

## Chapter 5

### **A Kinetic Model for the Synthesis of High-Molecular-Weight Alcohols over a Sulfided Co-K-Mo/C Catalyst**

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#### **ABSTRACT**

A statistically-designed set of experiments was run in a recycle reactor to evaluate the kinetics of the formation of higher alcohols and total hydrocarbon byproducts from synthesis gas (hydrogen and carbon monoxide) in a range of experimental conditions that mirrors the limits of commercial production. The alkali-promoted, C-supported Co-Mo sulfide catalyst that was employed in this study is well known for its sulfur resistance. The reaction was carried out in a gradientless Berty-type recycle reactor. A two-level fractional-factorial set consisting of sixteen experiments was performed. Five independent variables were selected for this study: temperature, partial pressure of carbon monoxide, partial pressure of hydrogen, partial pressure of inerts, and methanol concentration in the feed. The major oxygenated products were found to be linear alcohols up to n-butanol, but alcohols of higher carbon number were also detected, and analysis of the liquid product revealed also the presence of trace amounts of ethers in the products. Yields of hydrocarbons were non-negligible. The alcohol product distribution followed an Anderson-Schultz-Flory distribution. From the results of the factorial experiments, a preliminary power-law model was developed, and the statistically significant variables in the rate expression for the production of each alcohol were found. Based on the results of the power-law models, rate expressions of the Langmuir-Hinshelwood type were fitted. The observed kinetics are consistent with the rate-limiting step for the production of each higher alcohol being a surface reaction of the alcohol of next-lower carbon number. All other steps, including CO-insertion, H<sub>2</sub>-cleavage and hydrogenation steps do not appear to affect the rate correlations.

## INTRODUCTION

The modification of Fischer-Tropsch (FT) synthesis catalysts by adding an alkali promoter produces a variety of oxygenated compounds including alcohols. The direct synthesis of higher-molecular-weight alcohols from CO and H<sub>2</sub> has been practiced since the mid 1920's (Fischer, 1925; Frolich and Lewis, 1928; Frolich and Cryder, 1930; Morgan *et al.* 1932). These higher alcohols can be used as gasoline additives to improve octane number. Catalysts used for the production of higher alcohols are classified into the following three categories: (i) Modified High-Pressure Methanol-Synthesis catalysts (alkali-doped Zn-Cr oxides); (ii) Modified Low-Pressure Methanol-Synthesis catalysts (alkali-doped Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>); and (iii) Alkali-Doped Molybdenum Sulfide (ADM) catalysts. The modified methanol synthesis catalysts have been characterized and the reaction mechanisms over these catalysts have been identified (Smith and Anderson, 1983, 1984; Vedage *et al.*, 1983; Nunan *et al.*, 1989). Kinetic models for higher-alcohol synthesis over Cs-Cu/ZnO, K-Cu/ZnO/Cr<sub>2</sub>O<sub>3</sub>, K-CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>, and Zn-Cr-K catalysts have been reported (Smith *et al.*, 1991; Calverly and Smith, 1992; Boz *et al.*, 1994; Tronconi *et al.*, 1987; Tronconi *et al.*, 1992). These catalysts are not considered in this work.

ADM catalysts are of particular interest since they are tolerant of sulfur compounds in the feed stream. The use of such catalysts saves the considerable costs of ultra-desulfurization of the syngas feed stream. The patents from the Dow Chemical Company first describe a promoted molybdenum sulfide catalyst that produces higher alcohols (Conway *et al.*, 1987; Stevens, 1988) and is sulfur tolerant. The major oxygenated products over these catalysts are found to be linear alcohols following an Anderson-Schultz-Flory distribution (Santiesteban *et al.*, 1988; Klier *et al.*, 1988). The isotopic studies of Santiesteban (1989) suggest that higher alcohols are formed by a CO-insertion mechanism.

Herman *et al.* (1990) developed a kinetic model for higher-alcohol synthesis over a K-MoS<sub>2</sub>/C catalyst. But the literature still lacks a kinetic model developed from a set of statistically designed experiments. In the present study, a kinetic model for higher-alcohol synthesis over a Co-K-MoS<sub>2</sub> catalyst has been developed from a set of fractional-factorial experiments. The advantages of such a statistically designed experiment are two-fold. First, all of the several variables in the study have been investigated simultaneously, and over the entire range of their respective conditions. This affords a much greater opportunity for interactions between variables to exert influence on observed rates, leading to the development of a more-robust kinetic model. Second, we have been able to examine the statistical significance of each variable before any model is developed. If the average reaction rates at the high level of the variable are not significantly different from the rates at the low level of the variable, the variable is considered to have no real influence, and is eliminated. The early elimination of non-influential variables is a very real advantage of this approach.

Further, most of the kinetic studies reported in the literature were performed in plug-flow reactors. These reactors may be limited by external mass- and heat-transfer rates, and may not yield the intrinsic kinetics of the reaction of interest. In the present work, a Berty-type internal

recycle reactor was used for kinetic testing. Owing to the high linear velocities that are achievable in recycle reactors, it is possible to overcome external mass- and heat-transfer limitations. Hence it is possible to obtain better and more-reliable kinetic data.

The catalyst used in the present work was a C-supported, K-promoted Co-Mo sulfide. In earlier work (Liu *et al.*, 1997), we have compared related supported catalysts to unsupported catalysts. Addition of a support results in an increase in the yields of both alcohols and hydrocarbons, on a Mo basis. The clearly beneficial effect of K on (unsupported) MoS<sub>2</sub> catalysts was also reported.

## **EXPERIMENTAL**

### **Catalyst Preparation**

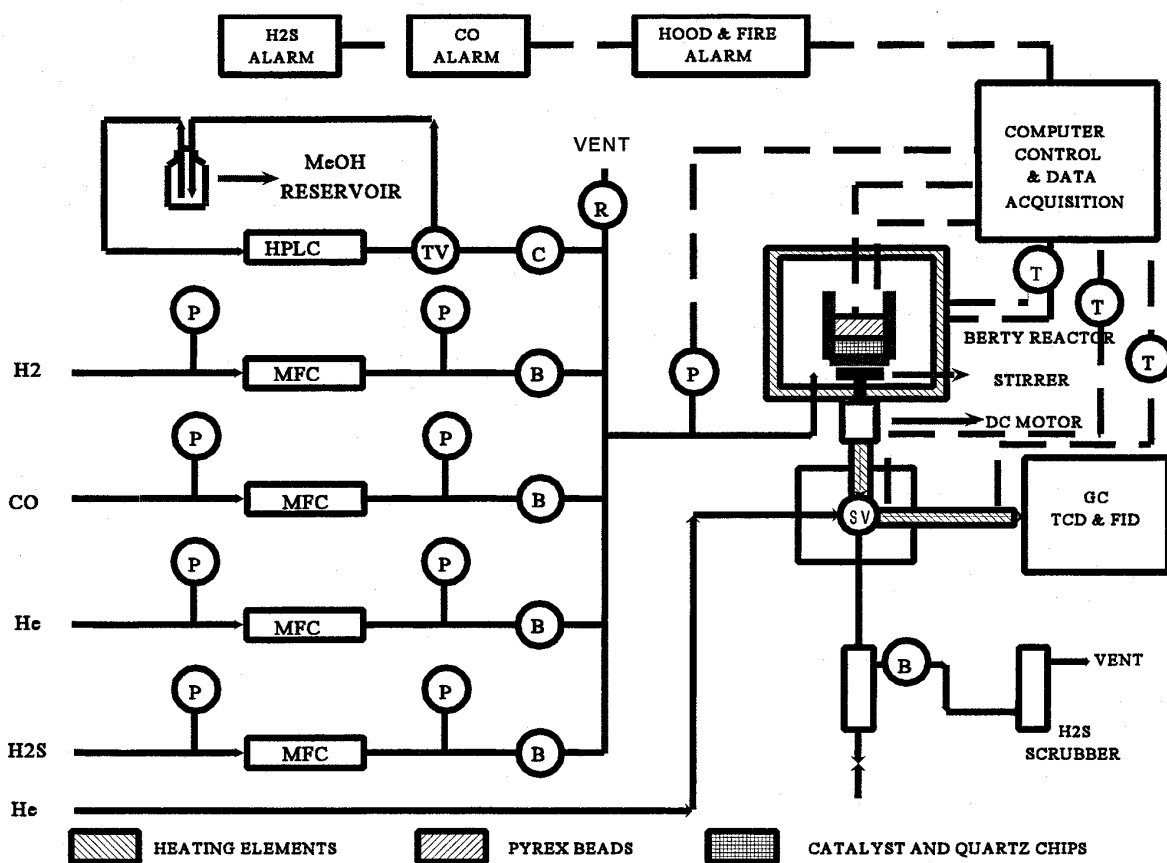
The C-supported, K-promoted Co-Mo sulfide catalyst was prepared by an incipient-wetness technique. Mo was impregnated first, followed by Co and K. The activated carbon support (20-40 mesh size, BET surface area of 655m<sup>2</sup>/g, pore volume of 0.93ml/g) was obtained from Aldrich Chemical Company (Lot # 00915PX). The soluble impurities on the activated carbon were removed by boiling it in water for about an hour. An aqueous solution of ammonium heptamolybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O) was prepared by dissolving 4.3g of ammonium heptamolybdate in approximately 10cc of water. This solution was used to impregnate 10g of washed activated carbon support. The sample thus obtained was dried at room temperature for four hours and then dried again at 100°C overnight in an oven. The dried material was impregnated with a cobalt nitrate solution prepared by dissolving 2.2g of cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) in approximately 10cc of water. After the impregnation, the sample was again dried at room temperature for four hours and then dried again at 100°C overnight. Finally, the material was impregnated with 5cc of 3.2M potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) solution and dried at 100°C overnight. This results in a catalyst containing 18% Mo by weight, and with a Co/Mo ratio of 0.34 and a K/Mo ratio of 1.3. The weight of catalyst used in all the runs was 2.0g.

The catalyst was then reduced to the sulfide form inside the reactor using 100cc/min (STP) of a gas mixture containing 10% H<sub>2</sub>S and 90% H<sub>2</sub> for one hour at 400°C and 1atm pressure. After the sulfidation the catalyst was purged in 100cc/min (STP) of pure H<sub>2</sub> for 90 minutes at 400°C.

### **Catalytic Testing**

The catalyst was tested in the experimental unit shown in Figure 1. The heart of the unit is a gradientless Berty reactor (PPI Inc., Model # 93U-00006-B) used as an internal recycle reactor to measure the catalyst performance. The unit is further equipped with four mass-flow controllers, a back-pressure regulator, a liquid pump, a gas chromatograph (GC) and a personal computer (PC). The PC is used to set all flow rates and temperatures, and to collect and log all data, using commercial software (Wonderware, InTouch 4.1). The carbon monoxide stream enters the system after passing through a trap of activated charcoal (not shown in Figure 1) in order to remove any iron carbonyl impurities. The inlet flow rates of carbon monoxide, hydrogen, helium and hydrogen sulfide are regulated individually by one of four mass-flow controllers (Brooks Model 5850E, range 0-500cc/min). A HPLC pump (ISCO model 2350) is used to inject

liquids such as methanol directly into the reactor. An on-line GC (HP-5890 Series II) samples the exit gases at regular intervals, using a sampling valve (VICI 6-port) located downstream of the reactor. The inorganic gases (CO, N<sub>2</sub> and CO<sub>2</sub>) are separated by a packed HayeSep DB packed-bed column, 30ft x 1/8in in column size and 100-120 mesh in particle size, and are analyzed using a thermal conductivity detector. The organic gases (hydrocarbons and alcohols) are separated by a capillary column (DB Wax, 20m x 0.1mm) and are analyzed using a flame ionization detector. The total CO conversion was calculated using nitrogen as internal standard. A pressurized trap at room temperature is placed downstream of the reactor to collect the liquid products of the reaction. A gas-chromatograph/mass-spectrometer (GC/MS, Varian, Saturn-3) is used off-line to identify the liquid products collected in the the trap.



**Figure 1.** Catalyst testing unit. MFC, mass flow controller; P, pressure gage; T, thermocouple; SV, sampling valve; B, back-pressure regulator; C, check valve; TV, three-way valve; HPLC, liquid pump; R, relief valve.

### Experimental design

The variables considered for the kinetic study were temperature, and partial pressures of carbon monoxide, hydrogen, inerts and methanol. A fractional-factorial experimental design for these

five variables was used in this study. The range of conditions used in the experimental design (and in which the kinetic expressions obtained are valid) was determined as follows. During catalyst screening runs in a plug-flow reactor (Liu *et al.*, 1996), the catalyst activity showed a maximum in the temperature range of 300-350°C. Hence, the kinetic runs were performed in this temperature range. The range of total pressure was chosen to be 400-1000 psi, and the ratio of CO/H<sub>2</sub> was varied from 0.5 to 2. These ranges for the two variables are expected to define the limits of commercial operation. All the experiments were performed at a gas hourly space velocity (GHSV) of 9000 l/hr/kg-catalyst, measured on a fresh-feed basis at 25°C and 1atm. This flow rate has been shown to result in measurable values of products being formed in the experimental range of conditions used. As a necessary characteristic of the experimental design, methanol reaction rates were measured on both sides of chemical equilibrium for the formation of methanol. Hence every run was repeated with and without the introduction of liquid methanol at a flow rate of 0.02 ml/min, measured at 25°C.

The experiments performed in this study are listed in Table 1. The factorial experiments were performed in a random order, as shown in Table 1, so as to make the catalyst age an additional independent variable. The center-point experiment was repeated after every four runs, in order to obtain a measure of the deactivation of the catalyst.

**Table 1. Fractional-Factorial Experimental Design.**<sup>a</sup>

LABEL	Temp [K]	Pressure [psig]	Vapor Flow Rates <sup>b</sup> [cc/min]			CH <sub>3</sub> OH Flow Rate <sup>c</sup> [cc/min]	SEQUENCE
			CO	H <sub>2</sub>	He		
A	573	600	100	100	100	0	13
B	573	600	100	100	100	0.02	4
C	573	600	200	100	0	0	11
D	573	600	200	100	0	0.02	12
E	573	600	100	200	0	0	20
F	573	600	100	200	0	0.02	19
G	573	1000	120	120	60	0	18
H	573	1000	120	120	60	0.02	17
I	623	400	150	150	0	0	5
J	623	400	150	150	0	0.02	16
K	623	800	150	75	75	0	7
L	623	800	150	75	75	0.02	15
M	623	800	75	150	75	0	8
N	623	800	75	150	75	0.02	10
O	623	800	150	150	0	0	2
P	623	800	150	150	0	0.02	3
CP	598	700	128.5	128.5	43	0.01	1,6,9,14,21

<sup>a</sup> Weight of catalyst used = 2.0 g<sup>b</sup> Measured at 25°C and 1 atm<sup>c</sup> Liquid-phase, measured at 25C

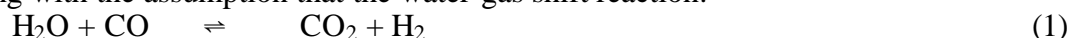
Each run was conducted for about twelve hours. The product rates and CO conversion were measured every two hours. Only when the rates were reasonably constant for at least three successive 2-hour periods was it assumed that the reactor had reached a steady state. Between the runs, when it was needed to shut down the reactor, the catalyst was kept under a constant inert gas flow of 50 cc/min.

## RESULTS

### Product Distribution Calculations

Both hydrocarbons and oxygenated products are observed with this catalyst. The major oxygenated products are found to be the linear alcohols methanol, ethanol, n-propanol, n-butanol and n-pentanol. In addition, occasional analysis of the liquid product by GC/MS revealed the presence of trace amounts of dimethyl ether and diethyl ether, as well as hydrocarbons and alcohols. All the individual hydrocarbons are not quantified in this study, but the major hydrocarbon product was found to be methane. Ethers and other oxygenates not explicitly identified as alcohols were lumped with the hydrocarbon fraction.

As mentioned earlier, the overall conversion of CO was obtained by using inert (nitrogen) as an internal standard. The rates of formation for CO<sub>2</sub> and for the individual linear alcohols were directly measured. A carbon balance was then used to obtain the total hydrocarbons. (Recall that this lump includes all products not explicitly identified as alcohols.) Finally, a hydrogen balance was used, along with the assumption that the water-gas shift reaction:



is in equilibrium, to estimate the amounts of hydrogen and water in the outlet stream. The detailed results from each run can be found in Gunturu (1997) and are summarized in Tables 2 and 3.

**Table 2. Rates of Production of Hydrocarbons and Alcohols for Factorial Experiments**

Sequence	Label	Observed rate of production (g/hr/kg-cat)				Catalyst Age (hr)
		Hydrocarbons	Methanol	Ethanol	Propanol	
1	CP	40.96	-79.23	40.00	5.52	12.00
2	O	43.09	50.86	26.60	6.03	25.50
3	P	94.04	-241.21	72.12	11.66	34.50
4	B	21.11	-97.98	44.24	1.14	55.50

		Observed rate of production (g/hr/kg-cat)				
5	I	21.69	34.95	11.95	1.84	69.00
6	CP	27.72	-70.22	40.34	5.08	79.50
7	K	23.36	20.95	11.43	2.76	91.50
8	M	13.41	21.23	7.55	1.39	103.50
9	CP	43.67	-83.60	37.92	5.20	12.00
10	N	83.45	-237.82	43.03	8.59	27.00
11	C	2.49	9.78	4.18	0.59	37.50
12	D	18.41	-100.19	36.59	1.52	49.50
13	A	3.49	16.00	4.98	0.75	61.50
14	CP	27.90	-70.14	36.31	4.53	73.50
15	L	87.12	-286.84	49.58	12.79	84.00
16	J	67.67	-195.69	41.22	6.79	97.50
17	H	25.41	-89.15	63.21	1.13	113.00
18	G	0.46	3.29	0.96	0.10	122.00
19	F	16.73	-55.99	47.11	0.57	131.00
20	E	0.96	11.33	1.96	0.15	140.00
21	CP	26.90	-46.56	34.47	4.31	149.00



**Table 3. Partial Pressures of Products in the Outlet Stream for Factorial Experiments**

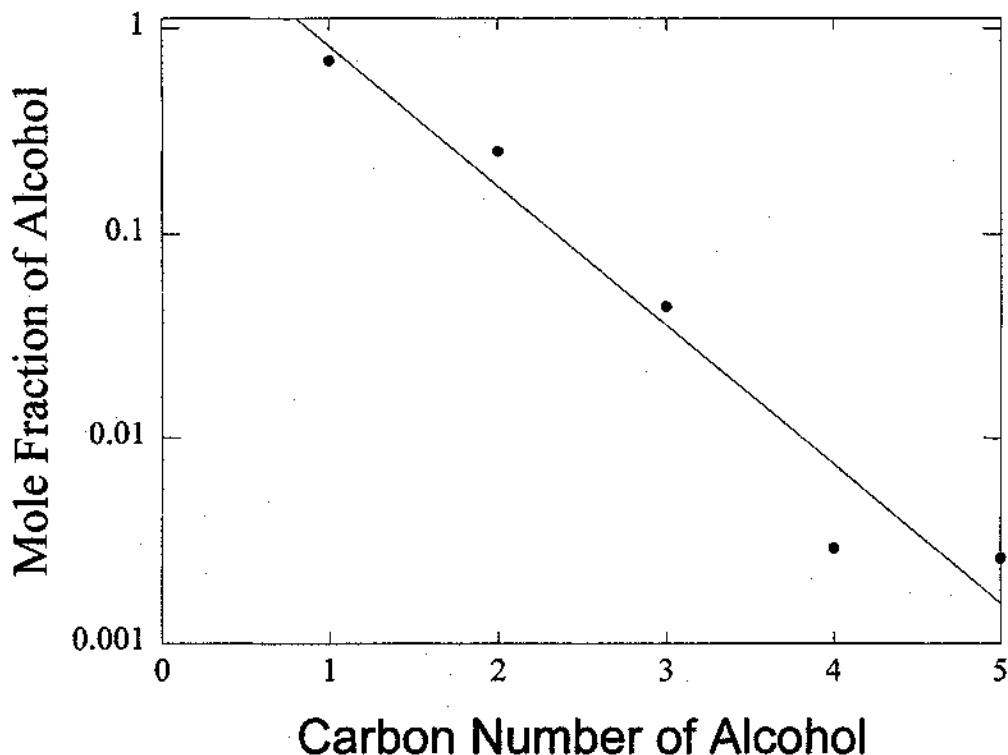
Sequence	Label	Partial Pressures (atm)								
		CO	CO <sub>2</sub>	H <sub>2</sub>	N <sub>2</sub>	He	H <sub>2</sub> O	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>3</sub> H <sub>7</sub> OH
1	CP	19.234	0.795	18.844	0.848	7.095	0.028	0.663	0.117	0.0124
2	O	25.538	0.692	26.711	1.130	0.000	0.036	0.244	0.089	0.0154
3	P	25.659	1.857	24.297	1.165	0.000	0.088	1.152	0.248	0.0308
4	B	13.213	0.391	10.844	0.572	14.292	0.008	1.370	0.112	0.0022
5	I	12.969	0.114	13.468	0.555	0.000	0.006	0.082	0.020	0.0023
6	CP	19.438	0.575	18.872	0.844	7.058	0.020	0.698	0.117	0.0113
7	K	25.845	0.328	13.150	1.108	13.848	0.008	0.099	0.037	0.0069
8	M	12.589	0.355	27.024	0.551	13.775	0.038	0.099	0.025	0.0035
9	CP	19.288	0.741	18.876	0.848	7.092	0.027	0.645	0.111	0.0117
10	N	12.374	1.336	24.441	0.575	14.369	0.132	1.153	0.146	0.0224
11	C	26.115	0.039	13.524	1.093	0.000	0.001	0.034	0.010	0.0011
12	D	26.814	0.489	10.888	1.141	0.000	0.005	1.359	0.093	0.0029
13	A	12.992	0.035	13.490	0.547	13.683	0.001	0.056	0.012	0.0014
14	CP	19.420	0.591	18.894	0.843	7.052	0.021	0.697	0.106	0.0101
15	L	25.868	1.593	10.390	1.144	14.302	0.032	0.910	0.168	0.0332
16	J	13.227	0.483	12.166	0.574	0.000	0.022	0.678	0.070	0.0088
17	H	26.505	0.721	22.660	1.149	14.365	0.016	2.348	0.268	0.0037
18	G	25.994	0.122	27.178	1.090	13.620	0.003	0.019	0.004	0.0003

		Partial Pressures (atm)								
19	F	13.300	0.281	25.012	0.573	0.000	0.014	1.526	0.120	0.0011
20	E	12.993	0.052	27.180	0.546	0.000	0.003	0.039	0.005	0.0003
21	CP	19.480	0.522	18.798	0.845	7.066	0.018	0.798	0.100	0.0100

The results of a typical run (Label O from Table 1) are used to illustrate the distribution of alcohols in the products. If the alcohols follow an Anderson-Schultz-Flory distribution, as observed previously by Santiesteban (1989), then the following relationship applies between the mole fraction of an alcohol  $y_n$ , and its carbon number  $n$ :

$$\log[y_n] = \log[1-\alpha] + (n-1) \log[\alpha] \quad (2)$$

Figure 2 indicates that such a relationship is obtained for this typical run. From the value of the intercept, the value of the chain-growth probability ( $\alpha$ ) is found to be 0.18, and the value of  $\alpha$  is found to be 0.20 from the value of the slope. Hence an average value of 0.19 can be assumed for  $\alpha$ .

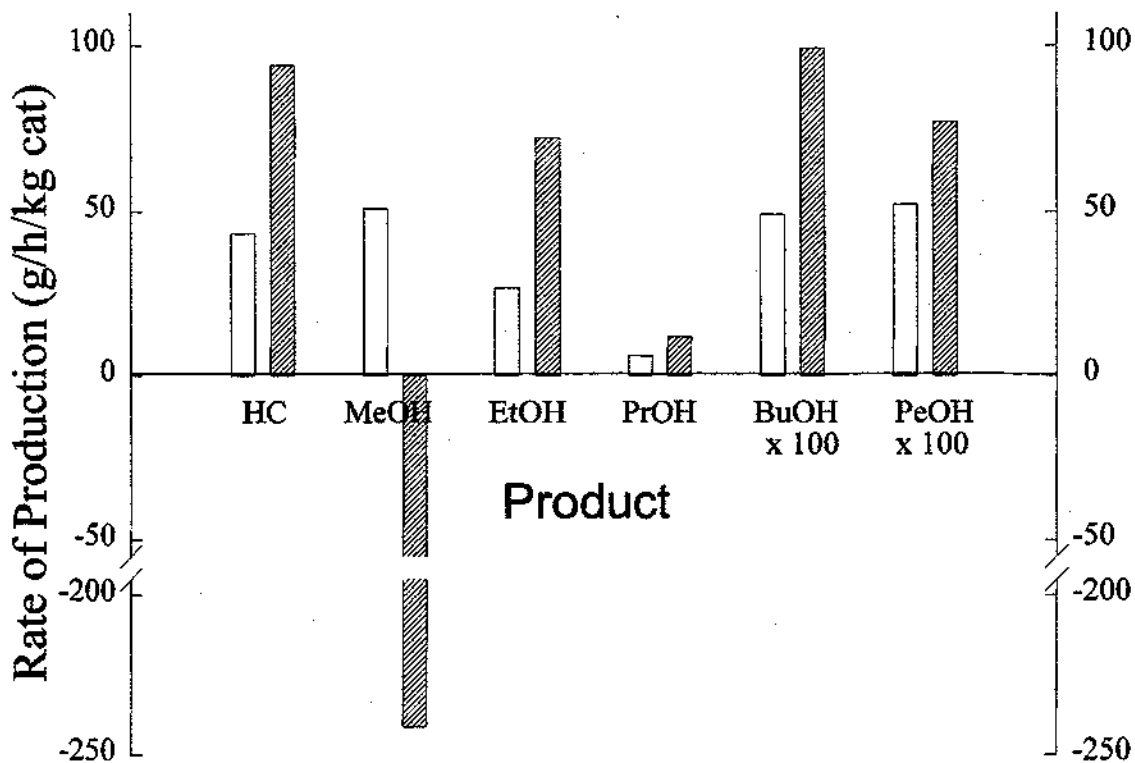


**Figure 2.** Product distribution of alcohols over Co-K-MoS<sub>2</sub>/C catalyst after Run Label O. Experimental conditions: 350°C; 800 psi; 2g catalyst; flow rates - CO, 150 ml/min; H<sub>2</sub>, 150 ml/min; He, 0 ml/min; CO conversion, 0.058.

### Effect of Methanol in Feed

To study the effect of products in the feed stream, methanol was injected into the reactor, along with CO and H<sub>2</sub>. Results of typical experiments with and without methanol in the feed (Labels P and O from Table 1 respectively) are shown in Figure 3. The fraction of CO converted increases from 0.058 to 0.082 when methanol is present in the feed. Methanol in the feed seems to increase the productivities of both higher alcohols and hydrocarbons. The increase in higher-alcohol productivities indicate that higher alcohols are generated from secondary reactions involving

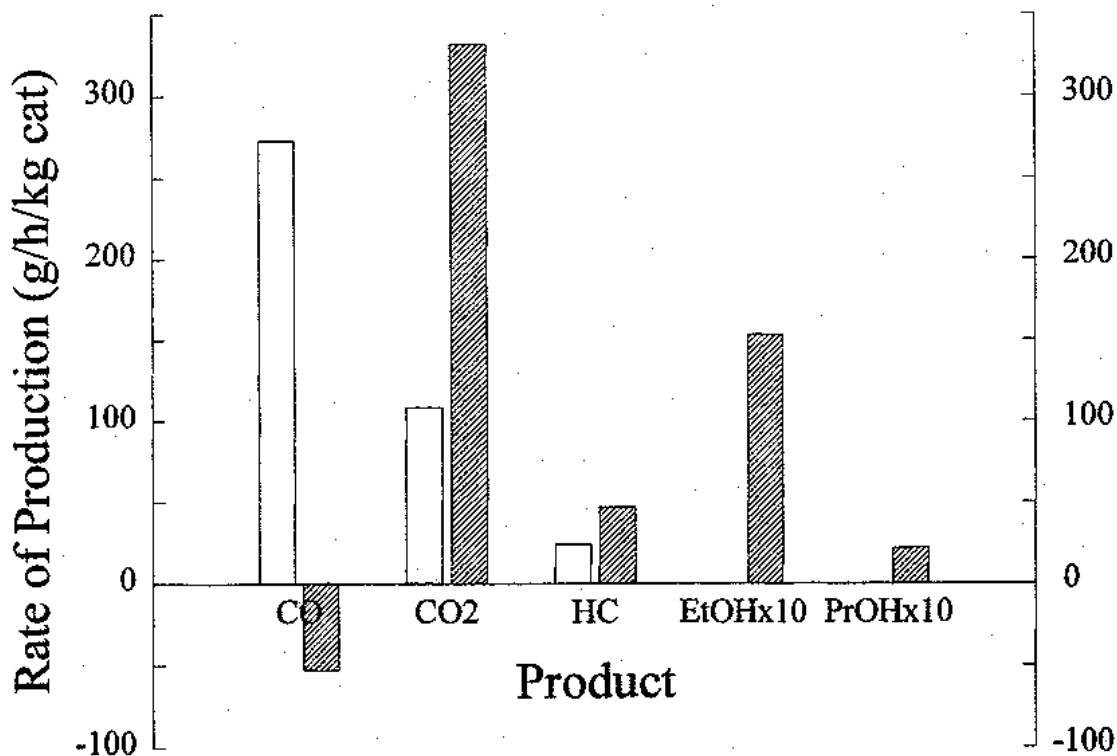
methanol. This result too is consistent with the work of Santiesteban (1989) using isotopic labeling experiments.



**Figure 3.** Comparison of rates of production of hydrocarbons and alcohols with and without methanol in the feed. Experimental conditions: 350°C; 800 psi; 2g catalyst; flow rates - CO, 150 ml/min; H<sub>2</sub>, 150 ml/min; He, 0 ml/min. Unshaded data: Run Label O, no MeOH in feed. Shaded data: Run Label P, 0.02 ml/min MeOH in feed.

### Methanol Decomposition over the Co-K-MoS<sub>2</sub>/C Catalyst

In order to test the hypothesis that higher alcohols may be formed from the condensation of lower alcohols, additional runs were carried out in which only methanol and helium were fed into the reactor. In the product stream from this experiment, no higher alcohols were found, as shown in the unshaded points in Figure 4. If the mechanism of higher-alcohol production involves only the condensation of lower alcohols, then significant amounts of ethanol would have been found in the product stream. The absence of ethanol in the products rules out the possibility of a condensation mechanism.



**Figure 4.** Comparison of methanol decomposition with and without CO in the feed. Experimental conditions: 350°C; 700 psi; 2g catalyst; methanol flow rates, 0.02 ml/min; hydrogen flow rates, 0 ml/min. Unshaded data: flow rates - CO, 0 ml/min; He, 300 ml/min; MeOH conversion, 0.92. Shaded data: flow rates - CO, 171 ml/min; He, 128 ml/min; MeOH conversion, 0.73.

When carbon monoxide was fed along with the methanol, with all other conditions maintained constant, then appreciable rates of production of ethanol and propanol were found. See the shaded points in Figure 4. This supports a mechanism in which CO is inserted into a lower-carbon-number alcohol to form an alcohol with a higher carbon number, the so-called CO-insertion mechanism.

#### Effect of Catalyst Age

As mentioned earlier, several runs were carried out at the conditions of the center point of the matrix of experimental ranges (CP in Table 1). These repeated runs are plotted in Figure 5 as a function of the catalyst time on stream. The results indicate qualitatively that there is no significant effect of catalyst age on the production of higher alcohols. We return to this later.

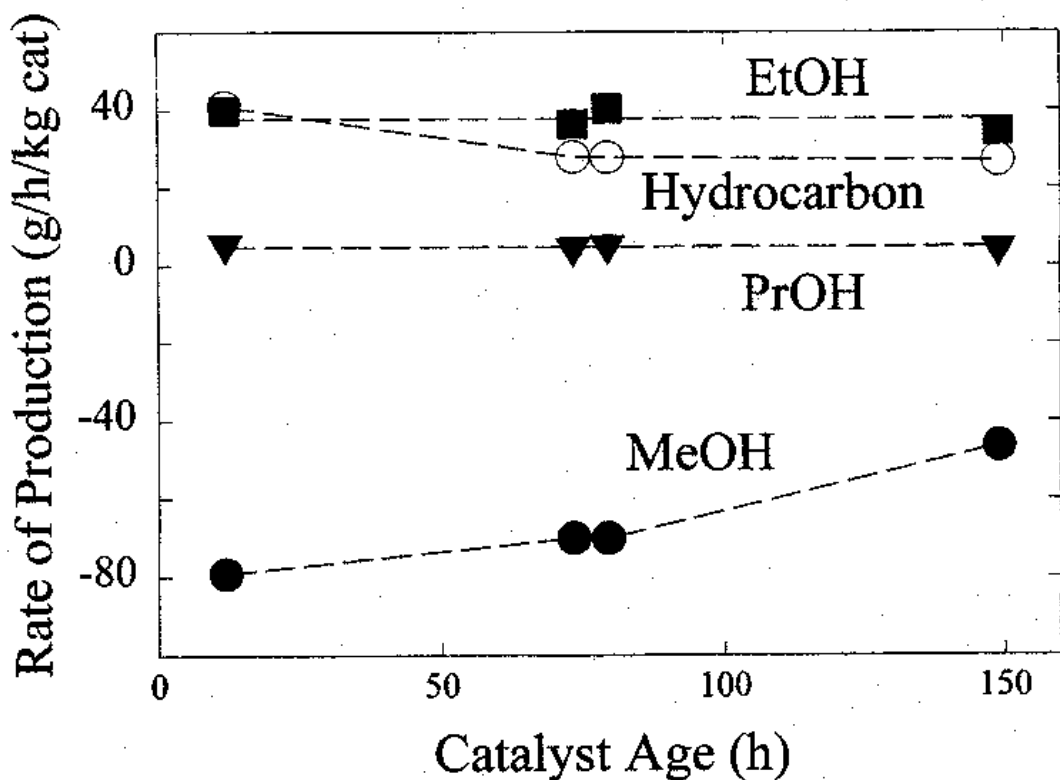


Figure 5. Effect of catalyst age on rates of production of alcohols and hydrocarbons after runs at center-point conditions, Run Label CP.

### Reaction Scheme

Santesteban (1989) suggested a detailed mechanism for the production of alcohols over  $\text{MoS}_2$  catalysts. A reaction network involving all the steps of this model would be very complicated, and it is difficult to obtain a statistically valid model for such complicated reaction schemes. So, the simplified reaction scheme shown below is assumed:



In this reaction scheme, the production of methanol from CO and H<sub>2</sub> is reversible. The subsequent steps proceed mainly via a CO-insertion mechanism and are assumed to be irreversible. The water-gas shift reaction, Equation (1), is assumed to be in thermodynamic equilibrium. Further, it is assumed that hydrocarbon products are composed exclusively of methane and are produced from methanol. As noted earlier, all products that were not identified as linear alcohols were also included in the hydrocarbon lump.

The reactions involved in the above scheme are sequential, that is, ethanol is produced from methanol by the insertion of CO, propanol is produced from ethanol by the insertion of another molecule of CO, and so on (although alcohols of carbon number higher than propanol are formed in quantities small enough to be neglected for present purposes). Further, methane is produced from reactions involving methanol. Hence the gross rate of production of methanol is equal to the sum of the observed (or net) rates of production of methane, methanol, ethanol and propanol, with all rates expressed in mol/hr/kg-cat to satisfy the carbon balance. Similarly, the gross rate of production of ethanol is equal to the sum of the observed (net) rates of production of ethanol and propanol. The gross rates of production, rather than the observed rates, are used for developing the kinetic models for the sake of simplicity. Kinetic models for the observed (net) rates are later back-calculated from the gross-rate models using the relationships above.

### Analysis of Kinetic Data

Since reactions occur at discharge conditions in recycle reactors, partial pressures at the outlet conditions have been chosen as the independent variables. It is necessary to ensure that the partial pressures of CO, H<sub>2</sub>, He and CH<sub>3</sub>OH, temperature and catalyst age at outlet conditions are indeed independent. Hence, a correlation analysis is used (Cropley, 1987a). The determinant of the correlation matrix is a useful measure to judge the independence of the corresponding set of variables. Values of the determinant close to unity indicate that the variable set is independent. The correlation matrix for the present study is shown in Table 4. Using the values of Table 4, the determinant of the correlation matrix is found to be 0.79. This is sufficiently close to unity that a regression analysis can be performed on the data of Table 3.

**Table 4. The SAS System Correlation Analysis**

X1 refers to outlet temperature; X2, X3, X4 and X5 refer to the partial pressures of CO, H<sub>2</sub>, He and CH<sub>3</sub>OH respectively in the products; and X6 refers to the catalyst age.

<b>Correlation matrix with catalyst age</b>						
	<b>X1</b>	<b>X2</b>	<b>X3</b>	<b>X4</b>	<b>X5</b>	<b>X6</b>
<b>X1</b>	1.0000	-0.0368	0.0080	0.0038	-0.2087	-0.2366
<b>X2</b>	-0.0368	1.0000	-0.0674	0.0287	0.1276	-0.1501
<b>X3</b>	0.0080	-0.0674	1.0000	-0.0442	-0.0235	0.2183
<b>X4</b>	0.0038	0.0287	-0.0442	1.0000	0.1119	0.0834
<b>X5</b>	-0.2087	0.1276	-0.0235	0.1119	1.0000	0.0216
<b>X6</b>	-0.2366	-0.1501	0.2183	0.0834	0.0216	1.0000
<b>Determinant value = 0.79</b>						

Two kinds of models were developed from the kinetic data: exponential models and Langmuir-Hinshelwood (LH) models. The form of the exponential models and of the LH models are given later. In the exponential models, parameters were estimated by minimizing the sum of the squares of the differences between experimental and predicted natural logarithms of the rates for each component:

$$\min \sum_{i=1}^N \left( \ln[r_i^{\text{exp}}] - \ln[r_i^{\text{mod}}] \right)^2$$

where N is the total number of observations (21 in this case),  $r_i^{\text{exp}}$  is the experimental rate of the component during observation i, and  $r_i^{\text{mod}}$  is the predicted rate of the component during observation i. Then Student's t test was used to test the statistical significance of the parameter estimates. The variables that were determined to be statistically significant in the exponential models were used in LH models. For the LH models, the parameters were estimated by using



DBCPOLE, an optimizing subroutine from IMSL. The two types of models are discussed further below.

### Exponential Model

Exponential rate equations of the following form were developed for the rates of production of ethanol, propanol and hydrocarbons:

$$r_{C_2H_5OH}^{gross} = A_1 e^{-(E_1/R)(1/T - 1/T_{cp})} \left[ \frac{P_{CO}}{P_{CO}^{cp}} \right]^{a_1} \left[ \frac{P_{H_2}}{P_{H_2}^{cp}} \right]^{b_1} \left[ \frac{P_I}{P_I^{cp}} \right]^{c_1} \times \left[ \frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right]^{d_1} \left[ \frac{t}{t^{cp}} \right]^{-I_1} \quad (6)$$

$$r_{C_3H_7OH}^{gross} = A_2 e^{-(E_2/R)(1/T - 1/T_{cp})} \left[ \frac{P_{CO}}{P_{CO}^{cp}} \right]^{a_2} \left[ \frac{P_{H_2}}{P_{H_2}^{cp}} \right]^{b_2} \left[ \frac{P_I}{P_I^{cp}} \right]^{c_2} \times \left[ \frac{P_{C_3H_5OH}}{P_{C_3H_5OH}^{cp}} \right]^{d_2} \left[ \frac{t}{t^{cp}} \right]^{-I_2} \quad (7)$$

$$r_{HC}^{gross} = A_3 e^{-(E_3/R)(1/T - 1/T_{cp})} \left[ \frac{P_{CO}}{P_{CO}^{cp}} \right]^{a_3} \left[ \frac{P_{H_2}}{P_{H_2}^{cp}} \right]^{b_3} \left[ \frac{P_I}{P_I^{cp}} \right]^{c_3} \times \left[ \frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right]^{d_3} \left[ \frac{t}{t^{cp}} \right]^{-I_3} \quad (8)$$

In the above equations, the  $A_i$  terms refer to pre-exponential factors in rate constants and  $E_i$  terms represent activation energies, *i.e.*, the temperature dependencies of the rate constants. Partial pressures of components  $i$  are denoted by  $P_i$ , and  $t$  refers to the catalyst age;  $P_i^{cp}$  refers to the value at the center-point condition, while  $t^{cp}$  refers to the mean catalyst age. Component  $I$  denotes the inert. As mentioned earlier, a log-linear regression was used to estimate the parameters in these equations.

Note that an exponential rate equation cannot be developed for the rate of methanol. The overall rate of formation of methanol is negative for those runs where methanol is a reactant, and

positive where methanol is not a reactant. Values which are both positive and negative cannot be accounted for in expressions of the form of Equations (6)-(8).

The results of the regression for Equations (6)-(8) are shown in Table 5. The values of the t-statistic for the rate of ethanol and the rate of hydrocarbons indicate that only the activation energy term and the exponent of the partial pressure of methanol are statistically significant, since only those values of the t-statistic are greater (in absolute magnitude) than the critical value of 3.0. For the rate of propanol, the statistically significant variables are found to be the activation energy and the exponent of ethanol. In all cases, the value of the exponent of the catalyst age is not statistically significant. This is consistent with the qualitative result noted earlier. Only the variables that are statistically significant (using the t-test) are retained in the LH models developed below.

**Table 5. Parameter Estimates for Exponential Models**

Exponential Model for Ethanol			Exponential Model for Propanol			Exponential Model for Hydrocarbons		
Parameter	Estimate	t-statistic	Parameter	Estimate	t-statistic	Parameter	Estimate	t-statistic
$\ln(A_1)$	-0.0420	-0.31	$\ln(A_2)$	-2.4035	-10.43	$\ln(A_3)$	0.9866	7.79
$E_1$	38.252	-5.11	$E_2$	97.852	-7.39	$E_3$	106.478	-15.23
$a_1$	0.1242	0.69	$a_2$	0.0893	0.29	$a_3$	-0.0273	-0.16
$b_1$	-0.3067	-1.89	$b_2$	-0.6406	-2.32	$b_3$	-0.5212	-3.43
$c_1$	-0.0411	-1.02	$c_2$	0.0216	0.31	$c_3$	-0.0123	-0.33
$d_1$	0.7307	19.06	$d_2$	0.5642	6.73	$d_3$	0.6636	18.53
$\lambda_1$	-0.1511	-1.96	$\lambda_2$	-0.3226	-2.43	$\lambda_3$	-0.2684	-3.74

$A_1$ ,  $A_2$ , and  $A_3$  are in [mol/hr/kg-catalyst];  $E_1$ ,  $E_2$ , and  $E_3$  are in [kJ/mol]; all other parameters are dimensionless.

### LH Expression for Methanol Gross Rate

A LH rate expression of the following form can be used for methanol synthesis:

$$r_{CH_3OH}^{gross} = \frac{A_m e^{-(E_m/R)(1/T - 1/T_{cp})} \left( \left[ \frac{P_{CO}}{P_{CO}^{cp}} \right] \left[ \frac{P_{H_2}}{P_{H_2}^{cp}} \right]^2 - \frac{1}{K_{eq}} \left[ \frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right] \right)}{\left( 1 + K_1 \left[ \frac{P_{CO}}{P_{CO}^{cp}} \right] + K_2 \left[ \frac{P_{H_2}}{P_{H_2}^{cp}} \right]^2 + K_3 \left[ \frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right] \right)^{n_m}} \quad (9a)$$

The form of Equation (9a) is widely used in the literature for methanol synthesis; see, *e.g.*, Cropley (1989). Note that this relation allows both positive and negative rates of formation to be obtained, by accounting for both forward and reverse rates of the reaction of Equation (3). Again, the gross rate of production of methanol (the sum of the observed rates of hydrocarbons, methanol, ethanol and propanol) is used instead of the observed rate, as discussed earlier. The parameters  $K_1$ ,  $K_2$  and  $K_3$ , in the denominator represent adsorption coefficients. The non-dimensional equilibrium constant  $K_{eq}$  in the numerator can be given by:

$$K_{eq} = K_a / (K_z K^{cp}) \quad (9b)$$

The parameter  $K_z$  is a fugacity correction factor which is estimated from the nonlinear regression. The equilibrium constant,  $K_a$ , is obtained as a function of temperature from software CHEMEQ.BAS developed by Sandler (1989). Table 6 shows the results of the calculation of  $K_a$  at the temperature values used here. Finally, the nondimensionalizing term  $K^{cp}$  is given by the ratio of the partial pressures at the central point:

**Table 6. Values of the Equilibrium Constant  $K_a$  <sup>a</sup>**

T (K)	$K_a \times 10^5$
573	20.83
598	8.686
623	3.868

<sup>a</sup> Sandler (1989)

$$K^{cp} = \frac{P_{CH_3OH}^{cp}}{P_{CO}^{cp} [P_{H_2}^{cp}]^2} \quad (9c)$$

For simplicity, the only temperature dependencies employed in Equation (9a) are that of  $K_a$  and that of the rate constant in the numerator, as given by the activation energy term  $E_m$ . This is consistent with previous uses of this type of kinetic relation (see, *e.g.*, Cropley, 1987b)

The results of the non-linear parametric estimation of Equation (9) are summarized in Table 7. Additional details can be found in Gunturu (1997). The coefficient of determination for the above model is 0.8148, that is, more than 80% of the variation in the rate data is explained by the model.

**Table 7. Parameter Estimates for Methanol Synthesis Model**

Parameter	Estimate
$A_m$ [mol/hr/kg-cat]	4.9047
$E_m$ [kJ/mol]	117.733
$K_z$ [dimensionless]	0.3359
$K_1$ [dimensionless]	0.0696
$K_2$ [dimensionless]	0.6400
$K_3$ [dimensionless]	0.6940
$\eta_m$	2
Coefficient of determination	0.8148
F-statistic	10.1160

### LH Expressions for Gross Rates for Ethanol, Propanol and Hydrocarbons

Recall that the catalyst age and partial pressures of carbon monoxide, hydrogen and inerts are statistically insignificant for the gross rates of ethanol, propanol and hydrocarbons. Hence the following forms of the LH rate expressions are selected:

$$r_{C_2H_5OH}^{gross} = \frac{A_e e^{-(E_e/R)(1/T-1/T_{cp})} \left[ \frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right]}{\left( 1 + K_e \left[ \frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right] \right)^{n_e}} \quad (10)$$

$$r_{C_2H_7OH}^{gross} = \frac{A_p e^{-(E_p/R)(1/T-1/T_{cp})} \left[ \frac{P_{C_2H_5OH}}{P_{C_2H_5OH}^{cp}} \right]}{\left( 1 + K_p \left[ \frac{P_{C_2H_5OH}}{P_{C_2H_5OH}^{cp}} \right] \right)^{n_p}} \quad (11)$$

$$r_{HC}^{total} = \frac{A_h e^{-(E_h/R)(1/T-1/T_{cp})} \left[ \frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right]}{\left( 1 + K_h \left[ \frac{P_{CH_3OH}}{P_{CH_3OH}^{cp}} \right] \right)^{n_h}} \quad (12)$$

In the above rate expressions,  $A_e$ ,  $A_p$  and  $A_h$  represent pre-exponential terms;  $E_e$ ,  $E_p$  and  $E_h$  represent temperature dependence terms; and  $K_e$ ,  $K_p$  and  $K_h$  represent adsorption coefficients.

The results of the non-linear parametric estimations are shown in Table 8. Additional details are given in Gunturu (1997). The coefficients of determination for the models are also given in Table 8. These values range from 0.92 to 0.97, *i.e.*, over 92 percent of the variation in the rate data is explained by the models.

**Table 8. Parameter Estimates for Langmuir-Hinshelwood Models**

LH Model for Ethanol		LH Model for Propanol		LH Model for Hydrocarbons	
Parameter	Estimate	Parameter	Estimate	Parameter	Estimate
$A_e$	1.5259	$A_p$	0.1101	$A_h$	4.6928
$E_e$	24.986	$E_p$	89.943	$E_h$	95.416
$K_e$	0.7367	$K_p$	0.2502	$K_h$	1.2472
$n_e$	1	$n_p$	1	$n_h$	1
Coefficient of determination	0.92	Coefficient of determination	0.92	Coefficient of determination	0.97
F-statistic	67.53	F-statistic	65.30	F-statistic	157.31

$A_e$ ,  $A_p$  and  $A_h$  are in [mol/h/kg cat];  $E_e$ ,  $E_p$  and  $E_h$  are in [kJ/mol]; all other parameters are dimensionless.

Note that partial pressures of CO and H<sub>2</sub> do not appear in Equations (10)-(12). The absence of the partial pressures of CO and H<sub>2</sub> in the LH rate expressions suggest that the CO-insertion, H<sub>2</sub>-cleavage, and hydrogenation steps implicit in Equations (3)-(5) do not effect the rates, at least in the range of conditions used here. A possible rate-limiting step might be a surface reaction of an adsorbed alcohol, perhaps a dehydration. However, we note that it is not advisable to infer mechanisms from kinetics obtained in this limited range of experimental conditions.

The values of the activation energy terms for methanol, ethanol and propanol are gathered in Tables 7 and 8. It is not very clear why the term for ethanol is so low compared to those for methanol and propanol. Perhaps ethanol could be forming oxygenated products such as esters and ethers at high temperatures in the actual reaction network. Since these compounds are not considered in this study, the temperature dependence of the gross rate of ethanol production could be lower than the actual value.

### Observed Rates of Formation

Equations (10)-(12) describe the gross rates of formation of methanol, ethanol, propanol and total hydrocarbons over the catalyst under the given conditions. Gross rates are used for ease in the fitting procedure, but expressions for the net (observed) rates are more convenient for reactor design. These expressions can be obtained from the sequential reaction scheme of Equations (3)-(5):

$$r_{HC} = r_{HC}^{gross} \quad (13)$$

$$r_{C_3H_7OH} = r_{C_3H_7OH}^{gross} \quad (14)$$

$$r_{C_2H_5OH} = r_{C_2H_5OH}^{gross} - r_{C_3H_7OH}^{gross} \quad (15)$$

$$r_{CH_3OH} = r_{CH_3OH}^{gross} - r_{C_2H_5OH}^{gross} - r_{HC}^{gross} \quad (16)$$

The gross reaction rates are given by Equations (10)-(12).

It is of interest to compare the experimental values of the rates with the values of the net rates obtained from Equations (13)-(16) and the model parameters. A comparison diagram for each of the species methanol, ethanol, propanol and total hydrocarbons is given in Figures 6 through 9. The fit of the models is generally good.



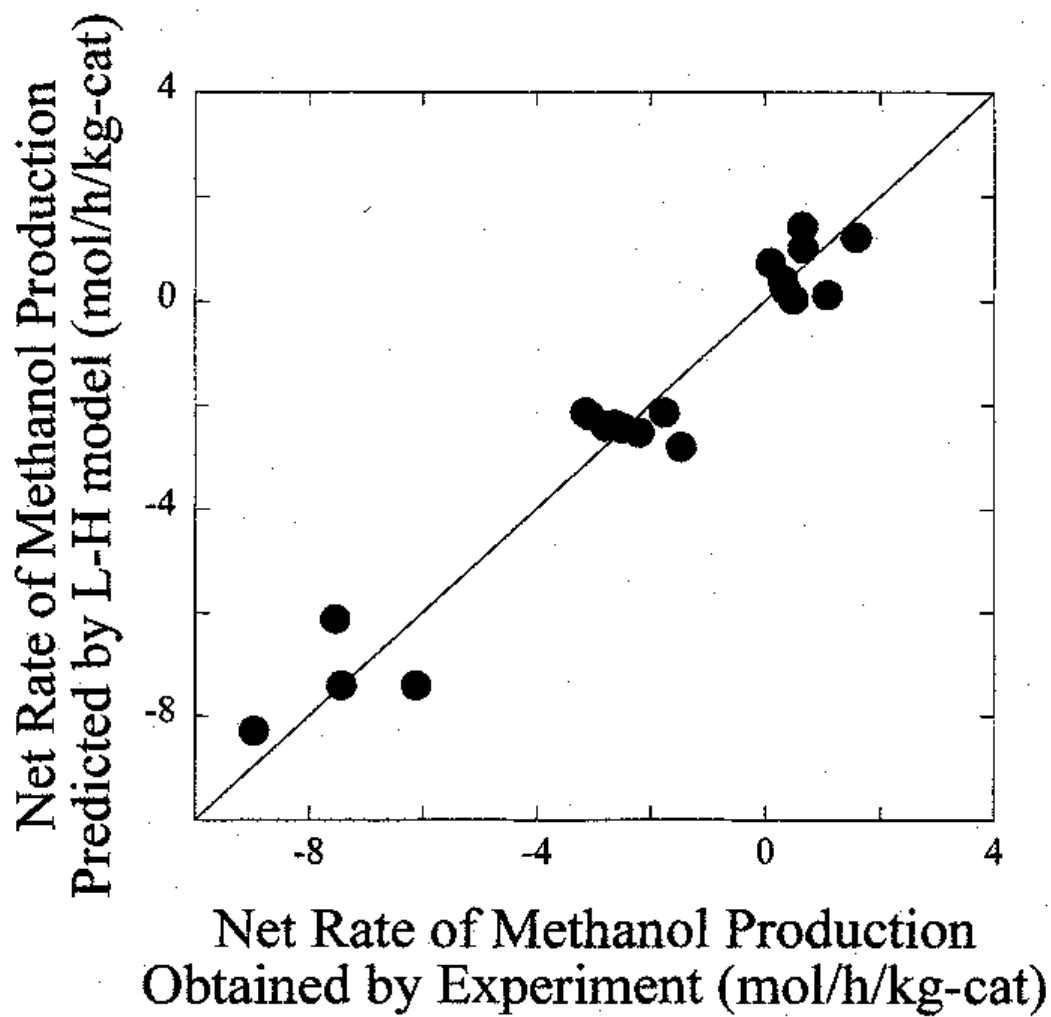
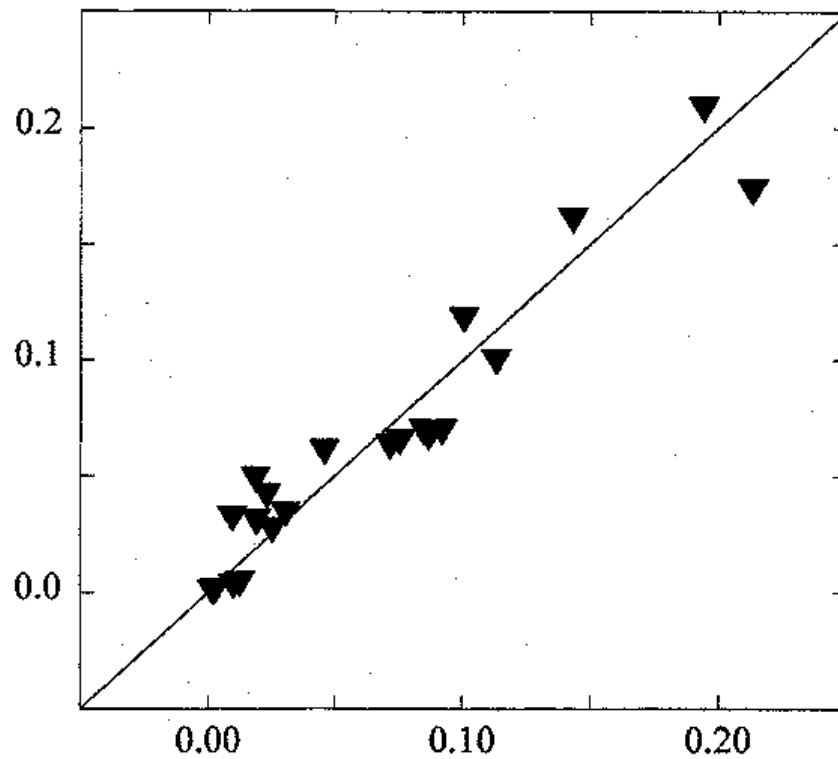


Figure 6. Comparison plot for net rates of methanol production.

Net Rate of Propanol Production  
Predicted by L-H model (mol/h/kg cat)



Net Rate of Propanol Production  
Obtained by Experiment (mol/h/kg cat)

Figure 7. Comparison plot for net rates of ethanol production.

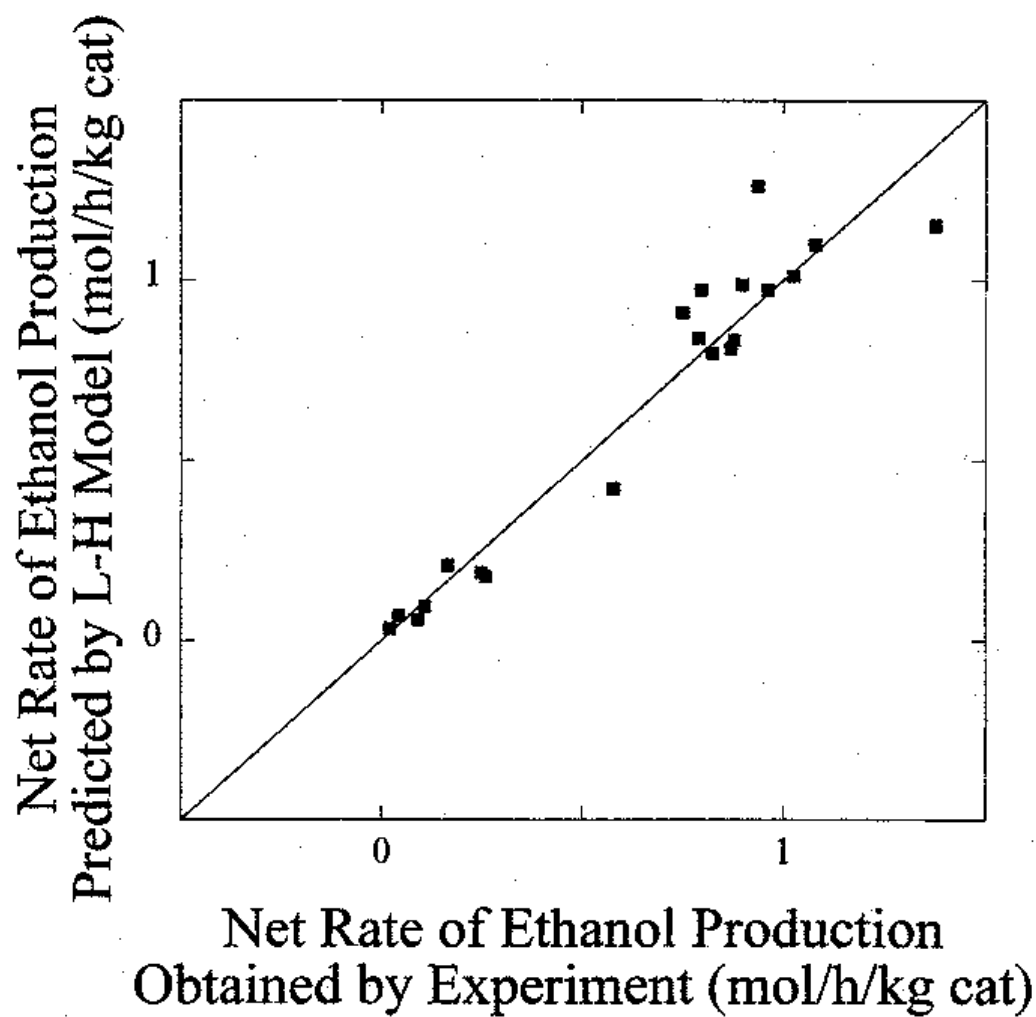


Figure 8. Comparison plot for net rates of propanol production.

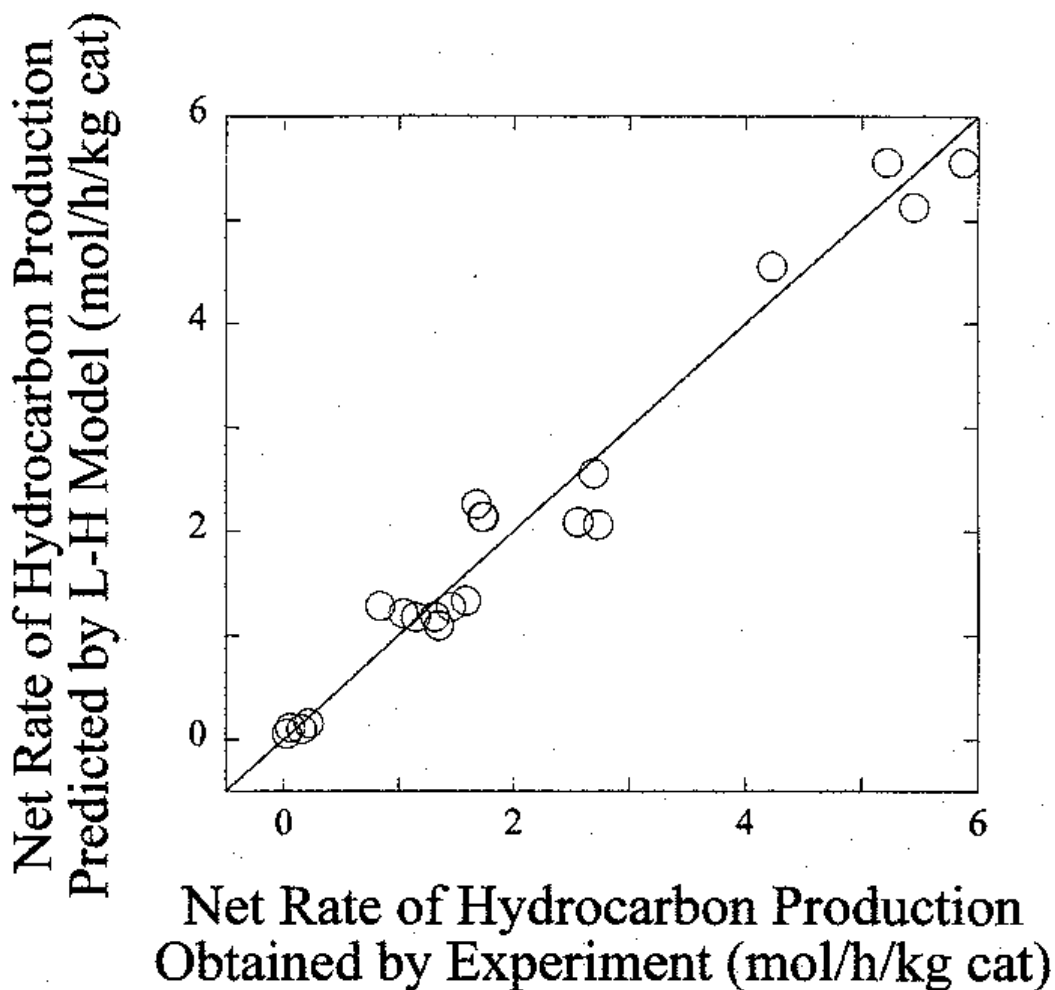


Figure 9. Comparison plot for net rates of hydrocarbon production.

## CONCLUSIONS

The formation of higher-molecular-weight alcohols over a sulfided Co-K-Mo/C catalyst was evaluated. Both hydrocarbons and oxygenated products were observed over this catalyst. The major oxygenated products were found to be linear alcohols such as methanol, ethanol, n-propanol and n-butanol. The major hydrocarbon product was methane. For the sake of simplicity, all oxygenates other than alcohols were lumped with the total hydrocarbon products. The alcohol product distribution follows an Anderson-Schultz-Flory distribution. Alcohol chain growth seems to occur via a CO-insertion mechanism, as suggested by Santiesteban (1989). A Langmuir-Hinshelwood type of kinetic model was developed to quantify the gross rates of

synthesis of each of the higher alcohols, and of the total hydrocarbons (as methane), in the temperature range of 300-350°C and in the range of partial pressures of CO and H<sub>2</sub> of 200-400 psi. The kinetic models suggest that, in the above temperature and partial pressure ranges, the rate-limiting step in the chain growth of the alcohols may be a surface reaction of the corresponding precursor alcohol. Other steps, including CO insertion, hydrogen cleavage, and hydrogenation, do not effect the rate correlations in the ranges used here. The models can be manipulated to predict the net (or observed) rates of formation of the higher alcohols. The predictions agree well with the experimental data.

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