BNL--42782

DE90 000534

ENHANCED CARBON CONVERSION OF LOW H_2/CO RATIO SYNGAS

FINAL REPORT

Dr. Richard S. Sapienza

April 1989

Prepared for the
U.S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER
PITTSBURGH, PA 15236

BNL-42782
Informal Report

ENHANCED CARBON CONVERSION OF LOW H_2/CO RATIO SYNGAS

FINAL REPORT

Dr. Richard S. Sapienza

April 1989

Prepared for the
U. S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER
PITTSBURGH, PA 15236

DEPARTMENT OF APPLIED SCIENCE
BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.

Under Contract No. DE-AC02-76CH00016 with the
U. S. Department of Energy

CONTENTS

REPORT SUMMARY

This report discusses the results of liquid phase methanol synthesis experiments conducted at 225C and 450 psi (starting pressure) in a 500 ml batch reactor, using a baseline methanol synthesis catalyst and a low temperature water gas shift catalyst, either singly or mixed. Polyglyme solvents were used as the liquid phase, because of their high thermal stability and the high gas and water solubility in them. Duration of the experiments was 20-40 minutes. The baseline methanol synthesis catalyst was sample L-450 of a C79-3 catalyst from United Catalyst, Inc., ground and sieved to below 60 mesh, then reduced. Its composition is 60 parts zinc oxide, 30 parts copper oxide, and 10 parts aluminum oxide, by weight. The low temperature water gas shift catalyst was sample 53-1 of a Katalco catalyst from ICI, ground and sieved to below 60 mesh, then reduced.. The composition is 30-35 parts copper oxide, 29-36 parts zinc oxide and balance, aluminum oxide, by weight.

A coal-derived synthesis gas was simulated by using a mixture of 36, 51 and 13 volume percent of H_2, CO and CO_2, respectively, as feed to the reactor. Carbon dioxide free synthesis gas having a 1:1 molar ratio of H_2 to CO was the feed gas used in baseline experiments. Water was added to the feeds to enhance carbon conversion.

Results from the water addition experiments indicate the formation of an intermediate with one hydrogen atom (a formate). Labeling techniques show that the methyl group of the methanol produced was composed of that water hydrogen a of methylene derived from the synthesis gas. The use of a water gas shift catalyst to provide additional formate intermediates and hydrogen showed increased activity.

Future work should emphasize solvent selection and continuous reaction data. Variables such as WGS to methanol catalyst weight ratios and catalyst composition effects should be studied, as they may be critical. The current BASF LPMeCH catalyst used by Air Products should also be studied.

PROJECT OBJECTIVES

A program to develop catalytic systems for the production of methanol from carbon monoxide and water, or alternatively from low H_2/CO ratio synthesis gas and water would offer a process of more desirable free energy and equilibrium considerations with the potential for improved process productivity.

Methanol is produced over heterogeneous zinc or copper oxide-based catalysts from synthesis gas (eq. 1). The low H_2/CO ratios

$$CO + 2H_2 \rightarrow CH_3OH \qquad (1)$$

available from current efficient gasifiers require that an external water gas shift step (eq. 2) be included in the process

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$

to improve reaction stoichiometry with the consequent loss in thermal efficiency and process simplicity. Current coal gasifier syngas limits theoretical yields to 17.5% methanol (100% H_2 utilization, 32% CO utilization). The use of carbon monoxide (or low H_2/CO ratio syngas) and water (eq. 3&4) for the direct production of methanol offers an alternative to the current process schemes.

$$3CO + 2H_2O \rightarrow CH_3OH + 2CO_2 \qquad (3)$$

$$2CO + H_2 + H_2O \rightarrow CH_3OH + CO_2 \qquad (4)$$

The approach to this goal centers around the fact that virtually all methanol catalysts have water gas shift activity under different process conditions. BNL has shown that these two reactions have been shown to involve a common intermediate. This species symbolizes the link between these chemistries and the potential route to developing water tolerant and water-utilizing methanol catalyst systems. A likely explanation for the differences in the course of equations 1 and 2 is that the hydrogenating function of methanol catalysts becomes inactive (or has low activity) in the presence of water and the modification of methanol catalysts for the water gas shift could give rise to new carbon monoxide-water methanol syntheses. These systems require the addition of water to the gas feed which generates <u>in situ</u> hydrogen which reacts with carbon monoxide (eq. 1) or with available carbon dioxide (eq. 5). Alternately, some of the

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad (5)$$

product methanol could be driven to form dimethyl ether, which would generate byproduct water (eq. 6). The water from this exothermic reaction could react with excess carbon monoxide to

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad (6)$$

form additional hydrogen (eq. 2) or methanol (eq. 3). These reactions will provide improved utilization of available carbon monoxide (>50%) from combine-cycle coal gasifiers.

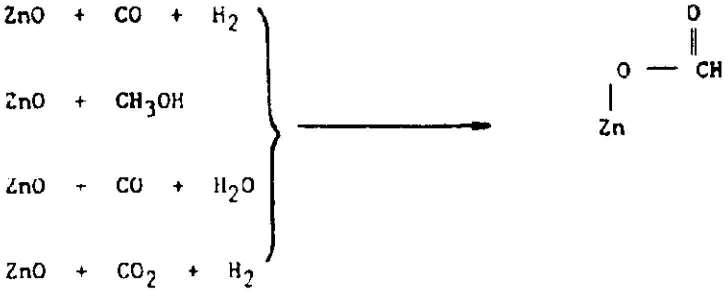
Table 1

Typical Coal-Derived Synthesis Gas Composition from the Texaco Gasifier

	Unbalanced	Balanced
H_2	35	55
CO	51	19
CO_2	13	5
Inerts	1	21
H_2/CO	.69	2.89
H_2/CO+CO_2	.5	2.08

Figure 1

Formate Surface Species



PROPOSAL GOALS

Productivity per reactor unit volume can be enhanced by the modification of, or additions to, the current slurry methanol catalyst employed in the Once-Through Liquid Phase Methanol Process. By applying <u>in situ</u> water gas shift reactions to yield hydrogen from water, the excess carbon monoxide in the feed gas can be converted to yield additional methanol. These techniques offer the possibility of a >50% gain in carbon utilization.

<u>Figure 2</u>

Theoretical Methanol Synthesis Reactions*

<u>With Unbalanced Gas</u> - stoichiometric limits

$$.35\ H_2 + .51\ CO + .13\ CO_2 \rightarrow .175\ CH_3OH + .335\ CO + .13\ CO_2$$

carbon utilization = 27%

<u>With Water Addition</u>

$$.51\ CO + .35\ H_2 \rightarrow .175\ CH_3OH + .335\ CO$$

$$.335\ CO + .223\ H_2O \rightarrow .112\ CH_3OH + .223\ CO_2 + .223\ CO$$

carbon utilization = 44.8%

or

$$.51\ CO + .25\ H_2 + .25\ H_2O \rightarrow .25\ CH_3OH + .25\ CO_2$$

$$.1\ H_2 + .033\ CO_2 \rightarrow .033\ CH_3OH + .033\ H_2O \qquad \text{(eq. 6)}$$

in the limit

carbon utilization = 44.2%

---

*All equations assume carbon dioxide is not consumed since this fact will not change the theoretical carbon utilization.

Relevant Thermodynamics

A catalyst system, which utilizes carbon monoxide and water, would offer more desirable free energy and equilibrium while yielding the potential for improved productivity per unit reactor volume. The thermodynamics of the following gas phase reactions for the production of methanol are:

		$H^{o}298^{o}K$ (kcal/mole)	
(1)	$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	-12.8	(eq.5)
(2)	$CO + 2H_2 \rightarrow CH_3OH$	-21.6	(eq.1)
(3)	$3CO + 2H_2O \rightarrow H_2 + 2CO_2$	-41.2	(eq.3)
(4)	$CO + H_2O \rightarrow H_2 + CO_2$	- 9.8	(eq.2)

Table 2

Equilibrium Constants as a Function of Temperature
Temperature, °K

Reaction	300	400	500	600
1	.15	1.3×10^{-3}	4.9×10^{-5}	4.8×10^{-6}
2	3×10^{4}	10.8	0.01	2.3×10^{-4}
3	5.8×10^{12}	2.07×10^{4}	1.02×10^{2}	.083
4	2.3×10^{5}	1.85×10^{3}	1.30×10^{2}	26.9

It is clear from these data that thermodynamically it is easier to prepare methanol via reaction 3 than direct hydrogenation of CO, reaction 2, or of CO_2, reaction 1.

This program was to focus on the currently utilized liquid phase methanol catalysts under study by DOE, and be based upon the understanding of the important factors that influence its activity and effectiveness under aqueous conditions, but this catalyst was never received. A commercial United Catalyst, Inc. L-540 methanol catalyst sample was substituted.

BACKGROUND

Although seemingly unrelated, the water gas shift reaction and the synthesis of methanol have unique similarities. Virtually all methanol catalysts are capable of water-gas shift activity. In fact, the low-pressure industrial methanol catalyst zinc oxide-copper oxide is chemically very similar to the low temperature industrial water-gas shift catalyst. Studies of these and related reactions have shown that a similar intermediate may be involved. This intermediate, identified as a metal formate, may be the catalytic link between these reactions and symbolizes the potential route to their integration. The role of formates in zinc oxide catalyzed water-gas shift reactions, carbon dioxide reductions, and methanol decomposition has been studied at varying surface coverages and temperatures by means of infrared spectroscopy (Figure 1). This link is revealing since zinc oxide is considered the most important component of the majority of widely used methanol catalysts. Formate intermediates have also been observed on magnesia, alumina, and iron-chromia shift catalysts and have been isolated in many homogeneous carbon dioxide reductions.

A bifunctional description of methanol catalysts allow us to explain various promoter effects. These are particularly noticeable in copper oxide systems. Pure copper oxide is practically inactive for the synthesis of methanol, but small amounts of promoter are sufficient in raising its activity to relatively high values. BNL Catalysis Group studies have shown copper to accomplish the hydrogenating function in methanol catalysts, therefore materials which promote formate formation should be good promoters for methanol synthesis with catalysts containing copper, and we believe this is the function of zinc oxide in the industrial catalyst.

Indeed copper oxide has been activated by orders of magnitude with the addition of trace alkali or when it is promoted or supported by carriers such as alumina, thoria, and zirconia, which are known to form formates under reaction conditions. In contrast, these materials alone have no catalytic effect, further demonstrating that aqueous methanol catalyst systems should be bifunctional.

Applying this concept, systems which are known to yield formate intermediates, but produce little or no methanol, need improvement in the hydrogenating function. Commercial methanol catalysts function best with extremely high H_2/CO ratios (10/1). This is also the probable reason that methanol is not generated by water-gas shift catalysts of the same composition. Various studies have shown that a reduced copper species is necessary for low temperature methanol catalysts to function, but in the presence of water this reduction is not possible. Therefore, to adapt methanol catalysts, or to convert water-gas shift catalysts into catalysts which utilize carbon monoxide or synthesis gas water, new or improved hydrogenating functionality must be designed for these systems.

Carbon monoxide and water can readily form formic acid under methanol reaction conditions. Potentially, metal oxides that have been shown to decompose this acid to formaldehyde could also be adapted into methanol catalysts with improved hydrogenating functionality.

Table 2 is a list of those oxides which have been shown to be water-gas shift catalysts, to promote methanol formation, and decompose formic acid yielding formaldehyde.

Table 3

Comparison of Activity of Various Oxide

	Water Gas Shift	Methanol	Formaldehyde
ZnO	+	+	+
Al_2O_3	+		+
FeO	+	+	+
MgO	+	+	+
ThO_2	+	+	+
Cr_2O_3	+	+	+
CuO	+	+	

+ Indicates Activity

The hydrogen activation for all these systems could be accomplished with metal or metal compounds, which under non-aqueous conditions would not be considered suitable for methanol synthesis. These metals under appropriate conditions can remain oxidized in an aqueous environment (i.e., iron-chromium oxide water-gas shift catalysts) eliminating this problem. These effects could be used in conjunction with supports known to retard metal oxide reductions or which interact with the metal oxide forming a solid solution. Control of the reduction of the methanol catalyst itself could offer some benefits as well.

In conclusion, it is our opinion that methanol catalysts have dual-functionality. If improvements in their activity, or if new catalysts for this reaction are to be developed, both a hydrogenating component and a formate forming component must be present.

EXPERIMENTAL

Catalysts and Reduction Procedures

A United Catalyst, Inc. sample L-540, C79-3 catalyst of composition, 60 parts zinc oxide/30 parts copper oxide/10 parts aluminum oxide, was utilized as the baseline methanol synthesis catalyst. This catalyst was ground and sieved to below 60 mesh before a sample was reduced in a tube furnace at 10 psi and 220-250°C under 4L/hr of 5% hydrogen in nitrogen for 18 hours. The catalyst was cooled under argon to room temperature before introduction to the reactor. The catalyst could be weighed before and after reduction so that 10 grams of reduced catalyst could be added.

A ICI Katalco sample 53-1 low temperature water gas shift catalyst of composition, 30-35 part copper oxide/29-36 parts zinc oxide and balance aluminum oxide was utilized due to the catalyst's ability to handle a high carbon monoxide, low steam feed stream. This catalyst was ground and sieved to below 60 mesh before a sample was reduced in a tube furnace under 1% and 2% hydrogen in nitrogen for 12 hours. The temperature and hydrogen breakthrough in these reductions had to be monitored (as specified by the manufacturer) to avoid over-reduction via thermal runaway and to provide maximum activity, repeatable performance and long life.

Solvent Selection

In the liquid phase methanol synthesis process, the solvent alleviates the problems resulting from the exothermic heat of reaction. It must be thermally stable and chemically inert and should possess the capacity to dissolve reactant gases (hydrogen, carbon monoxide and carbon dioxide) as well as addition reagents such as the water used in this study. Water plays an important role in equilibrium (both physical and chemical) as well as in product diffusion/mass transfer.

Polyglyme solvents were selected due to their high thermal stability, gas and water solubility. Previous work at BNL had demonstrated their beneficial effects on water gas shift and heterogeneous methanol synthesis. Stability measurements on tetraglyme were conducted to insure that hydrolysis and/or hydrogenation promoted cleavage would not cause problems via false methanol analysis. Treatments under reaction conditions in the presence of water, hydrogen, methanol + water, water + catalyst, and hydrogen + catalyst, indicated no decomposition.

Polyglyme-250 and tetraglyme gave identical baseline methanol synthesis results while a polyglycol demonstrated much poorer activity.

Apparatus

A 500 ml stainless steel MagneDrive II Packless Zipperclave reactor manufacrured by Autoclave Engineer's Inc. (AE) was used in this research. A dispersimax six-blade impeller was mounted on a shaft driven by an AE variable speed motor. Ports on the top of the reactor were provided for liquid additions and reagent gases, sampling vapor and liquid phase, cooling air inlet and outlet, and for inserting a thermocouple. The temperature of reactor was controlled by a Parr 4831 controller which controls an external heating mantle and internal air-cooling system. Pressure in the reactor was measured by a Weksler pressure gauge and a Setra Systems Model 204 pressure transducer. The transducer output was read from a Setra Systems digital pressure indicator and recorded by a two band Omega continuous chart recorder which also recorded the temperature from an Iron Constantan J type thermocouple.

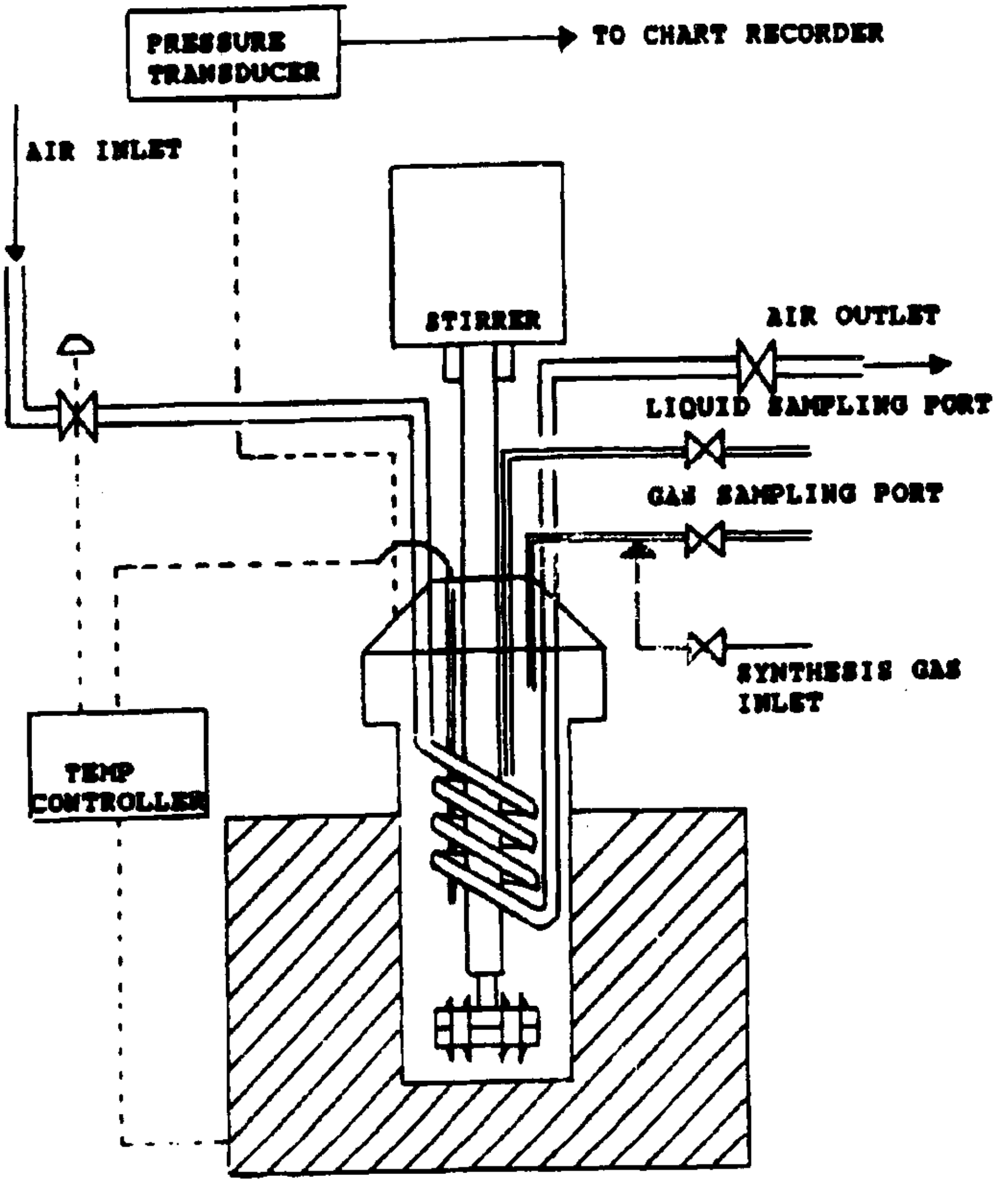


Figure 3. Schematic Diagram of Batch Reactor System

Operating Procedure

First, the heterogeneous catalyst (L540 or K 53-1) was reduced according to manufacturer procedures. The cooled catalyst (5, 10 or 15 grams) was then added to 100 ml of solvent under argon into the reactor. Then the reactor was quickly sealed. The sealed reactor was purged by pressurizing with 30 psig syngas and the gases were released. The system was purged and released by syngas twice. After releasing syngas from the reactor, if needed, water was injected using a syringe needle into the reactor through the injection port. The reactor was then pressurized with syngas to about 450 psig. The mixture in the reactor was stirred (1000 rpm.), and the temperature controller was turned on. During the reaction proceeding, the pressure and temperature were recorded. When the reaction had slowed (after 20-40 min.), the reaction was quenched by removing the heating mantle and placing the reactor into an ice-water batch. After the reactor was cooled to the initial temperature, the vapor and liquid samples were taken to do analysis.

Reactor Clean-Up

The inside of the reactor and the surfaces that were in contact with catalyst were cleaned by dilute nitric acid (6 M). After that all the surfaces were rinsed first with water and acetone and dried.

Analytical Techniques

Vapor phase samples were analyzed for hydrogen and carbon monoxide using a Perkin-Elmer model 154 vapor fractometer gas chromatograph. Peak areas were determined by Hewlett-Packard Model 3390A integrators. To detect CO, a molecular sieve column was used with helium carrier gas, while for H_2 a molecular sieve column was used with nitrogen as the carrier gas. The columns were calibrated daily by injecting standards of pure CO and H_2. Vapor phase GC measurements were reproducible to within 2%.

A Varian Aerograph series 1400 flame ionization detection (FID) gas chromatograph was used to detect methanol, dimethyl ether and methyl formate in the vapor phase. Peak areas were determined by a Hewlett-Packard Model 3390A integrator. Helium was used as the carrier gas. The column was calibrated by injecting standards of pure methanol, dimethyl ether and methyl formate.

Liquid phase samples were analyzed for methanol, methyl formate and higher alcohols with a Gow-Mac Series 550 thermal conductivity gas chromatograph. The liquid samples were injected into the GC after the syringe had been flushed three or four times with the sample. Peak areas were determined using a Hewlett-Packard Model 3390A integrator. The liquid phase GC was calibrated with a standar of 5% (by volume) methyl formate, 45% methanol and 50% tetraglyme. Liquid phase GC measurements were reproducible to within 10%.

Mass Balance Closure

Mass Balance calculations for the reactor system were done by summing moles of carbon, oxygen and hydrogen put into the reactor (initial charge) and moles of these elements found in final products and unreacted gas at end of run.

Typically mass balances could be closed for hydrogen, but small unaccounted mmoles of carbon and oxygen (unaccounted/consumed ratio of .05 - .15) often due to carbon dioxide solubility, were common.

RESULTS

Water additions utilizing carbon dioxide free 1/1:CO/H_2 syngas shown below, provide an interesting picture of carbon enhancement initiated by water gas shift activity. Calculations show that for 30 atm of 1/1 synthesis gas, 90 mmoles of water should provide ideal carbon utilization, assuming $3CO + 3H_2 + 1H_2O \rightarrow 2CH_3OH + 1CO_2$. This would be a carbon enhancement of 33%. Experiments indicate a more complex picture. Small amounts of water enhance catalyst activity (as has been reported elsewhere) and favorably change the carbon monoxide/hydrogen usage ratio. Higher than theoretical amounts inhibit catalyst activity and shift reaction pathway as expected by thermodynamics.

The rate of the UCI-L540 catalyzed water gas shift reaction is greater than the catalyst's methanol activity with no water present and is greater than methanol activity using a balanced carbon dioxide/hydrogen feed (3/1). Therefore, the rate enhancement seen with small amounts of water indicate a more complex picture than water gas shift (WGS) followed by syngas-only methanol synthesis. The common intermediate for these reactions, a surface formate, is responsible for the rate enhancement.

Also prominent in the data is the change in usage ratio as water is added to the feed. In fact, higher carbon utilization than desired occurs at only a 1/10 ratio of water to syngas feed with little or no loss of activity. Higher amounts of water lower activity. The UCI-L540 after being utilized as a WGS catalyst was treated with fresh 1/1 syngas giving surprisingly good performance compared to the catalyst not subject to the WGS reaction. This may be due to residual water in the solvent or to enhanced catalyst activity and carbon utilization.

Table 4

Water Additions to UCI-L540
$CO/H_2 = 1/1$
p = 450 psi
T = 225°C

H_2O ml	mmoles	H_2O/CO ratio	Activity $\text{Moles}_{MeOH}/\text{Kg}_{cat}/\text{hr}$	CO/H_2 usage ratio
0.0	--	--	13.1	0.5
0.5	28	.10	15.7	1.1
1.0	56	.20	12.3	1.25
1.5	83	.31	10.9	2.3
1.8	100	.37	10.7	2.6
3.0	165	.62	9.0	5.0
1.8repeat	100	.37	10.2	2.7
0.5repeat	28	.10	15.5	1.15
0.0*	--	--	15.5	0.91

WGS activity = 22.2 $\text{Moles}_{H_2}/\text{Kg}_{cat}/\text{hr}$ with .2 $\text{Moles}_{MeOH}/\text{hr}$

$CO_2 + 3H_2$ activity = 3.8 $\text{Moles}_{MeOH}/\text{Kg}_{cat}/\text{hr}$ with 18% reverse WGS

*WGS treated catalyst

The effect of carbon dioxide on feed gas composition and on in situ WGS activity should provide important information on using this technique with coal-derived synthesis gas. A mixture of ~51% CO, 36% H and 13% CO_2 was selected for study based upon LPMeOH feed used by Air Products.

Water additions utilizing this syngas mixture confirm water's ability to enhance carbon utilization with a gain, or little loss of catalyst activity.

Since the feed gas has a lower hydrogen to carbon monoxide rate than the carbon dioxide free gas investigated, lower activity is noted at comparable P,V,T conditions although at a slightly higher usage ratio. Less water is necessary to enhance this ratio. In fact, the feed ratio could be matched at an ~1/16 ratio of water to syngas with no loss in activity. As was reported for 1/1 syngas, higher amounts of water slightly suppressed activity but greatly enhanced carbon monoxide/hydrogen usage.

These results are encouraging when one considers the theoretical equation:

$$1\ H_2 + 1.4\ CO + .6\ H_2O \rightarrow .8\ CH_3OH + .6\ CO_2$$

because a carbon enhancement of 60% is possible compared to the

$$1H_2 + .5\ CO \rightarrow .5\ CH_3OH$$

equation in which the stoichiometric usage ratio occurs.

Table 5

Water Additions to UCI-L540
$CO/H_2 = 1.4/1$
p = 450 psi
T = 225°C

H_2O ml	mmoles	Activity $Moles_{MeOH}/Kg_{cat}/hr$	CO/H_2 usage ratio
0.0	--	11.1	.7
0.3	17	14.3	1.2/1
0.5	29	11.1	1.44/1
0.75	42	10.0	1.6/1
1.0	56	11.0	1.7/1
1.5	83	8.0	8/1
0.5repeat	28	10.0	1.3/1

Even though the UCI-L540 has water gas shift (WGS) activity, the reactions condition are not ideal for good performance. Therefore, a WGS catalyst (Katalco 53-1) more suited to the high carbon monoxide, low steam feed was selected and utilized with the UCI-L540. After numerous attempts, a good reduction procedure was selected to provide for a most active and repeatable performance. At 225°C and a carbon monoxide pressure of 225 psi and the addition of 4ml of water to the tetraglyme solvent: The Katalco 53-1 WGS activity = 41.0 $Moles/Kg_{cat}/hr$ with .5 $Mole_{MeOH}$. The K53-1 was also tested alone with syngas due to the surprisingly high methanol activity under these WGS conditions.

Table 6
K53-1 As Methanol Catalyst
P = 450 psi
T = 225°C

CO/H_2	H_2O mmoles	Activity $Mole_{MeOH}$/KgCat/hr	CO/H_2 Usage Ratio
1	--	15.8	.5
1.4	--	9.0	.9
1	28	16.7	1.0
1.4	28	10.7	1.2

The mixed catalyst tests provided additional information as to the significance of the water gas shift reaction on carbon enhancement. It appears that additional hydrogen via WGS is beneficial. Extraordinarily high activities were found, although these may be in part due to a new batch of UCI L-540 and the shorter run times due to larger amounts of total catalyst.

Excellent matches to feed gas composition coupled with the increase activity demonstrate this approach deserves further study.

Table 7

Water Additions to Mixed L-540/K53-1 = 2/1
CO/H_2 = 1/1
P = 450 psi
T = 225°C

H_2O ml	mmoles	Activity $Mole_{MeOH}/Kg_{cat}/hr$	CO/H_2 Usage Ratio
0.0	--	16.7	.55
0.3	17	14.6	1.0
0.5	28	23.3	1.2
1.6	90	12.9	1.95

Carbon dioxide could suppress this activity due to reverse WGS. Indeed, some loss in activity was noted with the carbon dioxide containing feed along with a change in usage, but the close match to feedgas at 17 and 28 mmoles water is interesting.

Table 8

Water Additions to Mixed L-540/K53-1 = 2/1
CO/H_2 = 1.4
P = 450 psi
T = 225°C

H_2O ml	mmoles	Activity $Moles_{MeOH}/Kg_{cat}/hr$	CO/H_2 Usage Ratio
0.0	--	12.7	.55
0.3	17	14.7	1.4
0.5	28	15.0	1.4
1.0	56	13.3	2.0

DISCUSSION

Plots of the data generated demonstrate the carbon enhancement effect. Any increase in carbon usage with an increase in activity means an enhanced carbon conversion. As activity drops with the increase in usage, parameter need to be defined to best accommodate this effect into the engineering constraints of reactor volume, gas flow, product removal and purification methods, and eventual unreacted gas utilization. It would be premature to define any of these limits at this point, although matching the feedgas CO/H_2 ratio would appear beneficial for methanol synthesis alone. Unreacted and product gases would have a lower heating value in these cases due to carbon dioxide formation. At very high carbon monoxide/hydrogen usages hydrogen replaces carbon monoxide as an "excess" gas.

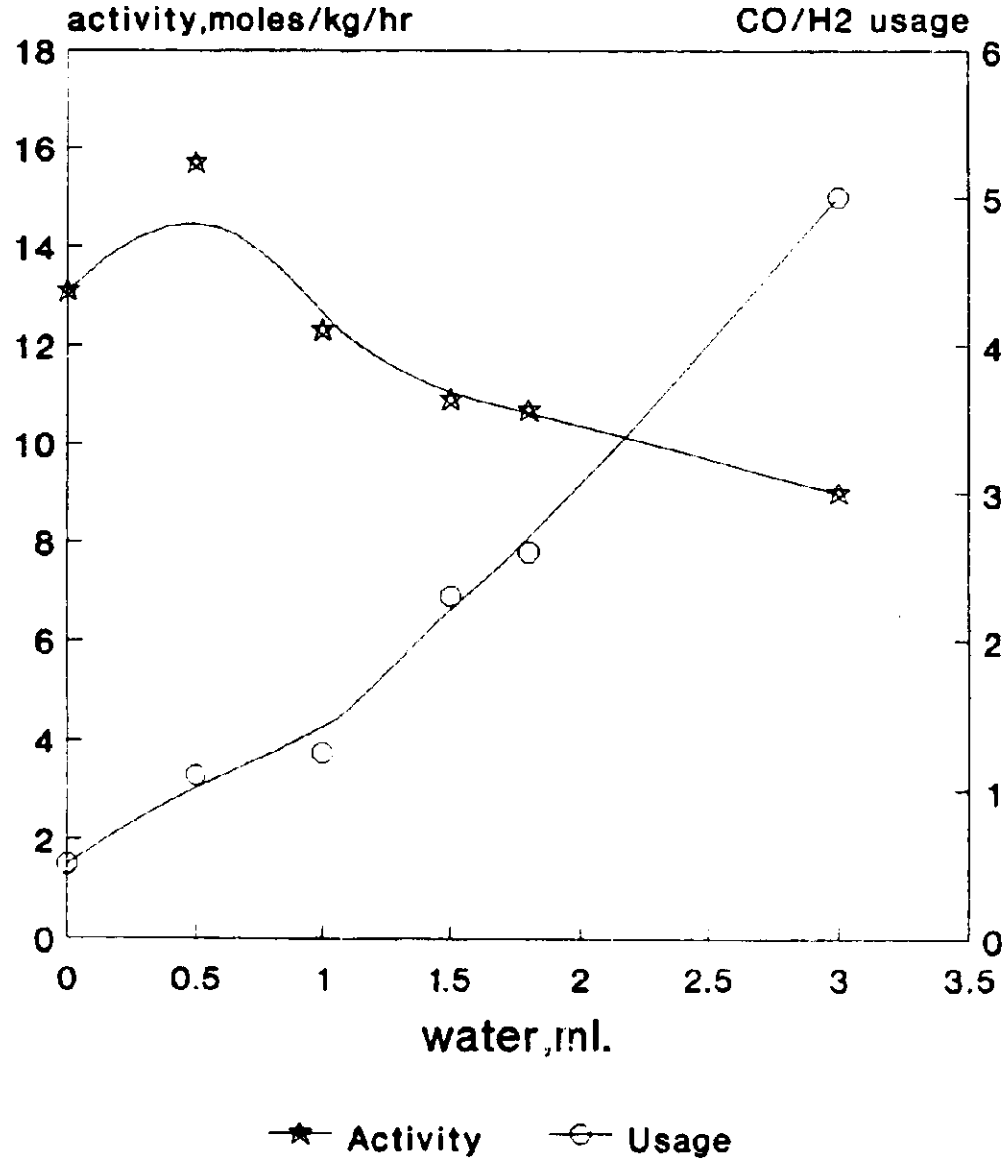


Figure Drawn from data in Table 4.

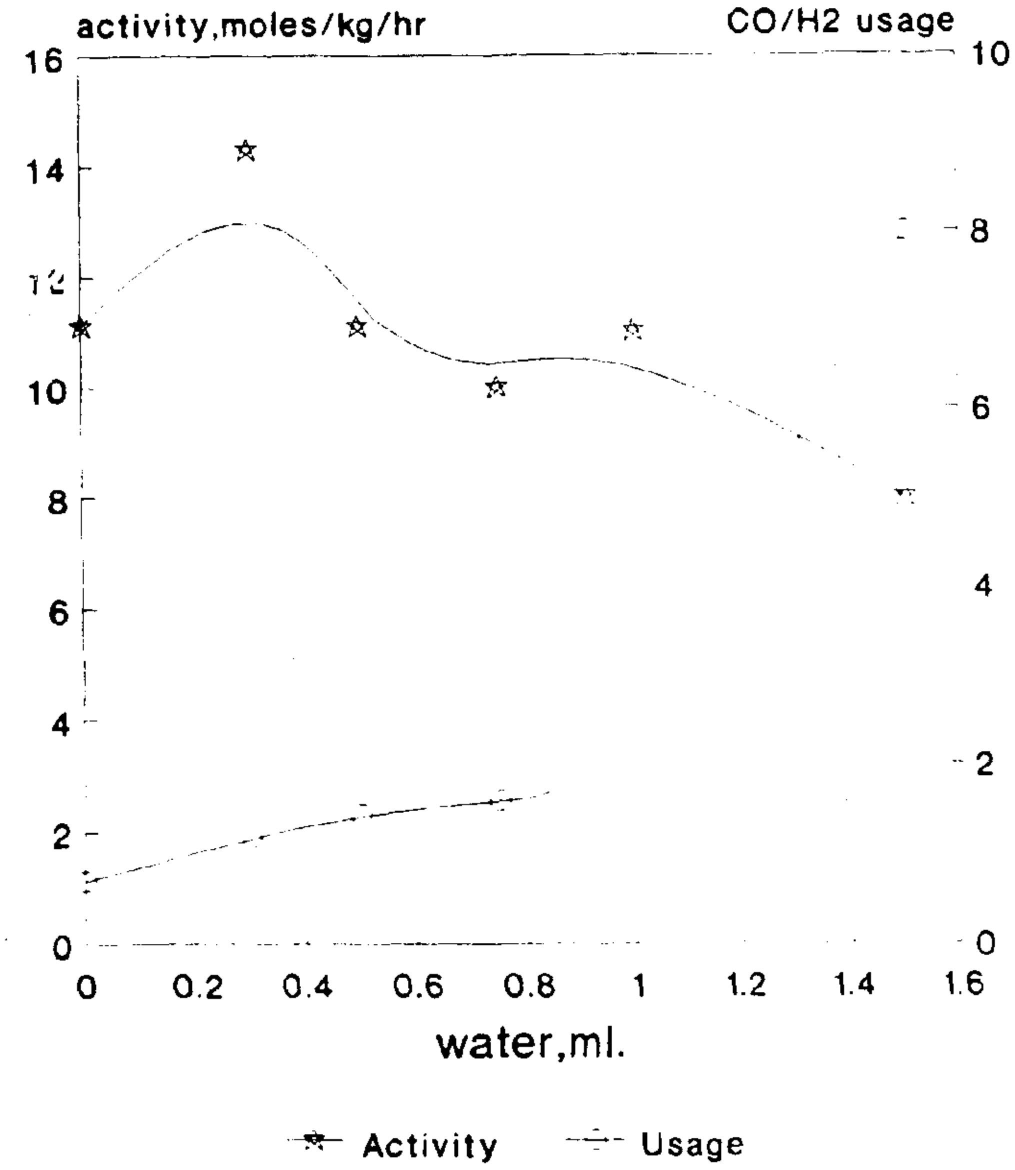


Figure 5. Drawn from data in Table 5.

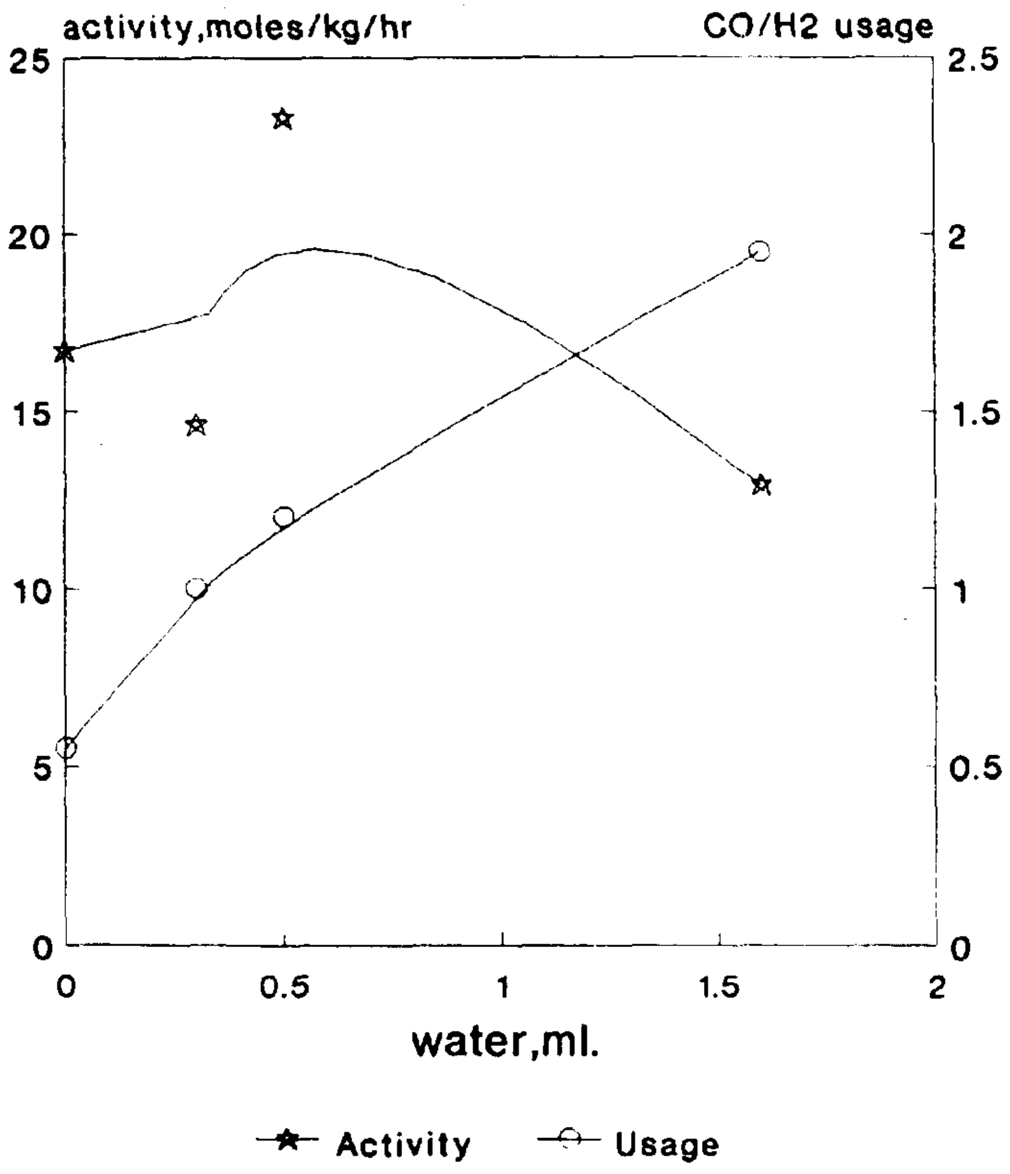


Figure 6. Drawn from data in Table 7.

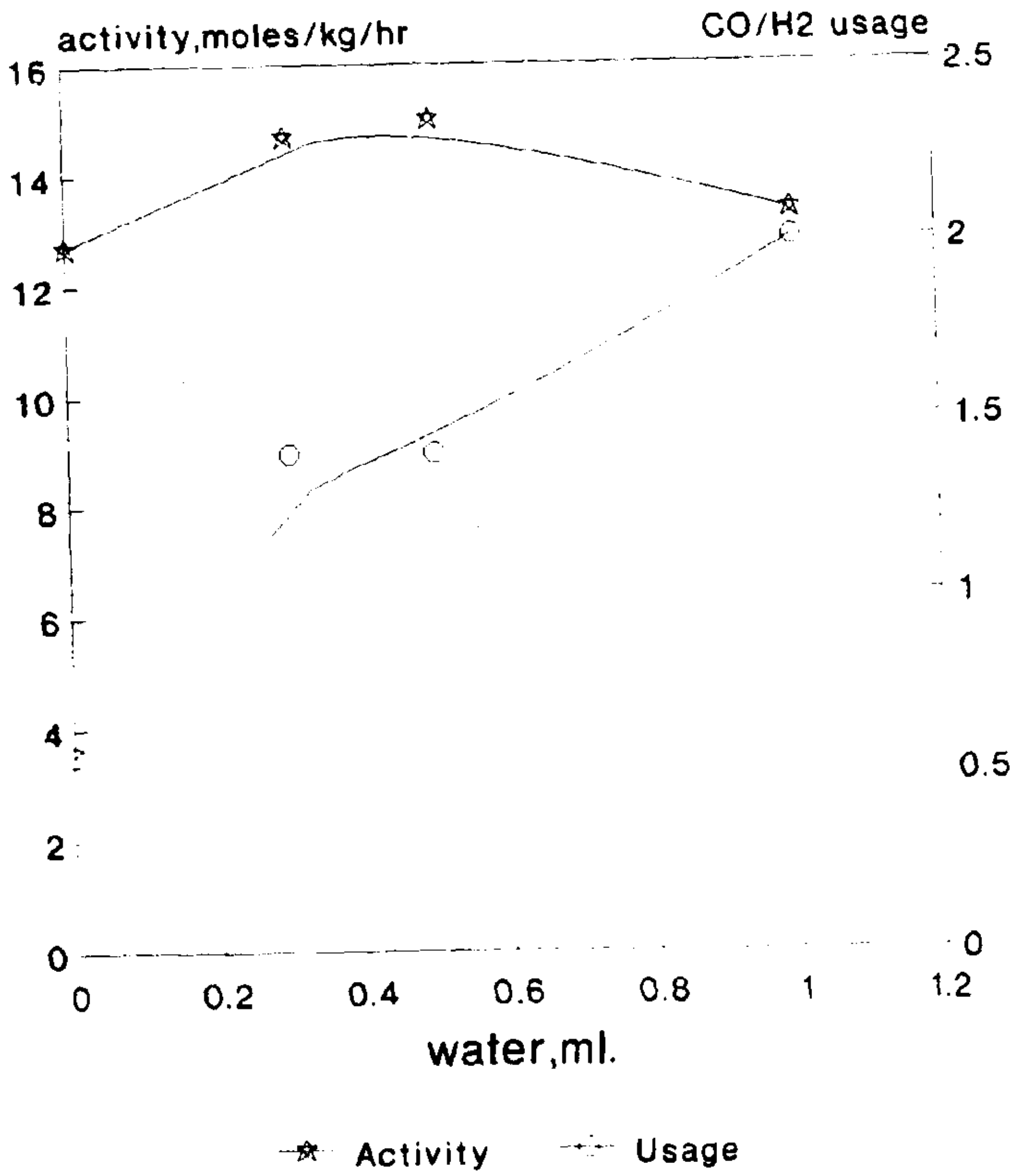


Figure 7. Drawn from data in Table 8.

CONCLUSIONS

It had been previously reported by us and others that the methanol synthesis rate over Cu/ZnO catalysts is greatly enhanced by small additions of water to the synthesis gas. Applying this effect to low hydrogen to carbon monoxide ratio coal-derived syngas for practical purposes has provided benefits.

Water additions indicate the formation of an intermediate with one hydrogen atom, a formate and using labeling techniques the methyl group of the resultant methanol was composed of that water hydrogen and a syngas-derived methylene. This observation indicates that a low ratio syngas with water could give enhanced activity and provide improved stoichiometric performance by trapping of the intermediate formate with available hydrogen. If the intermediate should "decompose" via completion of the water gas shift reaction, addition hydrogen would become available.

Carbon dioxide upon hydrogenation could also provide this intermediate (reverse water gas shift) and its promoting effect, although smaller, is related.

This investigation demonstrated that enhanced carbon utilization is possible in the liquid phase methanol synthesis. The use of a water gas shift catalyst to provide additional formate intermediates and hydrogen did show increased activity and the effects of carbon dioxide on rate in the presence of water demonstrated that a synergistic effect is possible at low water concentrations.

RECOMMENDATIONS

Although providing an interesting picture of potential carbon utilization enhancement, this investigation was an incomplete analysis which neglected engineering and economic considerations. Even without these application needs, insufficient time and funding did not allow for a complete study of water/carbon dioxide effects. Variables such as WGS catalyst/methanol catalyst ratios and catalyst composition effects could not be looked at, but may be critical. Work with the current BASF LPMeOH catalyst would also be necessary.

Future work should emphasize solvent selection and continuous reaction data. These should start with the appropriate completion of the batch phase of this work.