, Wt%	0.8	3.3	0.7	3.3
<u>Alkanol Weight Distribution, Wt%</u>				
Methanol	98.5	89.7	98.6	92.6
C ₂ -C ₆ Oxygenates	1.1	8.7	1.0	5.9
C ₄ -C ₉ H.C.	0.4	1.6	0.4	1.5

- (1) Synthesis gas has a 2/1 hydrogen/carbon monoxide ratio with 5 percent carbon dioxide content.
Synthesis pressure fixed at 1500 psig.
Impeller speed fixed at 1500 rpm.
- (2) carbon dioxide-free basis.

Appendix of this report). A calcined catalyst sample was reduced in the Berty reactor according to the standard reduction procedure described in Section IV. The final reduction temperature was 240°C. Synthesis testing was performed with a synthesis gas having a 2/1 hydrogen/carbon monoxide ratio with 5 percent carbon dioxide content. Synthesis temperature and space velocity were varied while synthesis pressure was kept constant at 1480 psig.

At these test conditions, the L-1122 catalyst demonstrated high selectivity to the production of methanol. Over the relative short on-stream time investigated, it appears that increasing temperature by about 50°C results in about a 5-7 percent increase in C₂-C₆ oxygenates content of the ALKANOLS mixture with a concomitant 6-9 percent decrease in the methanol content (see Figure V-4). The relatively high carbon monoxide conversion for test #1 might be a result of the hyperactivity of a freshly reduced catalyst (only 30 minutes on-stream time) placed in service.

These screening studies revealed that this catalyst formulation results in close to targetted selectivities (and conversion rates) to ALKANOLS and therefore was evaluated in more detail in the process variable scans of Task 2:

UCI L-1123 Catalyst (Run 213-60P)

UCI L-1123 catalyst was screened for initial catalyst performance in the plug-flow reactor using a 2/1 volume dilution with inert alumina beads. The catalysts was reduced under the same conditions as those used for reducing UCI L-1122 catalyst. Four synthesis tests were made as described in Table V-12 (detailed test data are provided in the Appendix). Over the first six hours of testing, the catalyst appeared to be deactivating as measured by carbon monoxide conversion per pass. The first test point obtained at about 24 minutes on-stream time probably demonstrated the hyperactivity of a freshly reduced catalyst placed on-stream. The corresponding carbon monoxide conversion of 22.4 percent was higher than that of an ensuing test made at a 45°C higher reaction temperature (and

TABLE V-12

INITIAL CATALYST PERFORMANCE OF UCI L-1123
CATALYST SCREENED IN THE DILUTED-BED, PLUG FLOW REACTOR

Test No. (213-60)	1	2	3	4
(1)				
<u>Test Conditions</u>				
Temperature, °C	306	352	351	350
VHSV, 1/hr/kg cat	3100	2960	2770	1930
Hours On-Stream	0.4	3.3	6.1	6.8
<u>Run Results</u>				
CO Conversion(2), Vol%	22.4	21.6	12.1	14.4
Alkanol Selectivity, Wt%	98.9	92.0	90.2	87.5
C ₁ -C ₃ H.C. Selectivity, Wt%	1.1	8.0	9.8	12.5
<u>Alkanol Weight Distribution, Wt%</u>				
Methanol	98.8	94.4	90.2	88.1
C ₂ -C ₆ Oxygenates	0.9	1.4	6.8	8.7
C ₄ -C ₉ Hydrocarbons	0.3	4.2	3.0	3.2

(1) Tests made with 2/1 H₂/CO synthesis gas having 5% CO₂ content.

(2) Reduction using 2% H₂/98% N₂, 1 atm., 500 VHSV.

