November 5, 1990

HETEROGENEOUS CATALYTIC CONVERSION OF SYN-GAS TO FUEL ALCOHOLS

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"Optimum Catalytic Process For Fuel Alcohols From Syngas"
DE-AC22-86PC90013
January, 1987 to July, 1990

The objective of our research is to discover and evaluate novel catalytic systems for the selective conversion of synthesis gas into a mixture of alcohols useful as a fuel extender or octane enhancer. These systems include both homogeneous and heterogeneous catalysts, and may involve two-stage operation through methanol.

Our work over the final 9 months of the contract has concentrated on the development of heterogeneous catalysts for the conversion of synthesis gas to C1-C4 alcohol mixtures. Specifically, heterogeneous catalysts consisting of one or more transition metals on mixed metal oxide supports with the spinel structure have been pursued. Catalysts for two different alcohol product mixtures have resulted. One catalyst type produces a Flory distribution of normal alcohols at mild conditions (260°C, 1000 psig) using a hydrogen rich ($H_2/CO=2$) synthesis gas. Alcohol yields as great as 13 lbs/ft^3 catalyst/hr have been observed. The second catalyst type produces an alcohol mixture consisting almost exclusively of isobutanol and methanol using a carbon monoxide rich synthesis gas ($H_2/CO=0.5$) at more elevated temperatures (400°C). Alcohol yields as great as 22 lbs/ft^3 catalyst/hr have been observed with isobutanol selectivities as great as 35 wt%.

Slurry phase reaction studies have been successfully performed using both a typical methanol catalyst and a spinel catalyst for the production of a C_1-C_4 normal alcohol mixture. The tests were run in a two-liter autoclave up to 1000 psig and 270°C using either dodecane or tetraglyme (Tetraethylene Glycol Dimethyl Ether). The kinetic models developed from these tests were used to predict the results of other published works.

AGENDA

I. Review Contract History

II. Current Work:

Direct syngas conversion using spinel
oxide basedheterogenous catalysts.

- A. Catalysts for linear alcohols
- B. Catalysts for iso-alcohols

III. Slurry Reactor Studies

- A. Methanol catalyst shake down studies.
- B. Linear alcohol spinel catalyst performance.

CONTRACT HISTORY

I. Novel Homologation Catalyst System

Objective: Improve upon known cobalt catalysts for conversion of methanol to acetaldehyde and ethanol.

Result: Discovery of diphosphine modified rhodium catalysts that reductively carbonylate methanol at low pressure and temperature with rates (5 mol/L/hr) that rival cobalt catalysts.

II. Direct Syngas Conversion By Homogeneous Catalysis

Objective: Improve upon known ruthenium based homogeneous catalysts discovered by Union Carbide under previous contract for the conversion of synthesis gas to methanol and higher alcohols.

Result: Novel catalyst additives found which improve catalyst activity (7 mol/L/hr) and selectivity to C_2^+ alcohols (40-50%).

III. Direct Syngas Conversion By Heterogeneous Catalysis

A. Alkali Promoted Molybdenum Sulfide

Objective: Explore modifications of the formulation and preparation of alkali promoted MoS2 catalysts in an effort to reduce methane formation while obtaining increased activity (>20 lb/ft^3/hr)

Result: Discovery of novel additive, A116, to increase rate by about 10% without significantly effecting selectivity.

B. Transition Metal(s) on Spinel Oxide Supports

Objective: To explore novel heterogeneous catalyst systems based primarily on transition metal(s) on spinel oxide supports.

Result: To be discussed.

TRANSITION METALS ON SPINEL OXIDES

Previous work

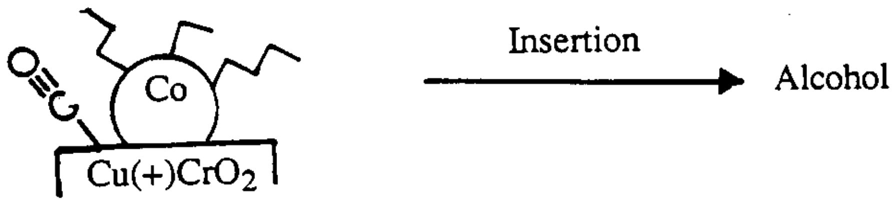
Literature: Insitut Francais du Petrole (IFP)
U.S. Patent 4,122,110 (1978)

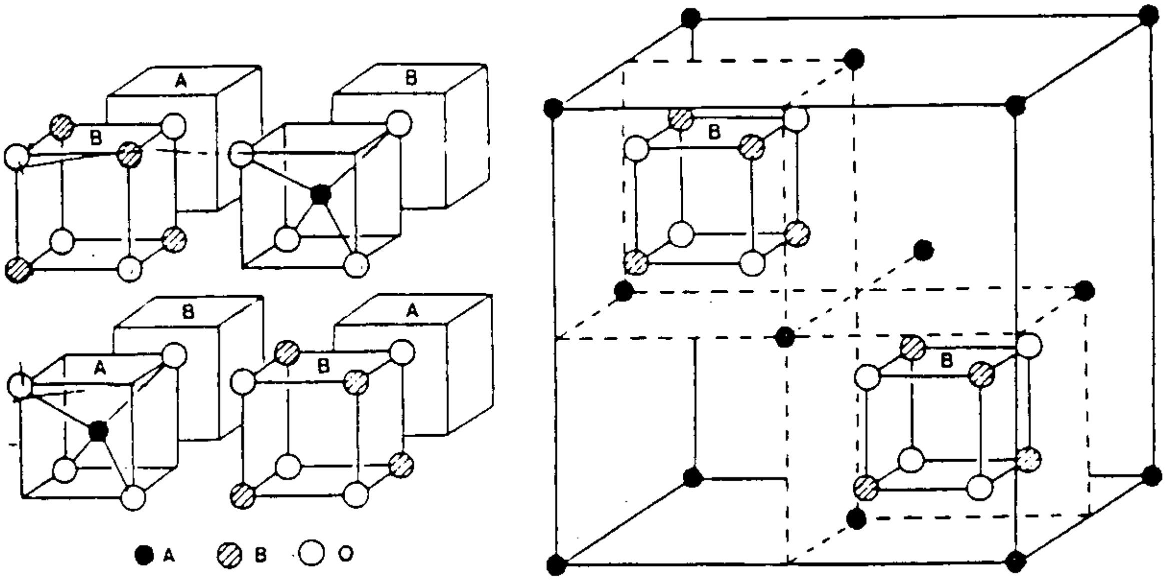
Discovery: Co / Cu / Cr or Al / alkali catalysts convert syngas to a Flory distribution of normal alcohols.

Activity = 0.1 to 0.3 g/g cat./hr (6 to 18 lb/ft^3/hr)

Selectivity = 70-99% alcohols (30-75% C_2+)

Postulated mechanism:





'The spinel structure, AB_2O_4. The structure can be thought of as eight octants of alternating AO_4 tetrahedra and B_4O_4 cubes as shown in the left-hand diagram; the O have the same orientation in all eight octants and so build up into a face-centred cubic lattice of 32 ions which coordinate A tetrahedrally and B octahedrally. The four A octants contain four A ions and the four B octants sixteen B ions. The unit cell is completed by an encompassing face-centred cube of A ions (●) as shown in the right-hand diagram; this is shared with adjacent unit cells and comprises the remaining four A ions in the complete unit cell $A_8B_{16}O_{32}$. The location of two of the B_4O_4 cubes is shown for orientation'. (From N. N. Greenwood, *Ionic Crystals, Lattice Defects, and Non-Stoichiometry*, Butterworths, London, 1968)

TRANSITION METALS ON SPINEL OXIDES

Previous Work
(continued)

Literature: King, T. S. and Sheffer, G. R. Appl. Catal. 1988, 44, 153.
J. Catal. 1989, 116, 95.

Performance: Activity = 0.12 g/g cat./hr (8 lb/ft^3/hr)

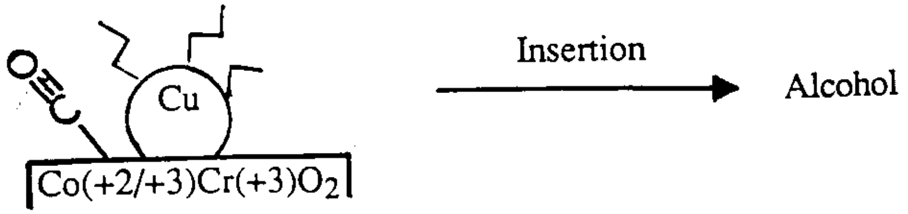
Selectivity = 70% alcohols (50% C_2+)

Discovery: Characterization indicated that the catalyst consisted of copper metal supported on a cobalt-chromium spinel.

Activity was sensitive to calcination temperature and correlated with copper metal particle size, especially the circumference.

Lithium promoted unsupported copper catalysts yielded a Flory distribution of alcohols and hydrocarbons.

Postulated mechanism:



TRANSITION METALS ON SPINEL OXIDES

Current Work

Objective: To optimize the transition metal(s) on spinel oxide class of higher alcohol catalysts with performance goals:

Activity = 20-25 lb/ft^3/hr (0.3-0.4 g/g cat/hr)

Selectivity = 90+% alcohols (30-40 wt% C_2+)

Strategy:

1. Use Hyper-Greco Latin Squares to determine relative importance and bracket catalyst preparation and formulation variables.
2. Use face centered factorial designs to map the response surface of the important variables.

Catalyst Preparation:

1. Continuous coprecipitation of spinel component metal nitrates using carbonate solution at fixed pH. Drying.
2. Impregnation of spinel precursor before calcination with alkali formate.
3. Calcination of precursor in air.
4. Impregnation of transition metals on a monolayer basis. (Ammonical solutions of metal carbonates preferred.)

Catalyst Testing:

1. Reactor - 4 ml, fixed bed, UCC built, system.
   Max. T = 400°C, Max. P = 1500 psig
2. Analytical - analysis for n-hydrocarbons, 1-olefins,
   n-alcohols, iso-alcohols, and n-aldehydes.

SPINEL OXIDE SUPPORTED TRANSITION METAL CATALYSTS

Variable Importance Rating by Magnitude of Influence on Catalytic Activity for Alcohol Formation

Item	Range Studied	Influence (lb/ft3/hr)
Choice of transition metal	A132, A129, Pd, Rh, Ag, Fe	6.5
Method of trans. metal intro.	carbonate, nitrate, coppt.	3.5
Choice of spinel components	A139, A144, A138, Ni, Fe, Al	3.0
Temperature of calcination	150 to 600°C	2.0
A132 transition metal loading	1/3 to 4 monolayers	2.0
Spinel metal component ratios	0.5 < A139/A144 < 2	1.5
Alkali impregnation step	before calc., after calc., w/ metals	1.2
pH of precipitation	7 to 11	1.2
Promoter loading	0 to 0.9 mole ratio	1.0
Promoter identity	all alkali elements, others	1.0
Temperature of precipitation	25°C to 100°C	0.8
Agent of precipitation	ammonium and alkali carbonates	0.8
Rate of reduction	0.5 to 4.0°C/min	0.3

SPINEL OXIDE SUPPORTED TRANSITION METAL CATALYSTS

Variable Importance Rating by Magnitude of Influence on Alcohol Selectivity

Item	Range Studied	Influence (wt%)
Choice of spinel components	A139, A144, A138, Ni, Fe, Al	50
Spinel metal component ratios	0.5 < A139/A144 < 2	25
Choice of transition metal	A132, A129, Pd, Rh, Ag, Fe	20
Temperature of calcination	150 to 600°C	18
Alkali impregnation step	before calc., after calc., w/ metals	15
Temperature of precipitation	25°C to 100°C	14
Promoter identity	all alkali elements, others	12
Agent of precipitation	ammonium and alkali carbonates	12
A132 transition metal loading	1/3 to 4 monolayers	11
Promoter loading	0 to 0.9 mole ratio	10
Rate of reduction	0.5 to 4.0°C/min	7
Method of trans. metal intro.	carbonate, nitrate, coppt.	6
pH of precipitation	7 to 11	4

SPINEL OXIDE SUPPORTED TRANSITION METAL CATALYSTS

CATALYST PERFORMANCE SUMMARY

	Alcohol selectivity (wt%)	C_2+ Alcohol selectivity (wt%)	Yield (lb/ft^3/hr)
Target	90+	30-40	20-25
Literature	70	50	6-8
Best Catalyst* (to date)	60	50	13

* Conditions: T = 260°C; P = 1000 psig; $H_2/CO = 2.0$
GHSV = 6000 hr^{-1}

FUTURE WORK

1. Try other methods of transition metal impregnations.
2. Face centered factorial design for response surface.
   a. Spinel component ratios
   b. Calcination temperature
   c. Transition metal loadings
   d. Promoter loadings.
3. Continue evaluation of other promoters.

TRANSITION METALS ON SPINEL OXIDES FOR ISO-ALCOHOL SYNTHESIS

Current Work

Objective: To optimize the transition metal(s) on spinel oxide class of higher alcohol catalysts with performance goals:

Activity = 20-25 lb/ft^3/hr (0.3-0.4 g/g cat/hr)

Selectivity = 90+% alcohols (60-70 wt% isobutanol)

Strategy:

1. Use Hyper-Greco Latin Squares to determine relative importance and bracket catalyst preparation and formulation variables.
2. Use face centered factorial designs to map the response surface of the important variables.

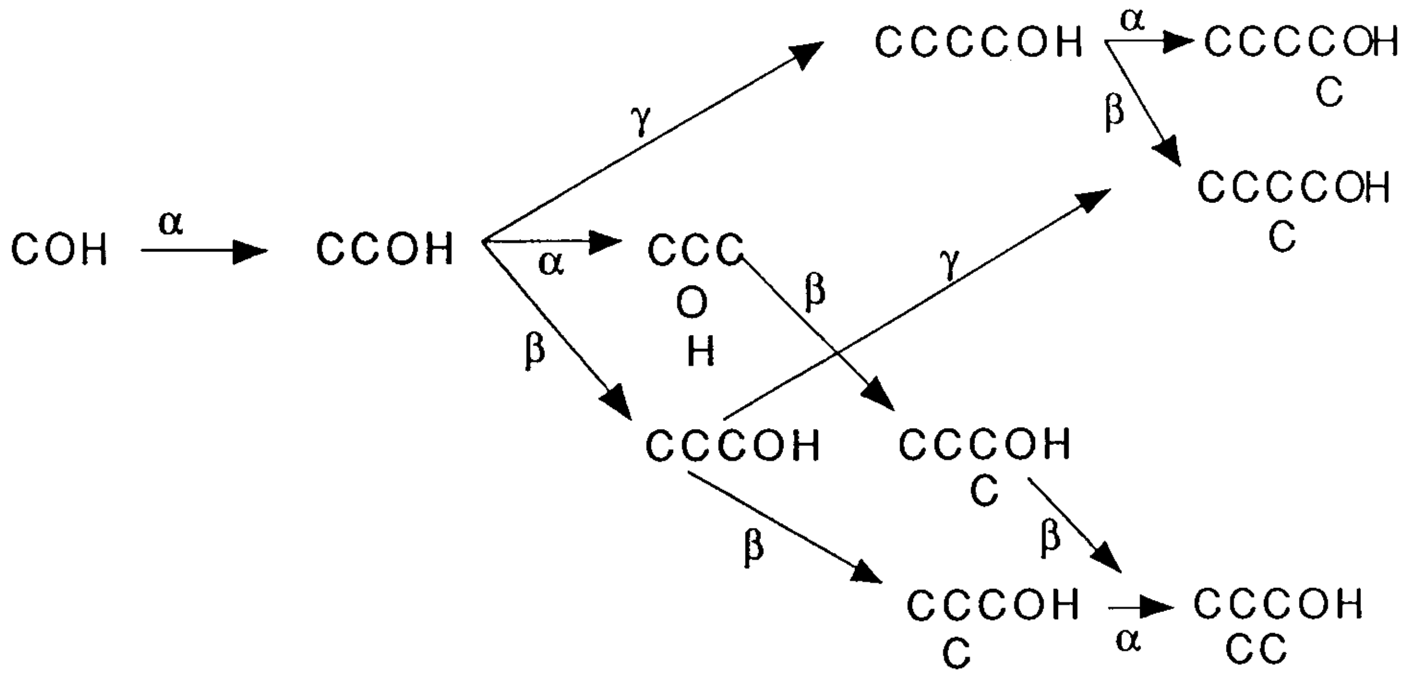
Catalyst Preparation:

1. Continuous coprecipitation of zinc-chromium based metal nitrates using carbonate solution at fixed pH. Drying.
2. Calcination of precursor in air.
3. Aqueous impregnation of transition metal, alkali, and other promoters on a surface area normalized basis.

Catalyst Testing:

1. Reactor - 4 ml, fixed bed, UCC built, system.
   Max. T = 400°C, Max. P = 1500 psig
2. Analytical - analysis for n-hydrocarbons, 1-olefins,
   n-alcohols, iso-alcohols, and n-aldehydes.

ISOBUTANOL SYNTHESIS   CHAIN GROWTH SCHEME



	RELATIVE RATE CONSTANTS				MOLAR HIGHER ALCOHOL DISTRIBUTION			
	α	β	γ	δ	C2	C3	i-C4	i-C5
K/Cu/Zn/Al	1	15	1	7	1	0.7	1.4	0.6
Hypothetical	1	10000	0	100	1	1.4	99.	1

SPINEL OXIDE SUPPORTED TRANSITION METAL CATALYSTS

Variable Importance Rating by Magnitude of Influence on Catalytic Activity for Alcohol Formation

Item	Range Studied	Influence (lb/ft3/hr)
Choice of spinel components	Zn, Cr, Al, Zr, A138	6.0
Choice of transition metal	Os, Rh, Ag,Cu, Au, Pd, Ir, Pt	3.0
Spinel component ratios	$0.5 < \text{Zn/co-component} < 4$	2.2
Other promoter loading	0 to 15×10^{18} atoms/m^2	2.1
Alkali loading	0 to 15×10^{18} atoms/m^2	2.0
Transition metal loading	0 to 15×10^{18} atoms/m^2	2.0
pH of precipitation	7 to 11	1.5
Alkali identity	all alkali elements	1.3
Other promoter identity	proprietary	1.2
Temperature of reduction	400 to 600°C	0.5
Temperature of precipitation	25°C to 100°C	0.5
Agent of precipitation	ammonium and alkali carbonates	0.4
Temperature of calcination	300 to 750°C	0.0

SPINEL OXIDE SUPPORTED TRANSITION METAL CATALYSTS

Variable Importance Rating by Magnitude of Influence on Alcohol Selectivity

Item	Range Studied	Influence (wt%)
Transition metal loading	0 to 15×10^{18} atoms/m^2	25
Agent of precipitation	ammonium and alkali carbonates	25
Temperature of reduction	400 to 600°C	20
Choice of transition metal	Os, Rh, Ag,Cu, Au, Pd, Ir, Pt	16
Alkali identity	all alkali elements	16
Choice of spinel components	Zn, Cr, Al, Zr, A138	12
Temperature of calcination	300 to 750°C	10
Other promoter loading	0 to 15×10^{18} atoms/m^2	10
Alkali loading	0 to 15×10^{18} atoms/m^2	10
Other promoter identity	proprietary	6
Spinel component ratios	$0.5 <$ Zn/co-component < 4	5
pH of precipitation	7 to 11	5
Temperature of precipitation	25°C to 100°C	5

SPINEL OXIDE SUPPORTED TRANSITION METAL CATALYSTS

Variable Importance Rating by Magnitude of Influence on Isobutanol Selectivity

Item	Range Studied	Influence (wt%)
Other promoter identity	proprietary	33
Alkali loading	0 to 15×10^{18} atoms/m^2	30
Spinel component ratios	$0.5 <$ Zn/co-component < 4	25
Agent of precipitation	ammonium and alkali carbonates	25
Transition metal loading	0 to 15×10^{18} atoms/m^2	20
Other promoter loading	0 to 15×10^{18} atoms/m^2	17
Alkali identity	all alkali elements	15
Choice of transition metal	Os, Rh, Ag,Cu, Au, Pd, Ir, Pt	12
Choice of spinel components	Zn, Cr, Al, Zr, A138	10
pH of precipitation	7 to 11	8
Temperature of precipitation	25°C to 100°C	5
Temperature of reduction	400 to 600°C	0
Temperature of calcination	300 to 750°C	0

SPINEL OXIDE SUPPORTED TRANSITION METAL CATALYSTS

CATALYST PERFORMANCE SUMMARY

	Alcohol selectivity (wt%)	Isobutanol selectivity (wt%)	Yield (lb/ft^3/hr)
Target	90+	60-70	20-25
Best Catalysts * (to date)	90	72	12
Best Catalysts * (to date)	80	35	23

* conditions: T = 400°C ; P = 1100 psig ; $H_2/CO = 0.5$
GHSV = 6000 hr^{-1}

FUTURE WORK

1. Continue evaluation of other promotersand interaction with alkalis.

2. Face centered factorial design for response surface.

   a. Spinel component ratios
   b. Transition metal loadings
   c. Promoter loadings.

INTRODUCTION

A series of tests was completed on the conversion of syngas to methanol using CCI #6341 Cu/Zn/Al catalyst in the slurry reactor. These tests were done in order 1) test the operation of the reaction system under reaction conditions, 2) demonstrate our ability to obtain kinetic information from the reactor, 3) determine a good solvent for use in future testing, and 4) develop a satisfactory *in situ* catalyst reduction technique. A second series of tests was completed on the conversion of syngas to C1 to C5 linear alcohols. These tests were run to demonstrate the performance of the slurry reactor in the production of higher alcohols.

The reaction system performed very well under reaction conditions. The kinetic data generated from the reactor was modeled and fit some literature values reasonable well. We also demonstrated that methanol has a strong inhibiting effect on the reaction even far from equilibrium. Dodecane appears to be a good solvent; tetraglyme is not.

EXPERIMENTAL RESULTS

Results using Tetraglyme (Tetraethylene glycol dimethyl ether)

The two-liter slurry reactor (shown in Figure 1) was charged with 25.9 grams of CCI #6341 Cu/Zn/Al catalyst which was crushed and sieved to 75 - 150 microns. Tetraglyme was added to the reactor and the catalyst was activated *in situ*. The catalyst was activated by feeding 150 sccm of a 1:1 H_2:N_2 mixture to the reactor which was at 100 psig while ramping the temperature from 150°C to 250°C over a 24 hour period. The hydroformylation reaction was carried out by feeding 450 sccm of a 2:1 H_2:CO mixture to the reactor which was at 240°C and 750 to 1000 psig. In order to keep a constant liquid level, tetraglyme was fed to the reactor at 60 ml/hr for the first 24 hours and 20 ml/hr for the rest of the test.

Figure 2 shows the results of this test. The initial methanol productivity was 0.04 g·methanol/g·catalyst-hr. The methanol productivity quickly dropped off to less than 0.002 g/g·hr in about 100 hours. There was a temporary decrease in the methanol productivity after 24 hours when the tetraglyme feed rate was decreased because of the accumulation of methanol in the liquid phase. After 168 hours, the CO was turned off and the catalyst was reactivated using the procedure described above. Reactivating the catalyst increased the methanol productivity to 0.015 g/g-hr, but the productivity quickly decreased and the test was terminated after 216 hours.

Modeling Methanol Production in Dodecane

The two-liter slurry reactor was charged with 25.6 grams of 75 - 150 micron CCI #6341 catalyst . Dodecane was added to the reactor and the catalyst was activated by feeding 200 sccm of a 1:3 H_2:N_2 mixture to the reactor which was at 200 psig while ramping the temperature from 150°C to 240°C over a 24 hour period. The pressure was increased to 750 psig and 200 sccm of H2 was fed for four hours. The hydroformylation reaction was then started by feeding 450 sccm of a 2:1 H2:CO mixture to the reactor which was at 240°C and 750 psig. In order to keep a constant liquid level, dodecane was fed to the reactor at 30 ml/hr for the first four days and 15 ml/hr for the rest of the test.

The catalyst required about 60 hours to lose its initial hyperactivity after activation. Figure 3 shows the initial methanol productivity for the first 200 hours of operation. During this time,the reaction was at 240°C and 750 psig with 450 sccm of a 2:1 H2:CO feed (GHSV = 1050 Sl/hr-Kg). After 160 hours, the first of two designed sets of experiments were started.

The first design set was developed in order to determine the effects of temperature, pressure, and feed ratio on the productivity. The conditions used for these tests are shown in Figure 4. Multiple regression of the methanol productivity rate produced the expression

$$\text{PRODUCTIVITY (g/g-hr)} = e^{(-0.445-8810/RT)}\langle H2\rangle^{1.018}$$
$$R^2 = 0.90$$

where <H2> is the hydrogen partial pressure in psia. This model provided a good fit of the data, but the low activation energy and first-order effect on hydrogen suggested that there were other important effects were not being considered.

A second design set was then run to determine the effect of methanol on the reaction rate. In this set the temperature and gas feed rate were varied and methanol was fed directly to the reactor in three of the runs. The results of this set are summarized in Table I.

TABLE I
SUMMARY OF DESIGN SET #2

PRESSURE = 950 PSIA
H2:CO = 2:1

RUN	TEMPERATURE °C	GAS FEED SCCM	MEOH FEED G/HR	MEOH PROD G/HR
1	260	1000	0	2.216
2	220	250	0	.564
3	260	250	3.5	.295
4	220	1000	3.5	.112
CP	240	500	1.7	.586

These data in Table I show clearly that feeding methanol to the reactor has a strong detrimental effect on the methanol productivity. This was unexpected because the reaction is far from equilibrium at 950 psig with less than ten percent conversion. Regression of the above data showed that the methanol partial pressure inhibits the reaction to the -1.23 power. The partial pressure of methanol can be used even though this is a liquid phase reaction by assuming that the vapor phase is an ideal mixture, (the vapor pressure equals the vapor fugacity) and by assuming vapor-liquid equilibrium (the vapor fugacity equals the liquid fugacity).

The equation for the methanol production is shown below.

$$\text{METHANOL PRODUCTIVITY (g/g-hr)} = e^{(27.448-27168/RT)} \langle \text{MeOH} \rangle^{-1.23}$$

$$R^2 = 0.895$$

As expected,[1] the activation energy is significantly higher when the methanol inhibition is accounted for. In order to simplify development of the model, a -1 order for methanol inhibition was assumed.

The reaction can be shown to be far from equilibrium by comparing the equilibrium constant with the ratio of the pressures of the product to the reactants. The run which produced the highest methanol partial pressure at the exit is the closest to equilibrium. In this run, $P_{MEOH} = 174$ psia, $P_{H2} = 521$ psia, and $P_{CO} = 254$ psia. From this, the ratio is calculated as

$$K_{OBS} = \frac{(174)}{(521)^2(254)} = 2.56 \cdot 10^{-6}\,\text{psi}^{-2} = 5.3 \cdot 10^{-4}$$

which is an order of magnitude away from the $\approx 6 \cdot 10^{-3}$ equilibrium constant reported for this reaction at 500K.[2] The other runs performed during this work were done with at least one-half to one-quarter the methanol partial pressure and correspondingly higher H2 and CO pressure. Thus, those runs were even further from equilibrium

The methanol catalyst was shown to decay at a rate of 0.28% per hour. This is shown in Figure 5. This figure shows the methanol productivity of our centerpoint runs (750 psig, 240°C, 2:1 H2:CO, 450 sccm) after correcting for the methanol inhibition. The dark points are those which were regressed to determine the deactivation rate.

The data from design set #1 were then regressed again. This time the catalyst deactivation rate and the methanol inhibition effect was built into the regression. The results from this regression

$$\text{PRODUCTIVITY (g/g-hr)} = e^{(3.071-24171/RT-0.002817)} \langle \text{H2} \rangle^{2.95} \langle \text{CO} \rangle^{0.74} \langle \text{MeOH} \rangle^{-1}$$

$$R^2 = 0.966$$

show a big difference from the original regression. The activation energy has increased to 24 Kcal/gmol, which is about what should be expected of this type of reaction, and the reaction is strongly influenced by the hydrogen partial pressure and less by the CO pressure. In order to simplify the model further, a second-order effect was assumed for hydrogen. Regressing the data with this assumption increased the effect of CO to the 0.92 power. Since there were only five conditions used in this design set, we can take some more liberties with the model without affecting the fit. Therefore, a first-order effect was assumed for CO and the model was regressed one last time to yield the equation

$$\text{PRODUCTIVITY (g/g-hr)} = e^{(6.241-22861/RT-0.002817)}\frac{\langle \mathrm{H2}\rangle^{2}\langle \mathrm{CO}\rangle}{\langle \mathrm{MeOH}\rangle}$$

This equation is a simple two-parameter model which does an excellent job of correlation our data as well as the data of others.

Figure 6 presents a parity plot which shows how well the above model fits our data. The model not only fits the data from the first design set, but also fits the data from the second set as well as the outliers which were run at H2:CO ratios of 0.75:1 and 3:1.

Figure 7 shows a comparison between the precision of the model developed above and published data from other researchers[3]. The model provides an relatively good fit of the data considering the differences between their experiments and ours. Their work was done gas-phase in a Berty reactor at six times the GHSV, with up to 24:1 H2:CO, and at pressures as low as 400 psig.

Figure 8 shows that our model does not do quite as well predicting the performance of the LaPorte PDU Unit[4]. Our model predicts only about 25 to 50 percent of the productivity reported in their unit. However, there are many differences between their unit and ours. The PDU unit uses 0.7:1 H2:CO with 13% CO_2 which is not accounted for in the model. The PDU alsu uses a smaller catalyst partical and operates at a space velocity up to twenty times higher than we used.

Figure 9 shows the production rate of CO2 as measured in our second design set. The production rate was regressed against temperature and methanol partial pressure. The regression shows that the CO2 production rate was only a function of temperature (activation energy = 16344 cal/gmole) and not methanol concentration.

Figure 10 shows the production rate of methane as measured in our second design set. As with the CO2, the production rate was regressed against temperature and methanol partial pressure. Again, the regression shows that the methane production rate was only a function of temperature (activation energy = 32228 cal/gmole). Thus, we can conclude that the methane and the CO2 are not being produced from the methanol.

Modification of Activation Technique

The two-liter slurry reactor was charged with 17.9 grams of CCI #6341 Cu/Zn/Al catalyst which was crushed and sieved to 75 - 150 microns. Dodecane was added to the reactor and the catalyst was activated *in situ*. The catalyst was activated by heating the reactor to 200°C under 400 psig N_2 then feeding 400 sccm of a 3:1 N_2:H_2 mixture to the reactor for 1.5 hours, then increasing the temperature to 240°C for two hours. The hydroformylation reaction was carried out by feeding 600 sccm of a 2:1 H_2:CO mixture to the reactor which was at 240°C and 750 psig. In order to keep a constant liquid level, dodecane was fed to the reactor at 4.5 ml/hr.

The experimental results compare well with the prediction using the model developed from the previous tests for the methanol and CO_2. The comparison between the methanol data and model is presented in Figure 11. It is interesting to note that it appears from Figure 11 to have taken about 70 hours for this catalyst to lose its initial hyperactivity. This was also what was observed in the previous test with this catalyst.

Experimental Results using Spinel Catalyst

The two-liter slurry reactor was charged with 15.0 grams of 53 - 420 micron catalyst. Dodecane was added to the reactor and the catalyst was activated *in situ* using the same method used for the methanol catalyst. The reactor was initially started up at 240°C and 750 psig with 600 sccm of 2:1 H_2:CO feed. After 16 hours the temperature was increased to 250°C and held for 92 hours. The temperature was then increased to 270°C and held for 48 hours. After this, the partial pressure of CO was increased (from about 225 psi to 450 psi) and the partial pressure of H_2 was held constant by increasing the reactor pressure to 975 psig and feeding 600 sccm of 1:1 H_2:CO.

The results from this tests are summarized in Table II. This table shows that above 250°C the product distribution of alcohols is insensitive to the temperature and pressure of the system. The product distribution of the test at 240°C appears out of line with the other tests and in most likely erroneous. The total production rate is very sensitive to temperature, with an apparent activation energy of 47 Kcal/mol K between 250°C and 270°C.

TABLE II
SUMMARY OF ALCOHOL PRODUCTIVITY USING SPINEL CATALYST

Temperature (C)	Pressure (PSIG)	Methanol (WT%)	Ethanol (WT%)	Propanol (WT%)	Butanol (WT%)	>C4 Alcohols (WT%)	TOTAL PRODUCTION RATE (G/KG-HR)
240	750	49.2%	0.0%	19.4%	24.1%	7.3%	1.0
250	750	49.1%	28.2%	11.3%	8.7%	2.7%	17.7
270	750	46.2%	35.6%	10.0%	6.4%	1.7%	83.9
270	975	46.1%	33.9%	10.0%	7.4%	2.5%	53.3

The efficiency of CO to alcohols (excluding CO_2) increases from about 45% to 55% with the increase in temperature from 250°C to 270°C. Thus, the production of alcohols increases more than the production of hydrocarbons with the increasing temperature. It is interesting to note that increasing the reactor pressure by increasing the CO partial pressure at constant H_2 partial pressure resulted in a decrease in alcohol production and a corresponding decrease in the hydrocarbon production (no change in CO efficiency).

The production rate of alcohol at 270°C using the spinel catalyst is similar to the production rate of methanol at 240°C using the Cu/Zn/Al catalyst.

CONCLUSIONS

- SLURRY REACTOR OPERATED FOR OVER 1000 HOURS WITHOUT ANY PROBLEMS
- WE WERE SUCESSFUL IS OBTAINING KINETIC DATA AND PREDICTING LITERATURE DATA
- METHANOL STRONGLY INHIBITS THE REACTION (BEYOND THE EFFECT OF EQUILIBRIUM)
- TERTRGLYME IS NOT A GOOD SOLVENT FOR THE REACTION
- CO_2 AND CH_4 PRODUCTION IS INDEPENDENT OF METHANOL CONCENTRATION (NO REVERSE REACTION)
- CATALYST PRODUCTIVITY NOT VERY SENSITIVE TO DETAILS OF *INSITU* ACTIVATION TECHNIQUE

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FIGURE 1
SLURRY REACTION SYSTEM

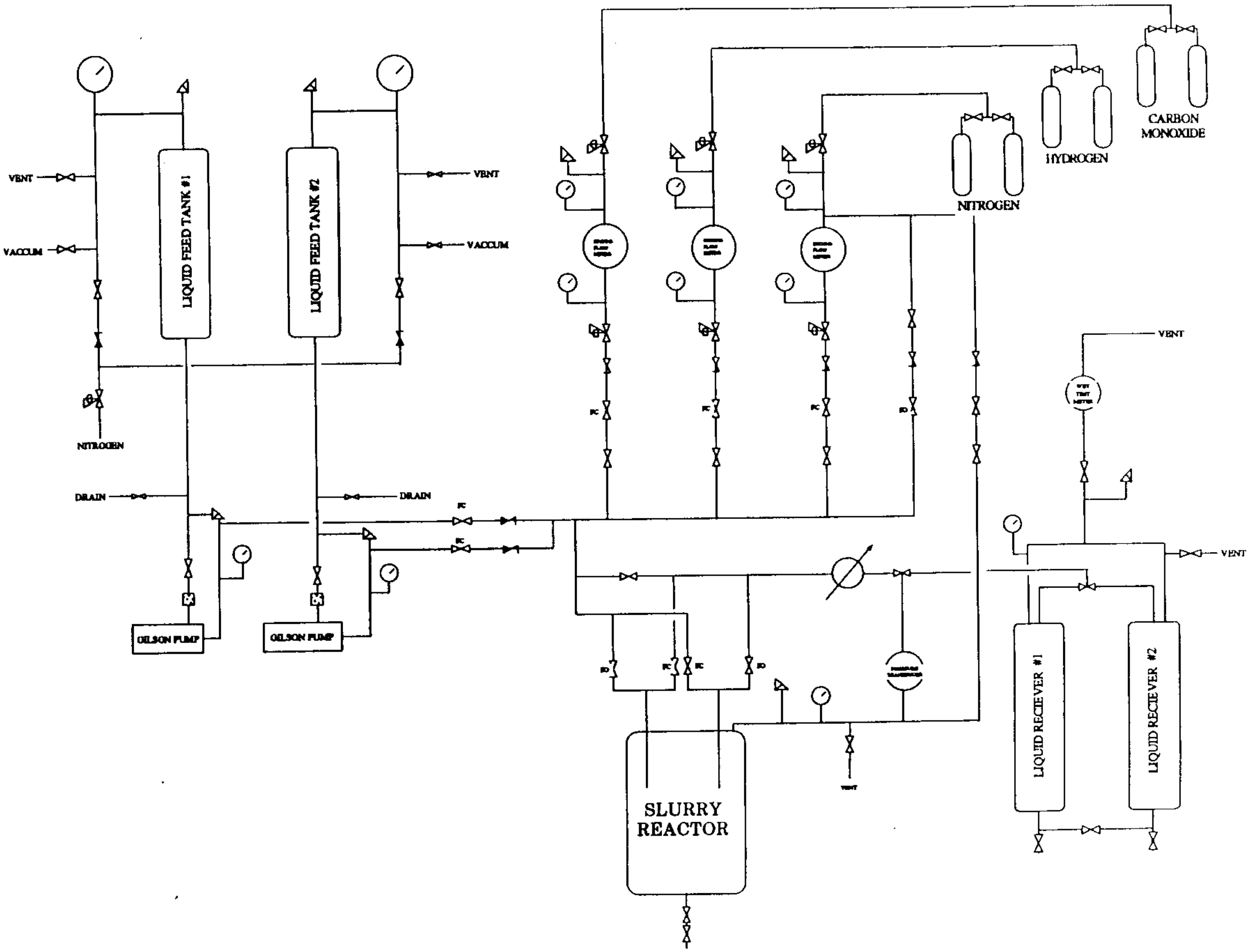
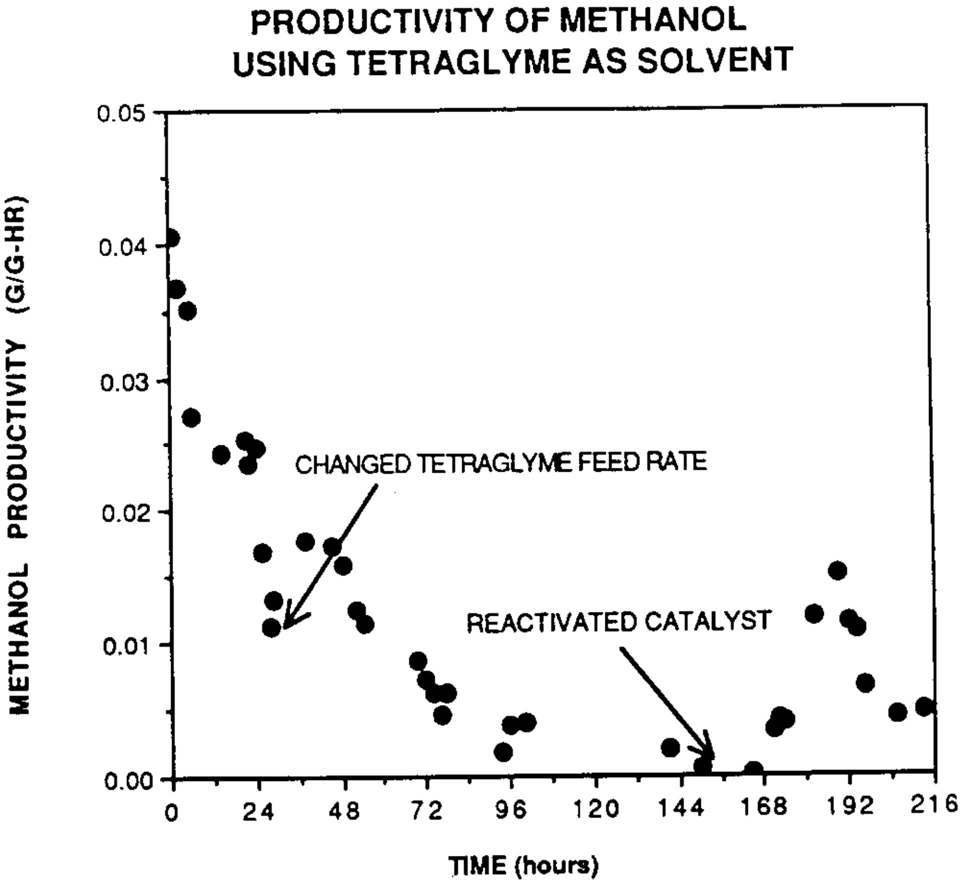


FIGURE 2



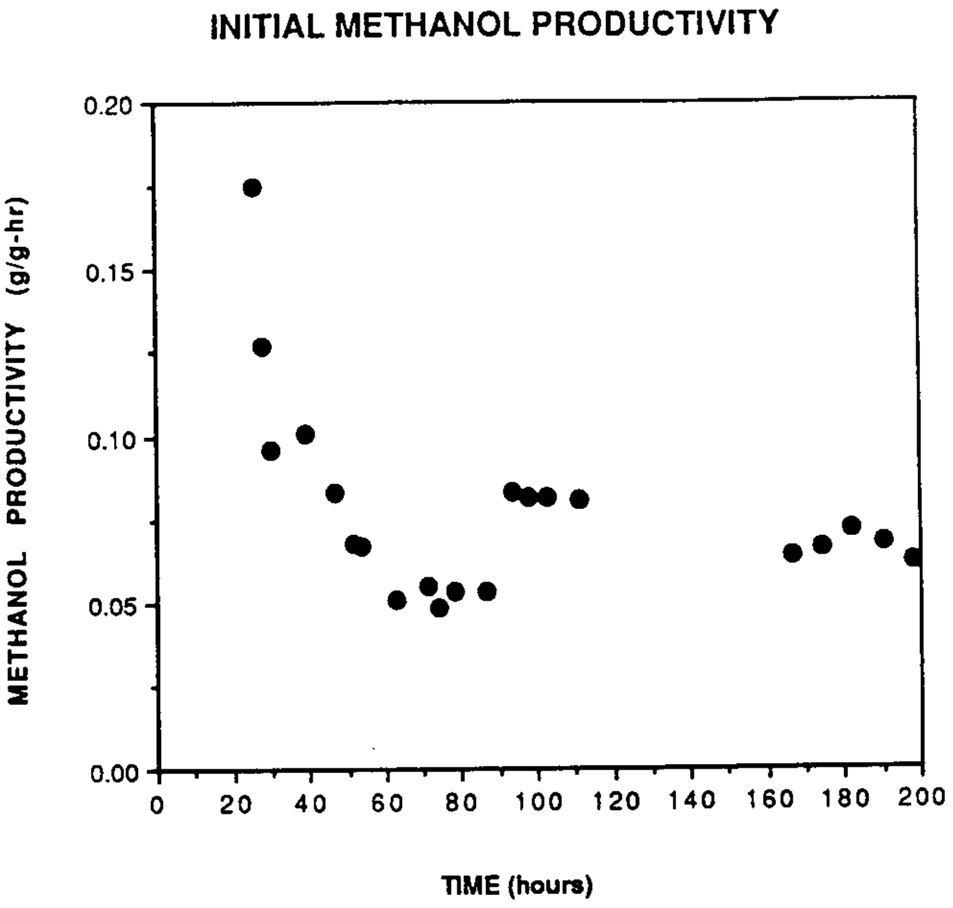
CONDITIONS:

240°C
750-1000 PSIG
2:1 H2:CO
GHSV = 1000 SL/KG-HR

CATALYST:

Cu/Zn/Al - CCI#6641
26 grams , 75-150 micron

FIGURE 3

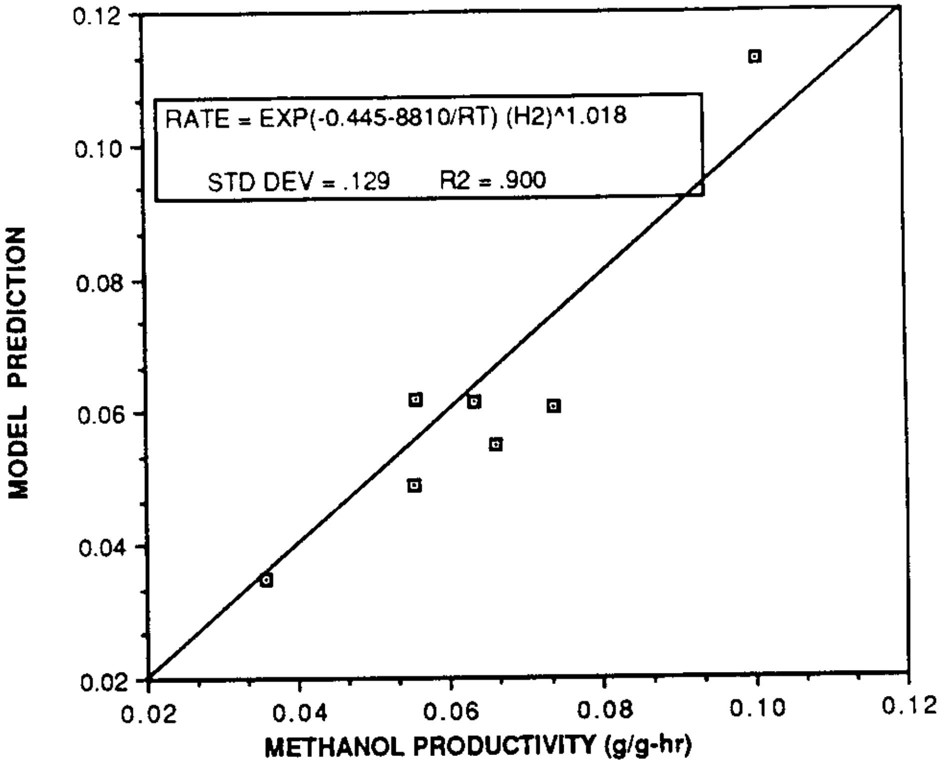


CONDITIONS:
240°C
750-1000 PSIG
2:1 H_2:CO
GHSV = 1000 SL/KG-HR

CATALYST:
Cu/Zn/Al - CCI#6641
26 grams , 75-150 micron

FIGURE 4

COMPARISON OF MODEL PREDICTION WITH RESULTS FROM DESIGN SET #1



CONDITIONS:

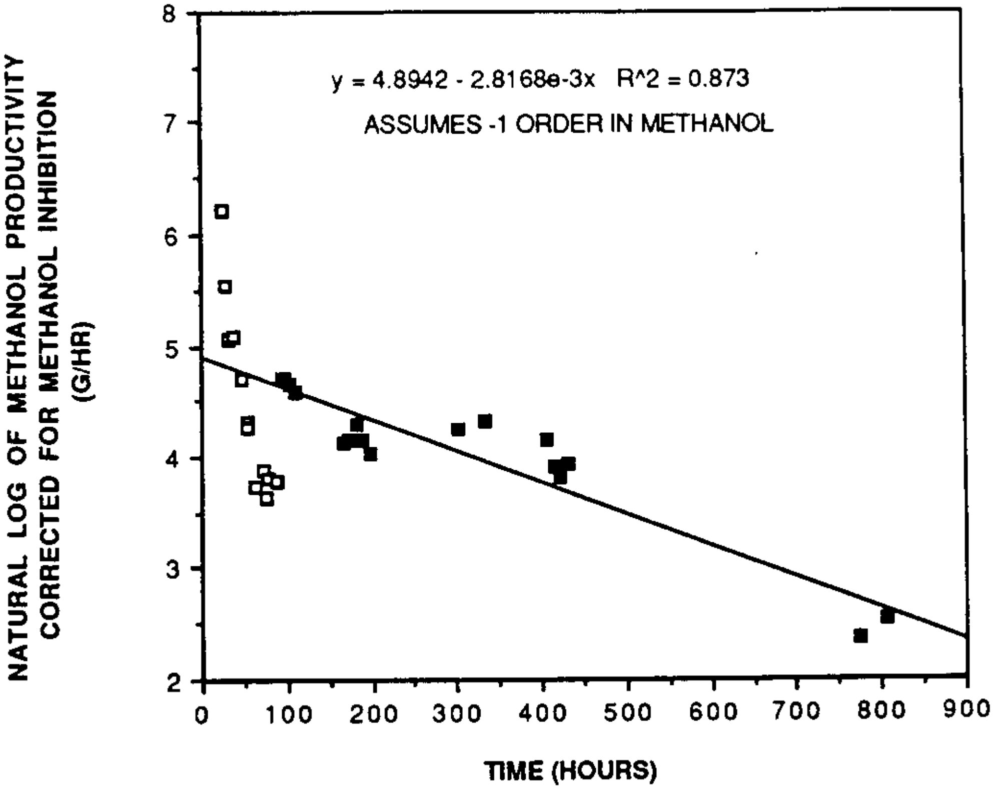
RUN	TEMPERATURE °C	PRESSURE PSIA	H2 FEED SCCM	CO FEED SCCM	H2:CO
1	220	550	323	131	2.5
2	220	950	272	181	1.5
3	260	550	272	181	2.5
4	260	950	323	131	2.5
CP	240	750	300	150	2.0

MODEL:

PRODUCTIVITY = $e^{(-0.445-8810/RT)} \langle H2 \rangle^{1.018}$ (g/g-hr)

FIGURE 5

METHANOL PRODUCTIVITY FROM CENTER-POINT RUNS SHOWING DEACTIVATION RATE OF CATALYST

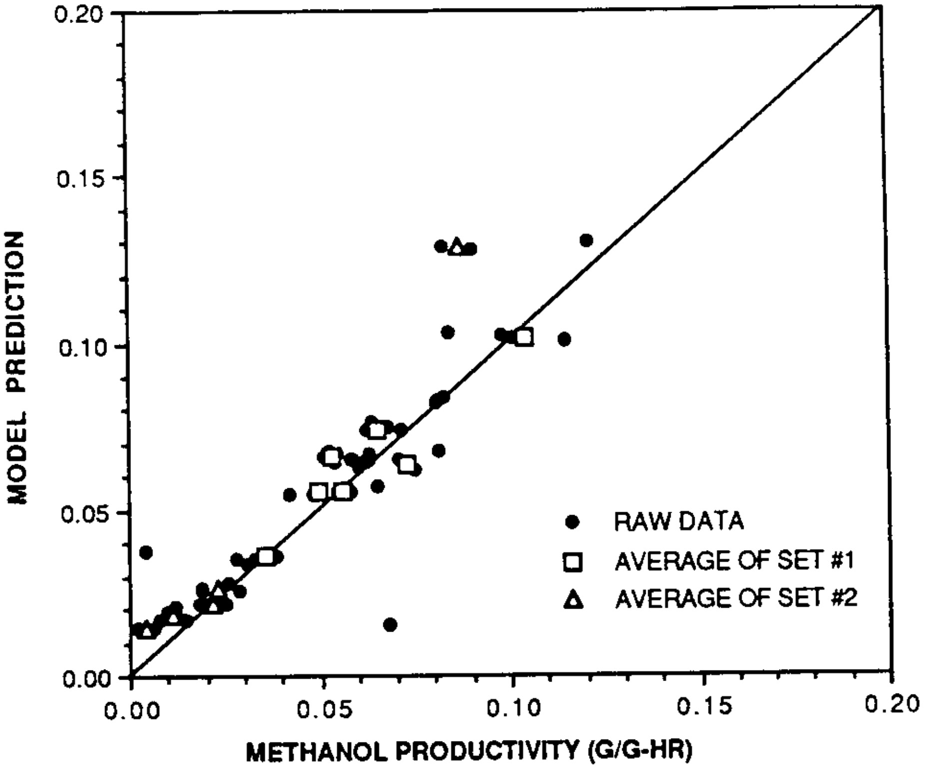


CONCLUSION:

REGRESSION SHOWS THAT CATALYST DEACTIVATES AT A RATE OF 0.28%/HOUR

FIGURE 6

COMPARISON OF METHANOL PRODUCTIVITY WITH MODEL PREDICTION



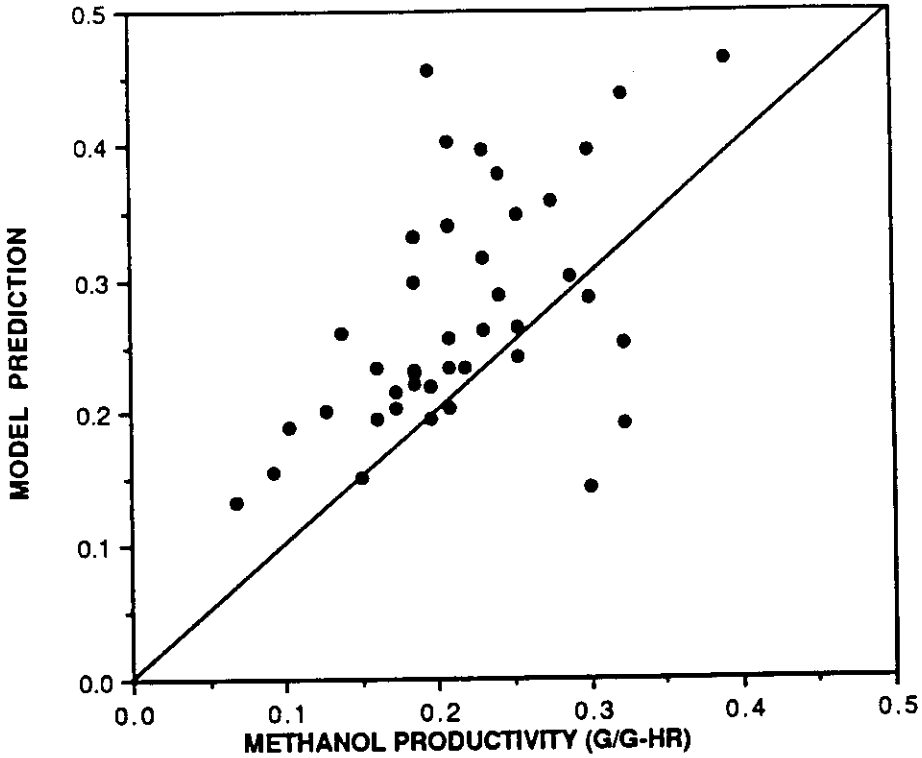
RATE = EXP(6.241 - 22861/RT - 0.002817t) (H2)^2 (CO) (MEOH)^-1

JGH 3-

$$RATE = e^{(6.241 - 22861/RT - 0.002817t)} (H_2)^2 (CO)/(MeOH)$$

FIGURE 7

COMPARISON OF MODEL PREDICTION WITH PUBLISHED DATA



DATA FROM BOS, et. al., CES 44 No. 11 p. 2444

RATE = EXP(6.241 - 22861/RT) (H2)^2 (CO) (MEOH)^-1

The reaction was carried out in a Berty reactor (gas-phase)

Pressure = 400 - 1000 psig

Temperature = 230 - 280 °C

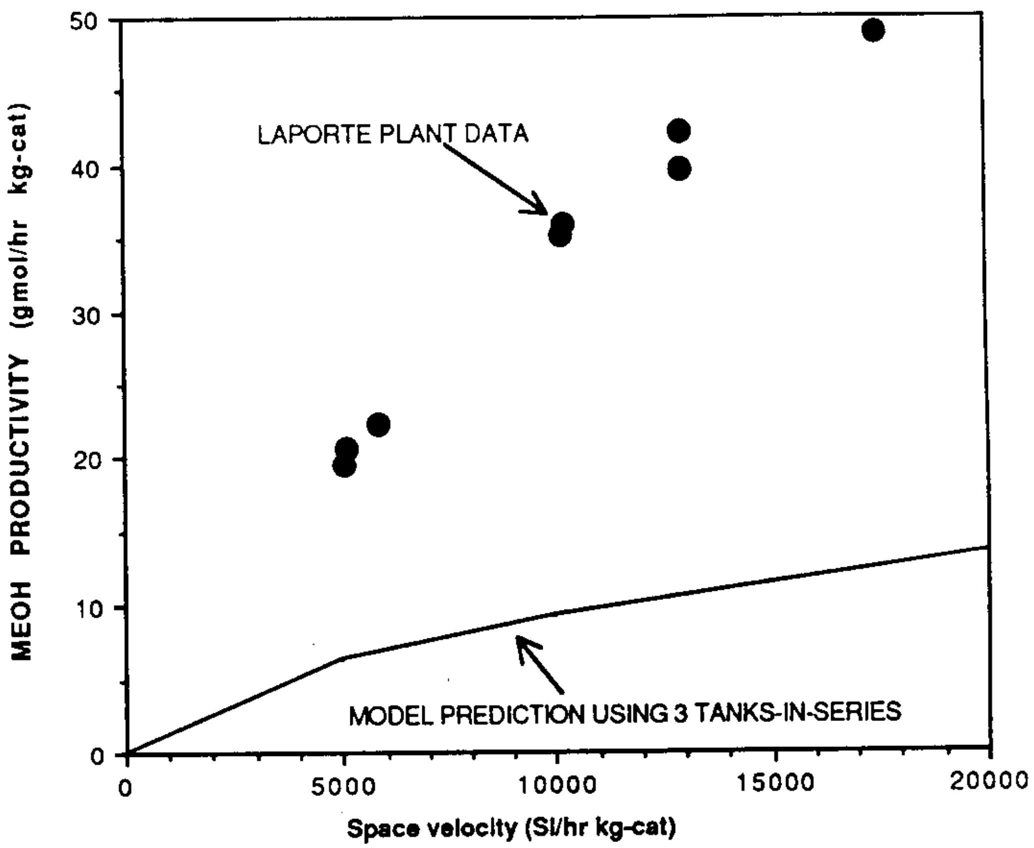
H2:C0 = 3.5:1 - 24:1

GHSV = 6000 SL/KG-HR

Catalyst = BASF S3-85 $Cu/ZnO/\alpha\text{-}Al_2O_3$

FIGURE 8

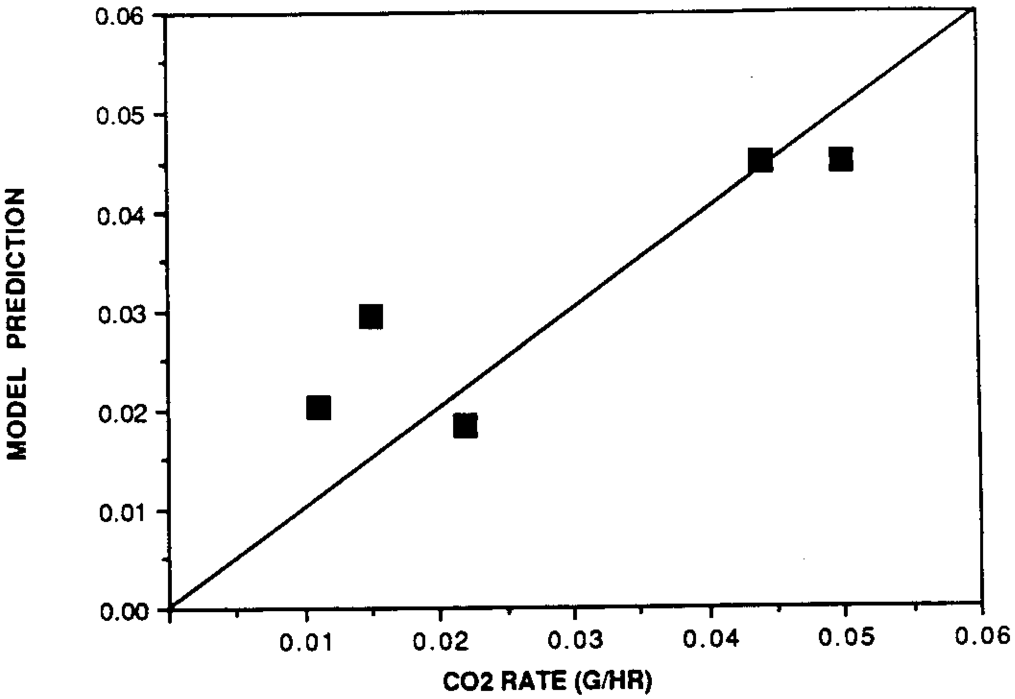
COMPARISON OF MODEL PREDICTION WITH PRODUCTIVITY FROM LAPORTE LPMEOH PDU REACTOR



CONTINUOUS SLURRY REACTOR (2' ID x 20' TALL)
750 PSIG
250°C
35% H_2; 51% CO; 13% CO_2; 1%N_2
MeOH PRODUCTIVITY = 5 - 10 TPD

FIGURE 9

PRODUCTION RATE OF CO2 IN DESIGN SET #2

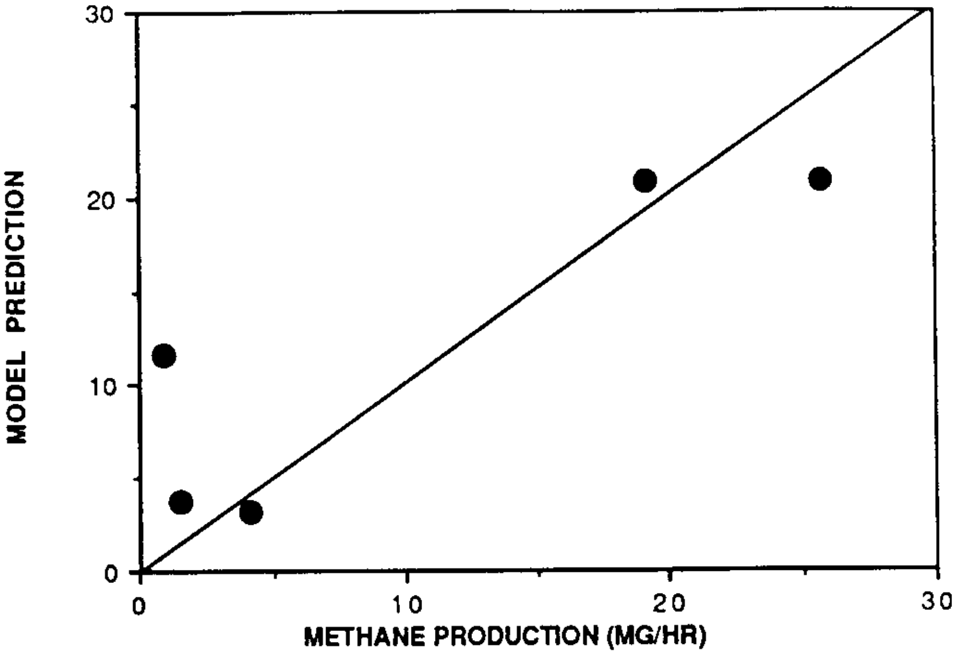


RATE (mg/hr) = $e^{(12.323-16344/RT)}$

INDEPENDENT OF METHANOL PARTIAL PRESSURE

FIGURE 10

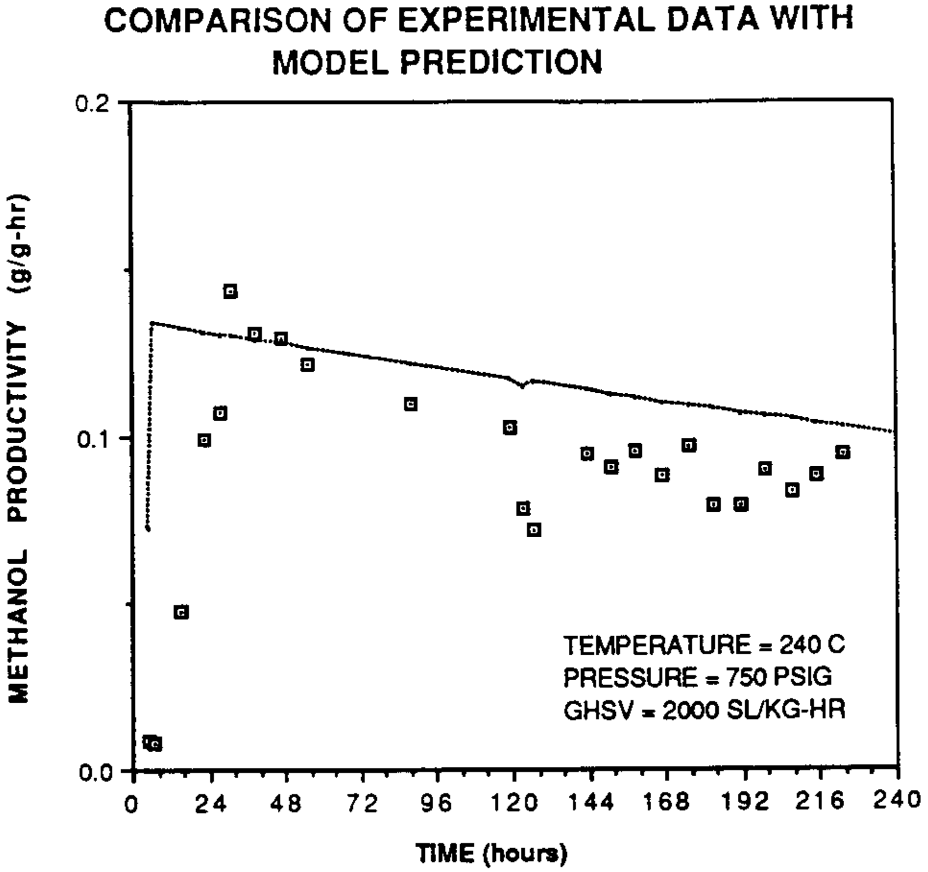
METHANE PRODUCTION FROM DESIGN SET #2



RATE (mg/hr) = $e^{(38.867-32228/RT)}$

INDEPENDENT OF METHANOL PARTIAL PRESSURE

FIGURE 11



MEOH = exp(6.241-22861/RT-0.002817t) <H2>^2 <CO>/<MEOH>

- ACTIVATION TECHNIQUE DID NOT AFFECT PRODUCTIVITY OF METHANOL CATALYST