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NOVEL APPROACHES TO THE PRODUCTION OF HIGHER
ALCOHOLS FROM SYNTHESIS GAS

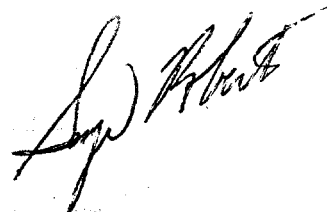
Quarterly Technical Progress Report No. 19

For The Period April 1, 1995 to June 30, 1995

Contractor

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NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report
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CONTRACT OBJECTIVES

- Task 1. Program Management.
- Task 2. Liquid-Phase, Higher Alcohol Process with Recycle of Lower Alcohols.
- Task 3. Novel Catalysts for Synthesis of Higher Alcohols. (Complete)
- Task 4. Synthesis of Higher Alcohols via Acid-Base Catalysis. (Complete)
- Task 5. Technology Evaluation. (Complete)

SUMMARY

Three runs were carried out in the continuous stirred autoclave reactor with Englehard Zn-0312 T 1/8 "zinc chromite" catalyst and with decahydronaphthalene (Decalin[®]) as the slurry liquid. One short run, which was prematurely terminated by operational problems, was designed to define the effect of stirrer speed on catalyst performance. Two longer runs completed the data base required for kinetic characterization of the unpromoted "zinc chromite" catalyst. Although analysis of the data is not complete, it is evident that:

- 1) stirrer speed has no significant effect on the measured reaction rate, and;
- 2) carbon dioxide appears to inhibit catalyst activity.

TECHNICAL DETAILS

A. Runs with "Zinc Chromite" Catalyst

Three runs were carried out in the continuous stirred autoclave reactor using Engelhard Zn-0312 T 1/8 catalyst with Decalin[®] (decahydronaphthalene) as the slurry liquid. This catalyst is a commercial, "high" pressure methanol synthesis catalyst with an atomic Zn/Cr ratio of about 3 and an "as received" BET surface area of about 140 m²/g.

1. Run #1 (April, 1995)

A set of experiments was conducted at different stirrer speeds in order to define the effect of gas-to-liquid mass transfer on the observed reaction rate. Process conditions were: 1000 psig pressure, 5000 GHSV (mol/kg cat - hr), 300°C, and H₂/CO = 2.0. These conditions were chosen so that the methanol synthesis reaction would not be close to equilibrium, and so that an effect of stirrer speed on methanol productivity could be observed if such an effect existed. The reactor inlet gas was fed through a dip tube extending below the agitator. The stirrer speed was set initially at 1750 rpm, then dropped to 1000 rpm, and then finally raised to 2250 rpm. The catalyst concentration was 20 weight percent.

Throughout this run, operational problems were experienced that resulted from an erratic air supply to the compressor. On several occasions, the unit shut down automatically during unattended operation, causing syngas to be purged from the system by N₂. These upsets may have resulted in some catalyst deactivation, and may have interfered with achievement of steady-state conditions. Therefore, the quality of the data from this run is questionable. Nevertheless, the data is presented for the sake of completeness.

Figure 1 shows the methanol productivities that were measured at the three stirrer speeds. The methanol productivity dropped significantly when the stirrer speed was decreased from 1750 to 1000 rpm. However, when stirrer

Figure 1

Effect of Stirrer Speed on Methanol Productivity
April 1995 Zinc Chromite Catalyst Run

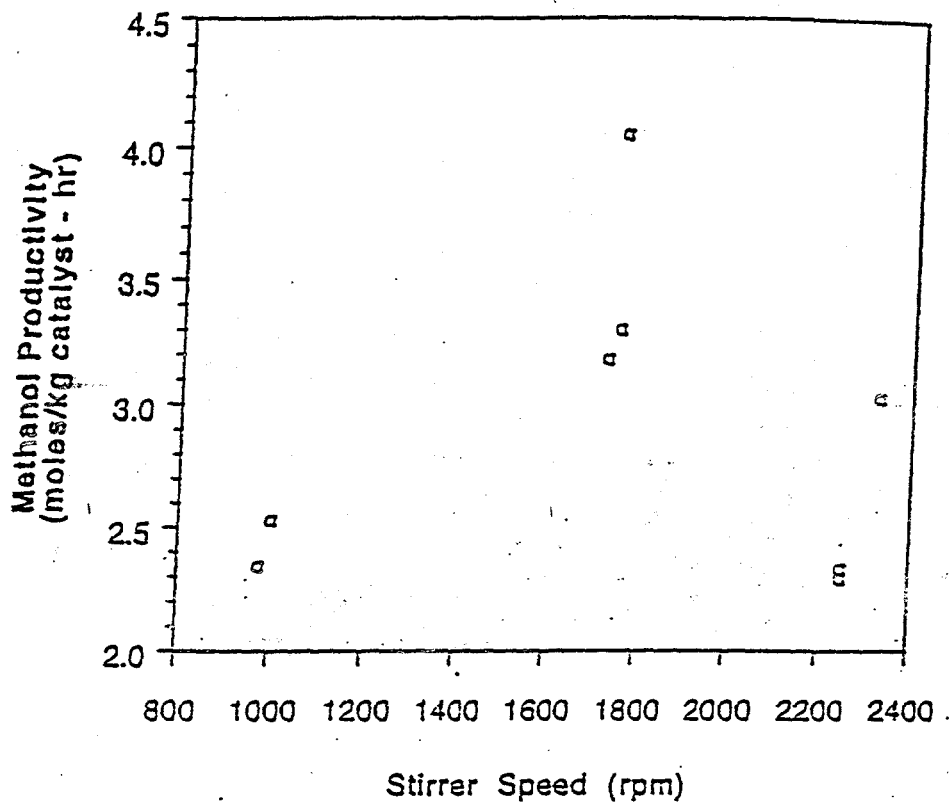
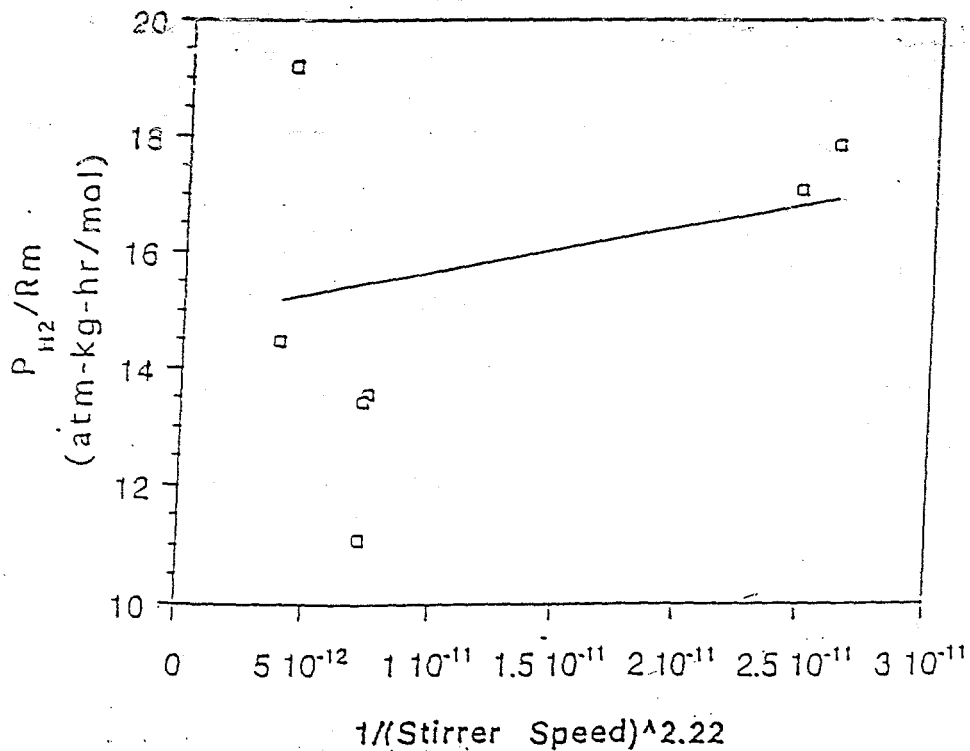


Figure 2

Effect of Stirrer Speed on Catalyst Performance
April 1995 Zinc Chromite Catalyst Run



speed was increased to 2250 rpm, the methanol productivity did not recover as expected.

The February, 1995 Monthly Status Report outlined the development of a simple relationship between the methanol productivity and the stirrer speed:

$$\frac{P_{H_2}}{R_m} = \frac{1}{k} + \frac{1}{AN^{2.22}}$$

where k = intrinsic rate constant (mol / (kg catalyst - hr - atm))

P_{H_2} = partial pressure of hydrogen in the bulk slurry (atm)

R_m = methanol productivity (mol / (kg catalyst - hr))

N = stirrer speed (revolutions per hour, or rph)

A = a physical constant (mol / (kg catalyst - hr - atm - rph^{2.22}))

Figure 2 shows the data from the present plotted according to this relationship. The resulting curve has some positive slope, indicating a dependency of stirrer speed on methanol productivity. However, the scatter of the data at the higher stirrer speeds (low x axis values) negates conclusive interpretation of this data.

This run was prematurely terminated due to problems with the compressed air system. In view of the questionable quality of the data, the run will be repeated to determine positively the effect of stirrer speed on catalyst activity.

2. Run #2 (May, 1995)

This run lasted for 17 days of continuous operation. Process conditions were varied to determine the effects of stirrer speed, reactor temperature, pressure, and space velocity on catalyst activity, as measured by methanol productivity. Table 1 lists the process conditions tested.

Table 1
May 1995 Zinc Chromite Catalyst Evaluation Run
 20 Weight % Catalyst Loading

Run #	H ₂ /CO Ratio	Temperature (°C)	Pressure (psig)	GHSV (sl/kg-hr)	Stirrer Speed (rpm)
1	2	300	1000	5000	1750
2	2	300	1000	5000	2350
3	2	275	1000	5000	1750
4	2	325	1000	5000	1750
5	0.5	325	1000	5000	1750
6	0.5	350	1000	5000	1750
7	2	350	1000	5000	1750
8	1	325	1000	5000	1750
9	2	325	2500	5000	1750
10	2	325	1750	5000	1750
11	2	325	1000	10000	1750
12	2	325	1000	2500	1750
13	0.5*	375	2000	2500	1750

*With about 10% CO₂ in the feed gas

Runs 1 and 2 were designed to determine the effect of stirrer speed; the results are shown in Figures 3 and 4. Figure 3 illustrates the direct relationship between stirrer speed and methanol productivity, while Figure 4 employs the previously-mentioned relationship, i.e.,

$$\frac{P_{H_2}}{R_m} = \frac{1}{k} + \frac{1}{AN^{2.22}}$$

Both figures show that stirrer speed had no significant effect on methanol productivity. Therefore, the gas/liquid mass transfer resistance for these experiments appeared to be insignificant relative to the intrinsic kinetic resistance.

Figure 3

**Effect of Stirrer Speed on Methanol Productivity
May 1995 Zinc Chromite Catalyst Run**

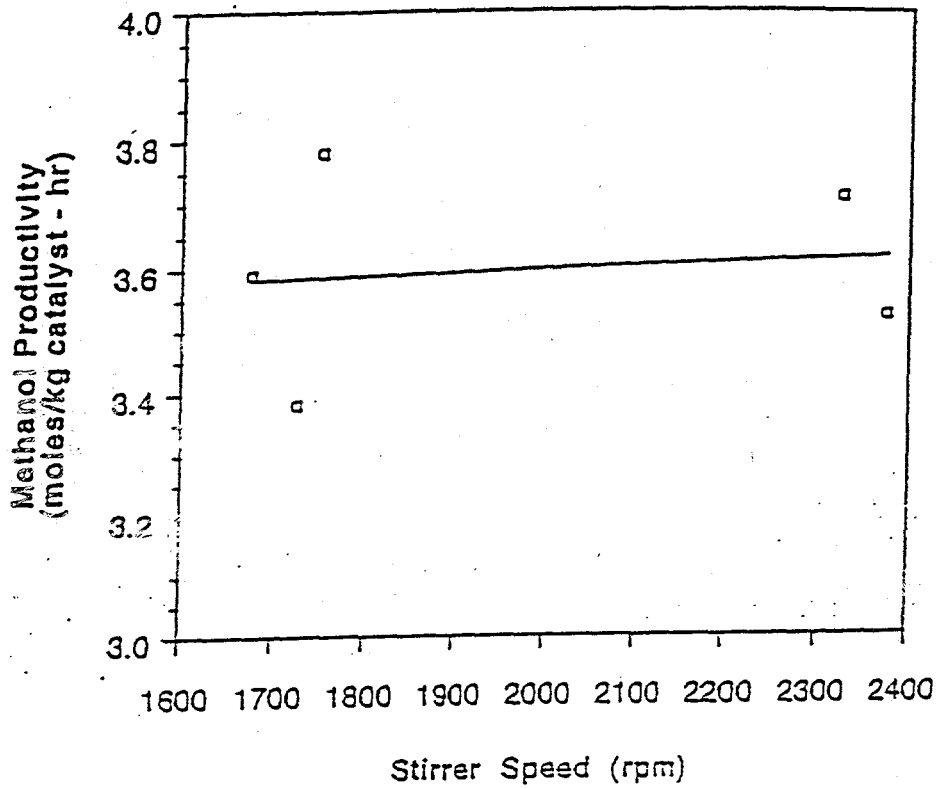
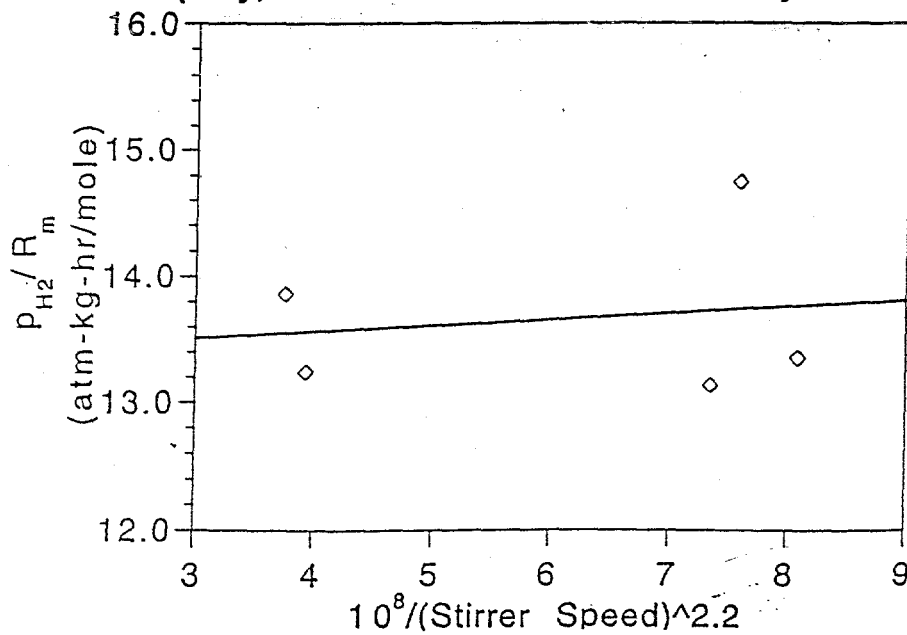


Figure 4

**Effect of Stirrer Speed on Catalyst Performance
(May, 1995 Zinc Chromite Catalyst Run)**



Note that the productivities shown in Figure 3, ca. 3.6 moles/kg-hr, are approximately equal to the initial productivity measured in Run #1 (April, 1995), i.e., the data at 1750 rpm in Figure #1. This suggests that the low productivities at 1000 and 2250 rpm in Figure 1 resulted from the compressor shutdowns described previously.

Figure 5 illustrates the effect of temperature on methanol productivity under operating conditions which should promote methanol synthesis (H_2/CO ratio of 2). The stirrer speed was 1750 rpm for all experiments in this figure. Clearly, 325°C is the optimum temperature for catalyst activity toward methanol synthesis at $H_2/CO = 2$, 5000 GHSV and 1000 psig total pressure.

Most of the remaining reactor conditions listed in Table 1 were designed to investigate the effect of pressure, H_2/CO ratio and space velocity on the reaction rate at the "optimum" methanol synthesis temperature of 325°C. Evaluation of the data from these runs led to a preliminary kinetic expression for methanol synthesis on the unpromoted zinc chromite catalyst:

$$R_m = \frac{kP_{H_2}^{1.5}P_{CO} \left(1 - \frac{P_{Methanol}}{P_{CO}P_{H_2}^2 K_{eq}} \right)}{1 + K_{CO_2}P_{CO_2}} \quad (1)$$

where R_m = methanol productivity (moles / (kg catalyst - hr))

P_i = partial pressure of component i (atm)

k = intrinsic rate constant (mol / (kg catalyst - hr - atm))

K_{eq} = methanol equilibrium constant (1/atm²)

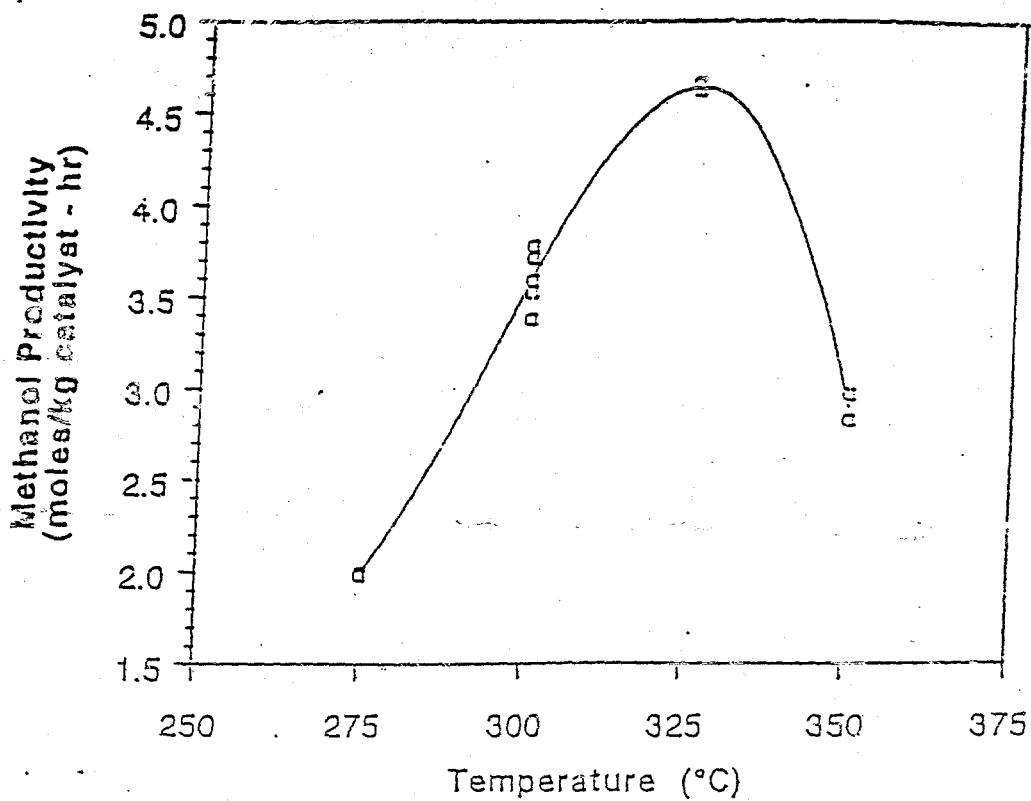
K_{CO_2} - equilibrium constant for CO_2 adsorption (1/atm)

This kinetic expression was developed using the data from the March, 1995 and May, 1995 runs, and was an attempt to describe the effect of CO_2 via a Langmuir-Hinshelwood form of rate equation.

As evident in the kinetic expression, CO_2 inhibits methanol formation. However, more data is needed at higher reactor temperatures and with CO_2 in the reactor gas feed to fully establish the magnitude of this inhibition.

Figure 5

Effect of Temperature on Methanol Productivity
May 1995 Zinc Chromite Catalyst Run
(5000 GHSV, $H_2/CO = 2$, 1000 psig)



Another run is planned to generate such data and to verify the reaction orders with respect to hydrogen and carbon monoxide.

3. Run #3 (June, 1995)

This run lasted for 20 days of continuous operation. Process conditions were varied to determine the effects of stirrer speed, reactor temperature, pressure, space velocity, and gas feed composition on catalyst product selectivity and activity. Table 2 lists the process conditions tested.

Table 2
June 1995 Zinc Chromite Catalyst Evaluation Run
20 Weight % Catalyst Loading

Run #	H ₂ /CO Ratio	Temperature (°C)	Pressure (psig)	GHSV (sl/kg-hr)	Stirrer Speed (rpm)
1	2	325	1000	4500	1750
2	2	325	1000	4500	2450
3	0.5	325	1000	4500	1750
4	1	325	1330	4500	1750
5	2	325	2000	9500	1750
6	2	325	2000	9500	2375
7	2	325	2000	4500	1750
8	2*	325	2000	4600	1750
9	2**	325	2000	4600	1750
10	0.5	325	2000	4600	1750
11	0.5	375	2000	4500	1750
12	2	375	2000	4500	1750
13	2*	375	2000	4700	1750
14	2**	375	2000	5000	1750
15	1	375	2500	4500	1750

*With about 10% CO₂ in the feed gas

**With 10% CO₂ in the feed gas

Runs 1, 2, 5 and 6 were designed to determine the effect of stirrer speed; the results are shown in Figures 6 and 7. Figure 6 illustrates the direct relationship between stirrer speed and methanol productivity, while Figure 7 employs the previously-cited relationship, i.e.,

$$\frac{P_{H_2}}{R_m} = \frac{1}{k} + \frac{1}{AN^{2.22}}$$

Both figures show that stirrer speed had no significant effect on methanol productivity. Therefore, the gas/liquid mass transfer resistance for these experiments appeared to be insignificant relative to the intrinsic kinetic resistance.

Figure 6

Effect of Stirrer Speed on Methanol Productivity
June 1995 Zinc Chromite Catalyst Run

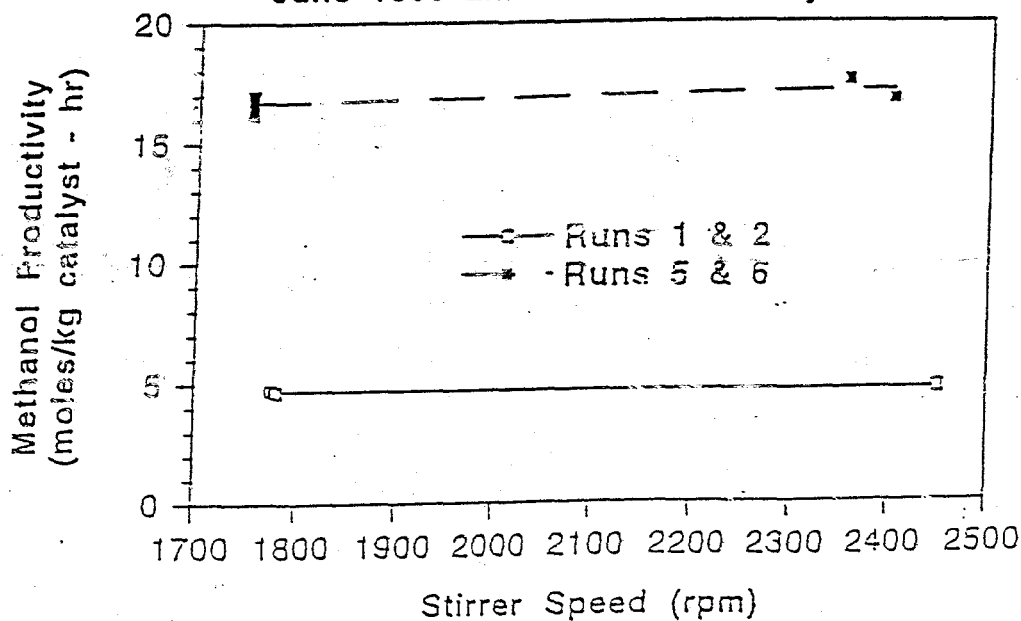
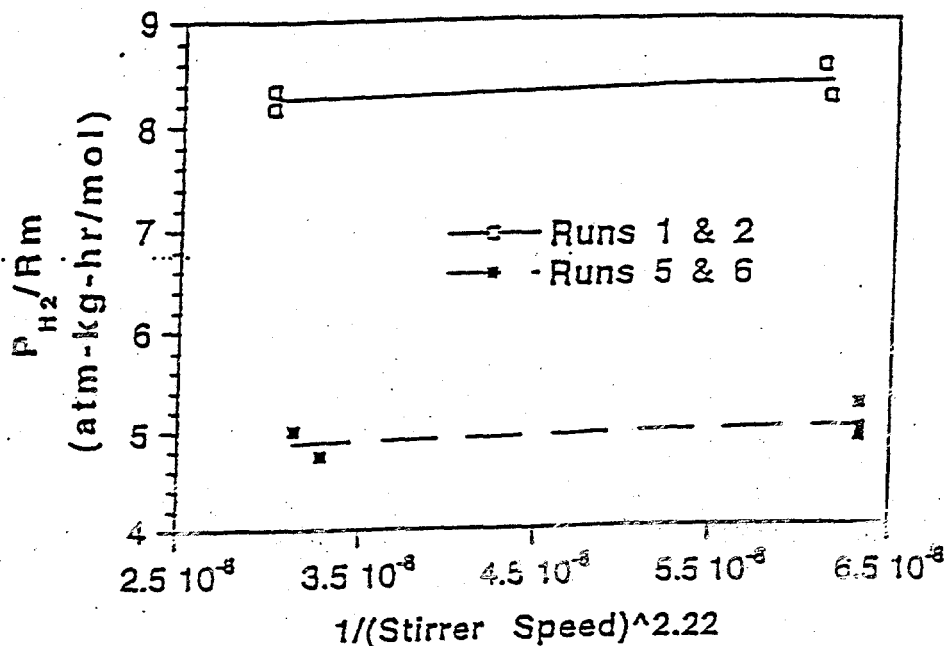


Figure 7

**Effect of Stirrer Speed on Catalyst Performance
June 1995 Zinc Chromite Catalyst Run**



4. Methanol Kinetics with the Zinc Chromite Catalyst

The remaining reactor conditions listed in Table 2 were designed to generate kinetic data for product formation. As a first guess for the kinetic expression for methanol synthesis, a "power law" expression based on the partial pressures of possible reactants in the formation of methanol, i.e., H₂, CO and CO₂, was used. Also, an equilibrium driving force term was included.

$$R_M = k P_{CO}^a P_{H_2}^b P_{CO_2}^c \left(1 - \frac{f_M}{f_{CO} f_{H_2}^2 K_{eq}} \right) \quad (2)$$

where k is the intrinsic rate constant, P_i is the partial pressure of species i , f_i is the fugacity of species i and K_{eq} is the equilibrium constant. The constant k is assumed to obey an Arrhenius form.

$$k = A \exp(-E_a/RT)$$

where A = the pre-exponential factor in $\text{gmol}/[\text{kg catalyst} \cdot \text{hr} \cdot \text{atm}^{(a+b+c)}]$,

E_a = the activation energy for the methanol synthesis reaction in cal/gmol,

R is the universal gas constant in cal/[gmol•K], and

T is the absolute temperature in Kelvin.

This expression was used to model the data from the three zinc chromite catalyst runs (March, May, and June, 1995), generating values for the exponents a,b, and c; and values for A and E_a . These values along with "goodness-of-fit" statistics are shown in Table 3.

Table 3
Goodness of Fit Statistics for the "Best Fit" Kinetic Model

Parameter	Estimate	Standard Error	Lower Confidence Limit	Upper Confidence Limit
a	0.519	0.082	0.358	0.680
b	0.741	0.072	0.592	0.891
c	-0.191	0.034	-0.265	-0.127
E_a	4370	1360	1790	7090
A	1.71	1.87	0.197	14.5

The values shown in this table yield considerable insight into the methanol synthesis kinetics, and will serve as a basis for a more mechanistic or fundamental model. First, the negative value of the exponent for CO_2 suggests it behaves as an inhibitor. Second, the value of the activation energy is lower than those reported in the literature, suggesting that this rate constant could actually be a combination of two or more constants, one being the true intrinsic rate constant, and others being adsorption constants. The apparent inhibitory effect of CO_2 would necessitate the presence of an inhibition constant in the denominator.

Finally, the exponents for hydrogen and carbon monoxide do not correspond with stoichiometric values for methanol synthesis from H_2 and CO (a=1 and b=2). This indicates that the actual reaction mechanism is

probably not limited by the CO hydrogenation reaction, but possibly by a reactant adsorption or a product desorption step. Also, even though CO₂ is showing an inhibitory role, the relative value of its exponent is small, possibly indicating the CO₂ could directly be involved with methanol synthesis, i.e. CO₂ hydrogenation, as well as causing inhibition due to competitive adsorption.

With this information, a more fundamental model will be developed. Specifically, Langmuir-Hinshelwood rate equations of the form of Equation 1 will be evaluated. The differences between the exponents on CO and H₂ in Equations 1 and 2 probably result from: 1) Equation 2 is based on the complete set of data (March, May and June, 1995 runs), whereas Equation 1 does not include the June, 1995 data, and; 2) the form of the dependence on CO₂ is different in the two equations.

B. Other Results

1. Decahydronaphthalene Density Estimates

Due to a lack of liquid density data at typical operating conditions for the zinc chromite catalyst, an estimation of the density of Decalin was performed. The estimation method that was used was developed by Yen and Woods¹. The estimated liquid density of decahydronaphthalene at 375°C is 0.46 grams/mL. The density at 25°C is 0.896 grams/mL.

Clearly, when the reactor temperature is increased from ambient to 375°C, almost a two-fold volumetric expansion takes place. To date, all stirred autoclave runs using Decalin have initially contained 150 mL of liquid. Although the total reactor volume is 300 mL, the volume below the gas exit port is about 250 mL. Therefore, some slurry could have been "expanded" out of the reactor due to thermal expansion of the liquid. Based on these results, only 100 mL of liquid will be used as an initial charge in future runs in order to reduce the possibility of catalyst/slurry carryover.

¹Yen, L. C. and S. S. Woods, *AIChE J.*, 12: 95 (1966).

2. Decahydronaphthalene Thermal Stability Test

A thermal stability test was conducted with decahydronaphthalene containing 20 weight % zinc chromite catalyst. The test started by reducing the catalyst according to the standard reduction procedure using a hydrogen/nitrogen mixture and temperature ramping to 375°C. Then the reactor temperature was held at 375°C, and pure hydrogen was fed through the reactor. The reactor gas effluent was analyzed via gas chromatography to detect trace amounts of hydrocarbons that might indicate possible liquid decomposition.

At 375°C, the hydrocarbon loss rate was about 0.0015 grams/hour, less than that determined during the November, 1994 decahydronaphthalene standard (without catalyst) thermal stability test (about 0.005 grams/hr), also conducted at 375°C. The reactor temperature was then increased to 400°C, and the loss rate increased to about 0.05 grams/hr after about 62 hours of operation at the higher temperature. However, this value was less than half of the 0.15 g/hr hydrocarbon loss rate reported at the conclusion of the Drakeol 34 high temperature blank run (August, 1994 Monthly Status Report).

The reactor temperature was then increased further to 425°C, and additional components were detected by the gas chromatograph. These were C₆₊ compounds, with exact identification not yet determined. The hydrocarbon loss rate increased to 0.11 grams/hour, approaching that seen at the conclusion of the Drakeol 34 blank run.

After run completion, only about 7 grams of liquid remained in the reactor, and the liquid was dark brown and possessed a "burnt" smell. This was uncharacteristic of decahydronaphthalene obtained after previous zinc chromite catalyst runs where the liquid was clear and had a "sweet" smell. Based on these preliminary results, no "zinc chromite catalyst" runs will be planned for temperatures exceeding 375°C until further evaluation is completed.