ALCOHOL SYNTHESIS IN A HIGH-TEMPERATURE SLURRY REACTOR

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SUMMARY

Objective:

The overall objective of this contract is to develop improved process and catalyst technology for producing higher alcohols from synthesis gas or its derivatives. Recent research has been focused on developing a slurry reactor that can operate at temperatures up to about 400°C and on evaluating the so-called "high pressure" methanol synthesis catalyst using this reactor.

Accomplishments and Conclusions:

A laboratory stirred autoclave reactor has been developed that is capable of operating at temperatures up to 400°C and pressures of at least 170 atm. The overhead system on the reactor is designed so that the temperature of the gas leaving the system can be closely controlled. An external liquid-level detector is installed on the gas/liquid separator and a pump is used to return condensed slurry liquid from the separator to the reactor. In order to ensure that gas/liquid mass transfer does not influence the observed reaction rate, it was necessary to feed the synthesis gas below the level of the agitator.

The performance of a commercial "high pressure" methanol synthesis catalyst, the so-called "zinc chromite" catalyst, has been characterized over a range of temperature from 275 to 400°C, a range of pressure from 70 to 170 atm., a range of H_2/CO ratios from 0.5 to 2.0 and a range of space velocities from 2500 to 10,000 sL/kg.(catalyst),hr. Towards the lower end of the temperature range, methanol was the only significant product. At the highest temperatures, the methanol synthesis reaction was close to equilibrium. However, there were significant quantities of methane, dimethyl ether and olefins in the product at these temperatures. Formation of higher alcohols was insignificant, although small amounts of isobutanol were detected at the highest temperatures and pressures, with 10 mole percent CO_2 in the feed gas.

Plans:

The next phase of this research will be devoted to modifying the "high pressure" methanol synthesis catalyst to increase the production of higher alcohols and to decrease the production of methane and ethane. The initial approach to this objective will involve adding alkali metals such as cesium to the commercial catalyst.

INTRODUCTION

The synthesis of higher (C_2^+) alcohols from mixtures of H_2 and CO (synthesis gas) has been an active area of research for the last several decades, and continues to be an important element of the Department of Energy's indirect coal liquefaction program. Table 1 summarizes the types of catalysts that have been studied for this reaction.

TABLE 1
HIGHER ALCOHOL SYNTHESIS CATALYSTS

	Water Gas Shift Activity?	
	Yes	No
Anderson-Schulz-Flory Product Distribution	Molybdenum Sulfide (+ promoters) Cu/Co/Cr (IFP)	Rhodium, other Group VIII metals
Non Anderson-Schulz-Flory Product Distribution	Methanol Synthesis: Cu/ZnO ZnCrO	None

The synthesis gas that is produced by modern, thermally-efficient coal gasifiers has a H_2/CO ratio in the range of 0.5 to 1. With such a feedstock, it is advantageous to use a catalyst that has some water-gas shift (WGS) activity since H_2 is the limiting reactant for alcohol synthesis at these ratios. When the H_2/CO ratio approaches or exceeds 2, as it can when synthesis gas is manufactured from natural gas, substantial WGS activity is not desirable since this reaction now causes a loss of the limiting reactant, CO.

Heydorn et al (1) and Minahan and Nagaki (2) have pointed out the advantages associated with an alcohol synthesis process that produces roughly one mole of methanol (or ethanol) and one mole of a 2-methyl alcohol such as isobutanol or 2-methyl 1-butanol. Such a product distribution could lead to the production of established octane enhancers such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE) and tertiary amyl methyl ether (TAME), with relatively small amounts of methanol, ethanol, propanol, etc. that would have to be sold as by-products. By definition, the catalysts that produce an Anderson-Shulz-Flory distribution of products cannot approach this target. However, some modified methanol synthesis catalysts have yielded product distributions in which methanol and isobutanol are the predominant products (1,2,3,4,5,6). None of these catalysts are completely satisfactory either because the molar rate of methanol formation has exceeded that of isobutanol formation by a substantial amount, and/or because the overall rate of alcohol formation has been low.

The synthesis of alcohols, particularly C_2^+ alcohols, is highly exothermic. Excellent temperature control is essential to good selectivity, long catalyst life and, in the case of methanol synthesis, to high conversions because of the reversibility of the reaction. The slurry reactor provides an essentially isothermal environment, on both the scale of the reactor and the scale of the catalyst particle. Therefore, this type of reactor has received a great deal of attention for methanol synthesis (7), for dimethyl ether synthesis (8) and for the synthesis of C_2^+ alcohols. A cesium-promoted Cu/ZnO methanol synthesis catalyst, a modification of the so-called "low pressure" methanol synthesis catalyst, has been demonstrated in a slurry bubble column reactor at the Department of Energy's Alternate Fuels Development Unit in La Porte, Texas (1).

Most of the studies of alcohol synthesis and related reactions (e.g., 9) that have been carried out in slurry reactors have been at temperatures below about 310°C. There are several reasons for this temperature limit. First, most of the previous work has involved catalysts, such as the Cu/ZnO "low pressure" methanol synthesis catalyst, that lose activity rapidly above about 300°C (7). Second, as will be discussed in more detail below, the liquids that have been used to slurry the catalyst are thermally unstable in the presence of high partial pressures of H_2 at temperatures significantly in excess of 300°C.

The specific objectives of the work described in this paper were to extend the operating range of slurry reactors for alcohol synthesis to a temperature of about 400°C, and to characterize the performance of a commercial, high-pressure methanol synthesis catalyst in a slurry reactor at temperatures up to 400°C. This research is intended to set the stage for the synthesis and evaluation of catalysts for the production of C_2^+ alcohols that are derived from this "zinc chromite" methanol synthesis catalyst.

EQUIPMENT

A schematic diagram of the equipment employed is shown in Figure 1. Gases are fed from cylinders through activated carbon traps to remove impurities and then through mass flow controllers to measure and control the flow rate. The mixed gas is compressed to the desired pressure, typically in the range of 70 to 200 atm., and the compressed gas is passed through another activated carbon trap specifically to remove any iron and/or nickel carbonyl that may have formed during and after compression. The gas is then fed into a 300 $cm.^3$ Autoclave Engineers stirred autoclave reactor. The gas leaving the reactor passes into a gas/liquid separator that contains a cooling coil. The temperature of the gas/liquid separator is carefully regulated. The gas then passes through a back pressure regulator that controls the reactor pressure. After leaving the regulator, the gas passes through heated lines to prevent condensation and through a wet test meter to measure the gas flow rate. Samples of the reactor feed and effluent are periodically diverted to a dual column gas chromatographic system containing a Carboxen 1000 column followed by a thermal conductivity detector and a Poroplot Q column followed by a flame ionization detector. The former system is used to measure the fixed gases, H_2, N_2, CO, CO_2 and H_2O. The organic species are measured on the second system.

Several features of the equipment merit further discussion: the carbonyl traps, the overhead system and the location at which gas is fed into the stirred autoclave reactor.

Carbonyl Traps

Iron and nickel carbonyl are known to poison both types of methanol synthesis catalyst, even at very low concentrations (7,10,11). Two types of trap have been employed to remove these volatile species from the feed gas, a low-temperature adsorptive trap, typically containing activated carbon (12,13), and a high-temperature catalytic trap, in which the carbonyls are decomposed and the metal is deposited on the catalyst at a temperature of about 300°C. Only the former type of trap should be used at the CO partial pressures that are typical of methanol synthesis. Thermodynamic calculations have shown that high-temperature traps are relatively ineffective at high CO partial pressures, and can even result in the formation, rather than the destruction, of metal carbonyls. Moreover, the iron and nickel that are deposited on the catalyst might lead to the formation of large quantities of carbon through catalysis of the Boudouard reaction.

Overhead System

At the high reactor temperatures employed in this research, the vapor pressure of the inert liquid that is used to suspend the catalyst can be appreciable. Therefore, the quantity of liquid that is condensed in the overhead system and returned to the stirred autoclave can be significantly greater than with, for example, a liquid-phase methanol synthesis reactor that operates in the region of 250 to 300°C. Unless the hydraulics of the overhead system are carefully designed, some of the condensed liquid can fill the gas/liquid separator and overflow through the back pressure regulator. Simple gravity return of the condensed liquid may not be sufficient to avoid this loss. Three important features of the actual overhead system are not shown in Figure 1. First, an ultrasonic liquid level sensor is mounted on the exterior of the gas/liquid separator to provide a warning in the event that the liquid level in the separator reaches a position that is high enough to threaten liquid loss through the back pressure regulator. Second, a high-pressure piston pump is used to return condensed liquid from the separator to the reactor. These two features have permitted the overhead system to be operated reliably over long periods of time without any significant mechanical loss of the slurry liquid.

Under certain circumstances, it may be necessary to operate the overhead system at a relatively high temperature in order to avoid condensing and returning a high-boiling product or a product that has a high partial pressure in the reactor effluent. When the effluent temperature from the gas/liquid temperature is sufficiently high, a small loss of the slurry medium as vapor can occur. For long periods of operation, the cumulative loss of slurry medium by this mechanism can be significant. Therefore, the actual overhead system is equipped with a high pressure pump to return slurry liquid that is condensed downstream of the back pressure regulator to the reactor, or to feed fresh slurry liquid in lieu of returning low-pressure condensate.

Feed Location

Figure 2 shows the results of two sets of experiments designed to determine the optimum agitation rate and gas-feed location. These experiments were carried out with BASF S3-86 "low pressure" (Cu/ZnO) methanol synthesis catalyst. The methanol productivity is defined as the rate of methanol production per unit weight of catalyst (g. moles of methanol/kg. catalyst, hr.) at a standard set of operating conditions: reactor temperature - 250°C; total pressure - 51 atm.; feed composition - 35 mole % H_2, 51% CO and 14% CO_2, and; gas hourly space velocity (GHSV) - 5000 sL/kg.,hr. Two feed gas locations were tested in each experimental set: 1) through a dip tube that extended into the slurry, and; 2) directly into the "headspace" above the liquid. The data has been normalized by dividing each data point by the catalyst productivity at infinite stirrer speed, as determined by extrapolating the data in each set that was obtained with the feed through the dip tube to infinite stirrer speed. The basis for the abscissa, the reciprocal stirrer speed raised to the 2.2 power, is a publication by Yagi and Yoshida (14) showing that the k_La for the reactor depends on stirrer speed raised to this power.

Only the data obtained with the gas feed introduced below the level of the agitator (designated "extended dip tube" in Figure 2) showed no dependence on the agitation rate. This is strong evidence that gas/liquid mass transfer had no significant influence on the overall reaction rate. The data for the "short dip tube", which terminated about 1 cm. above the agitator, shows a strong dependence of catalyst productivity on agitation rate, suggesting that gas/liquid mass transfer influenced the overall reaction rate to a significant extent. The effect of agitation rate was present even at the highest stirrer speed, 2500 rpm. However, the data extrapolated to essentially the same productivity that was measured in the run with the extended dip tube.

The manufacturer of the stirred autoclave reactor recommends feeding gas into the headspace above the liquid. The "dispersimax" agitator in the reactor has a hollow shaft and the blades at the bottom of the shaft are designed to draw gas down the shaft from the headspace, creating bubbles in the shear field of the agitator. The two runs that were done with this feed location exhibited a significant effect of agitation rate. Moreover, neither "headspace" run extrapolated to a normalized productivity of 1 at an infinite stirrer speed. Apparently, the "headspace" feed location has a deficiency that is more than just an insufficient value of k_La. One possible explanation of the failure of the data for the two "headspace" feed runs to extrapolate to a normalized productivity of 1 is that gas by-passing occurred.

The "extended dip tube" has been used for all runs with the "zinc chromite", "high pressure" methanol synthesis catalyst. The stirrer speed has been varied on several occasions, with no noticeable effect on catalyst productivity.

RESULTS AND DISCUSSION

Liquid Stability Testing

The literature (15,16,17) suggests that the "zinc chromite", "high pressure" methanol synthesis catalyst is typically run at temperatures of 350 to 410°C in commercial, fixed-bed methanol synthesis reactors. Moreover, the research that has been carried out to date on the addition of alkali metals to this catalyst in order to shift the product distribution towards the higher alcohols (e.g., 3,4,5) has involved similar temperatures. Therefore, a target operating temperature of 375°C was set for slurry reactor operation and a series of tests was carried out to evaluate the stability of various liquids in the presence of H_2 at this temperature.

The stability of a liquid was evaluated in two phases. First, a "thermal" stability test was carried out by charging a measured amount of the liquid to the stirred autoclave reactor, pressurizing to the range of 54 to 68 atm. with hydrogen, heating to 375°C, continuously sparging hydrogen through the liquid and holding the system at these conditions for about three days. Catalyst was not present in the reactor during this test. The gas leaving the reactor was analyzed periodically by gas chromatography to determine whether any hydrocarbons were present, and, if so, their identities and concentrations in the sampled gas. At the end of the test period, the liquid remaining in the reactor was measured and a number of analytical tests were carried out, including molecular weight, density, refractive index and nuclear magnetic resonance (NMR) spectroscopy.

Table 2 shows the performance of four different liquids in this testing protocol.

TABLE 2
RESULTS OF THERMAL STABILITY TESTING OF VARIOUS LIQUIDS

Liquid	Run Duration[1] (hr.)	Molecular Weight Reduction (%)	Rate of Liquid Loss (wt. % of initial charge/hr.)	
			Maximum	Steady-State
Drakeol 34	69	35	1.2	0.10
Durasyn 180	65	86	1.8	0.12
A	71	Pending	0.44	0.044
B	73	Pending	0.095	0.0040

[1] - at a temperature of 375°C, H_2 pressure of 60 to 70 atm. and H_2 flow rate of 3.8 sL/min.

Liquids A and B were much more stable than either Drakeol 34 or Durasyn 180, as indicated by both of the rates of hydrocarbon loss in the effluent gas stream. NMR analyses (^1H and ^{13}C) were carried out on samples of Liquids A and B taken from the reactor at the end of the thermal stability test and on samples of the original liquids for comparison. There was no evidence of hydrocracked products in the final sample of

Liquid B. However, there were traces of compounds that could have resulted from hydrocracking in the final sample of Liquid A. Because the stability of Liquid B appears to be higher than that of Liquid A, the former has been used exclusively to date in slurry reactor operation.

Performance of Commercial Catalyst

A commercial high pressure methanol synthesis catalyst (Zn-0312 T1/8) was obtained from Engelhard Corporation in a reduced and stabilized form. The catalyst contained 60 wt. % Zn and 15 wt. % Cr, with ZnO and $ZnCr_2O_4$ detectable by x-ray diffraction. The as-received BET surface area was 145 m^2/g. The catalyst was ground and sieved to -120 mesh. All runs were made with a 20 wt. % slurry of catalyst in Liquid B. The catalyst was activated in-situ by: pressurizing the reactor to 69 atm. with N_2 and heating it to 130°C while sparging N_2 through the slurry; heating from 130 to 300°C at about 40°C /hr. with a sparge gas consisting of 5% H_2 in N_2; heating to 375°C at 25°C/hr. while progressively increasing the hydrogen mole fraction in the sparge gas from 0.05 to 1, and; holding at 375°C with a pure H_2 sparge until no water was present in the gas leaving the reactor.

A series of experiments was conducted at a total pressure of 69 atm., temperatures in the range of 300 to 375°C and gas hourly space velocities (GHSV) between 1500 and 10000 sL/kg.,hr. The feed was a mixture of H_2 and CO, with H_2/CO ratios between 0.5 and 2. A typical operating pressure for a methanol synthesis process based on the "zinc chromite" catalyst is about 300 atm. (15,16,17). The equilibrium concentration of methanol decreases as the pressure is decreased. In order to limit the amount of methanol formed in a higher-alcohols process, it seems reasonable to presume that the pressure would be lower than that used for methanol synthesis. An operating pressure of 69 atm. was chosen for the initial series of runs in order to characterize the performance of the "zinc chromite" catalyst in a slurry reactor at conditions that might be reasonably characteristic of a higher-alcohols process, and were not likely to lead to the formation of excessive amounts of methanol.

Figure 3 shows the product distributions that were obtained in two runs at 375°C, 5000 sL/kg.,hr. GHSV and H_2/CO ratios of 0.5 and 1. Methanol was the only alcohol detected in the outlet stream. Dimethyl ether (DME) was the only other oxygenate present in significant quantities. DME probably formed by the condensation of two molecules of methanol, a reaction that is catalyzed by mildly acidic surfaces such as γ-alumina (8). A portion of the product, slightly less than 10 % of the carbon atoms, was C_2 through C_4 olefins. Olefin formation in these quantities has not been reported previously for this type of catalyst in research carried out in gas-phase, fixed bed reactors. However, the formation of C_2 through C_4 alcohols has been reported. It is tempting to speculate that the olefins that were observed in this run may have resulted from the dehydration of the corresponding alcohol. It has been reported that the dehydration of isobutanol to isobutene is catalyzed by the same kind of acidic materials that catalyze the formation of dimethyl ether from methanol (9). The formation of about 15% methane plus ethane is a negative feature of the performance of this catalyst.

The production of a large quantity of CO_2 demonstrates that the catalyst has a substantial activity for the water-gas shift reaction, as suggested by Table 1. The water produced by the formation of alkanes, olefins and dimethyl ether was shifted to CO_2 and H_2 essentially quantitatively.

The product distributions at the two different H_2/CO ratios are similar except for the higher relative amount of methanol and the lower relative amount of CO_2 at the higher ratio. Both changes are conceptually reasonable; the 1:1 H_2/CO ratio should increase the rate of methanol formation because it is closer to the stoichiometric ratio, and should decrease the driving force for the water-gas shift reaction.

Figure 4 shows the product distribution at a H_2/CO ratio of 1 and at a lower space velocity of 1500 sL/kg.,hr. The most pronounced change is the increase in the ratio of dimethyl ether to methanol. This is probably the result of the factor of three increase in contact time, which permitted a higher conversion of methanol into DME.

Figure 5 compares the product distribution at 375°C with that at 300°C, for a GHSV of 5000 sL/kg.,hr. and a H_2/CO ratio of 0.5. At the lower temperature, methanol is the only product that is formed in substantial quantities. The formation of hydrocarbons is substantially lower, as is the formation of dimethyl ether. The small quantity of CO_2 that is produced does not necessarily indicate that the shift activity of the catalyst is substantially diminished at 300°C. The reactions that result in the formation of water, i.e., hydrocarbon formation and DME formation, do not occur to any substantial extent at 300°C. The low rate of water formation, compared to the rate at 375°C, limits the amount of CO_2 that can be formed.

The experimentally measured rate of methanol production is compared to the rate that would be observed if chemical equilibrium were achieved in Figure 6. The "equilibrium" catalyst productivity is calculated by assuming that the methanol synthesis reaction is in equilibrium in the gas stream leaving the reactor, thus defining the methanol production rate. At 375°C and 350°C, the measured and theoretical rates are reasonably close, which suggests that the presence of the liquid has not had a significant inhibiting effect on the activity of the catalyst. On the contrary, the close approach to equilibrium at a temperature of 350°C is somewhat surprising. It has been reported (15) that the effectiveness factor of the pelleted commercial catalyst is only about 0.7 in the temperature range from 370 to 410°C. Thus, the surprising low-temperature activity of the catalyst in the slurry reactor may be associated with a reduction in the resistance to pore diffusion as a result of the much smaller particle size of the catalyst in the slurry reactor.

As the reactor temperature is further decreased, the actual catalyst productivity decreases to a relatively small fraction of the equilibrium productivity. However, at 300°C, the lowest temperature investigated, the methanol productivity of the catalyst was higher than it was at any of the higher temperatures. This reflects the fact that the reaction equilibrium becomes more favorable as the temperature decreases. For comparison, the methanol productivity obtained with the "zinc chromite" catalyst at 300°C is one-quarter to one-fifth of the productivity obtained with the Cu/ZnO catalyst at 250°C at otherwise comparable conditions.

Figure 7 shows the effect of space velocity and H_2/CO ratio on the methanol productivity at a temperature of 300°C. As expected, the reaction rate increases as the H_2/CO ratio is increased from 0.5 to 2 and as the space velocity is increased.

The experiments described above required about fifteen days of continuous reactor operation. The liquid in the reactor at the end of this period was analyzed to determine whether any degradation had taken place. Some of the data is still pending. However, there was no decrease in the molecular weight. The conversion and product distribution were measured periodically during the run at a standard set of conditions: 375°C, 5000 sL/kg.,hr. GHSV and a H_2/CO ratio of 1. The results are shown in Figure 8. There is no trend with time in the rate of paraffin production, there is a modest increase in the rate of methanol formation and the rates of olefin and DME production decrease with time. The BET area of the catalyst that was recovered at the end of the run was about 110 $m^2/g.$, about 25% lower than the "fresh" value.

One of the disappointing features of the data presented above is the lack of a substantial rate of C_2^+ alcohol formation. However, it was theorized that the olefin formation that was observed may have resulted from the dehydration of the corresponding alcohol. Therefore, in a subsequent series of experiments, 10 mole percent CO_2 was added to the feed gas in order to suppress the water-gas shift reaction, increase the concentration of water in the reactor and shift the alcohol dehydration reaction to the left. This experiment resulted in the production of very small amounts of isobutanol, which lends some credence to the alcohol dehydration theory.

CONCLUSIONS

The studies reported above are significant in several respects. First, operation of the slurry reactor at 375°C, with no apparent degradation of the slurry liquid and with what appears to be a reasonable level of catalyst activity, represents a significant extension of the operating temperature range of this type of reactor. A number of operating and equipment problems associated with the overhead system had to be overcome before reliable operation was possible.

The "zinc chromite" catalyst showed some promising performance features. First, the commercial version of this catalyst appears to be compatible with slurry reactor operation in that a high level of activity was observed, there was no catastrophic deactivation of the catalyst over the course of two weeks of continuous operation, and the catalyst did not appear to cause any degradation of the slurry liquid. Second, some features of the product distribution at 375°C are encouraging, particularly the formation of substantial quantities of dimethyl ether and olefins. The high production rates of methane and ethane are a negative element of the performance of this catalyst, which will have to be addressed in future research.

REFERENCES

1. Heydorn, E. C., Schaub, E. S., Stein, V. E. E., Underwood, R. P. and Waller, F. J., "Recent Progress on Syngas Conversion to Isobutanol", paper presented at U. S. Department of Energy, Pittsburgh Energy Technology Center Coal Liquefaction and Gas Conversion Contractor's Review Conference, Pittsburgh, PA, September 7-8, 1994

2. Minahan, D. M. and Nagaki, D. A., "Heterogeneous Catalytic Process for Alcohol Fuels from Syngas", paper presented at U. S. Department of Energy, Pittsburgh Energy Technology Center Coal Liquefaction and Gas Conversion Contractor's Review Conference, Pittsburgh, PA, September 7-8, 1994

3. Riva, A., Trifiro, F., Vaccari, A., Busca, G., Mintchev, L., Sanfilippo, D. and Manzatti, W., "The Promoting Role of Cr and K in Catalysts for High-Pressure and High-Temperature Synthesis", *J. Chem. Soc., Faraday Trans. 1*, **83**, 2213-2225 (1987)

4. Tronconi, E., Lietti, L., Groppi, G., Forzatti, P. and Pasquon, I., "Mechanistic Kinetic Treatment of the Chain Growth Process in Higher Alcohol Synthesis", *J. Catal.*, **124**, 376-390 (1992)

5. Tronconi, E., Lietti, L., Forzatti, P. and Pasquon, I., "Higher Alcohol Synthesis over Alkali Metal-Promoted High-Temperature Methanol Catalysts", *Applied Catalysis*, **47**, 317-333 (1989)

6. Vedage, G. A., Himelfarb, P. B., Simmons, G. W. and Klier, K., "Alkali-Promoted Copper-Zinc Oxide Catalysts for Low Alcohol Synthesis", *ACS Symp. Series*, **279**, 295-312 (1985)

7. Roberts, G. W., Brown, D. M., Hsiung, T. H. and Lewnard, J. J., *Ind. Eng. Chem. Res.*, **32**, 1610 (1993)

8. Brown, D. M., Bhatt, B. L., Hsiung, T. H., Lewnard, J. J. and Waller, F. J., *Catalysis Today*, **8**, 279 (1991)

9. Armstrong, P. A., Bhatt, B., Heydorn, E. C. and Toseland, B. A., "Isobutanol Dehydration: A Key Step in Producing MTBE from Syngas", paper presented at U. S. Department of Energy, Pittsburgh Energy Technology Center Coal Liquefaction and Gas Conversion Contractor's Review Conference, Pittsburgh, PA, September 27-29, 1993

10. Supp, E., "Technology of Lurgi's Low Pressure Methanol Process", *Chemtech*, July (1973), 430-435

11. Satterfield, C. N., *Heterogeneous Catalysis in Industrial Practice (2nd Edition)*, McGraw-Hill, 447 (1991)

12. Bhatt, B. L., Golden, T. C. and Hsiung, T. H., "Adsorptive Removal of Catalyst Poisons from Coal Gas for Methanol Synthesis", *Separation Science and Technology*, **26**, 1559-1574 (1991)

13. Golden, T. C., Hsiung, T. H. and Snyder, K. E., "Removal of Trace Iron and Nickel Carbonyls by Adsorption", *Ind. Eng. Chem. Res.*, **29**, 502-507 (1991)

14. Yagi, H. and Yoshida, F., "Gas Absorption by Newtonian and Non-Newtonian Fluids in Sparged Agitated Vessels", *Ind. Eng. Chem., Process Des. Dev.*, **14**, 488-493 (1975)

15. Pasquon, I. and Dente, M., "Heat and Mass Transfer in Methanol Synthesis - Optimum Operating Conditions of the Reactors", *J. Catal.*, **1**, 508-520 (1962)

16. Strelzoff, S., "Methanol: Its Technology and Economics", *Chem. Eng. Prog. Symp. Series*, No. 98, **66**, 54-68 (1970)

17. Stiles, A. B., "Methanol, Past, Present and Speculation on the Future", *AIChE Jnl.*, **23**, 362-375 (1977)

Figure 1

STIRRED AUTOCLAVE PROCESS FLOWSHEET

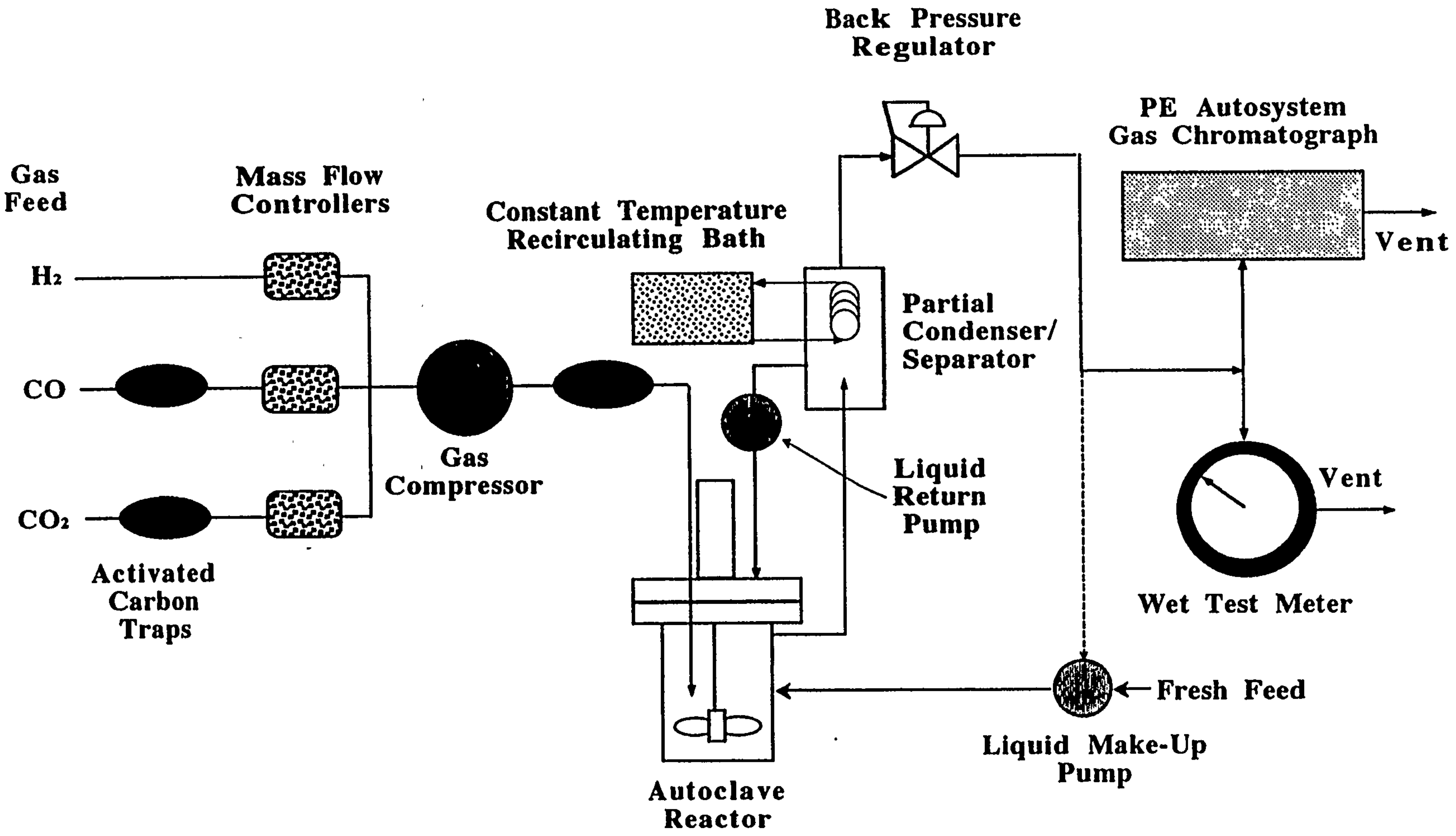

Figure 2

Effect of Reactor Gas Feed Configuration on Catalyst Performance

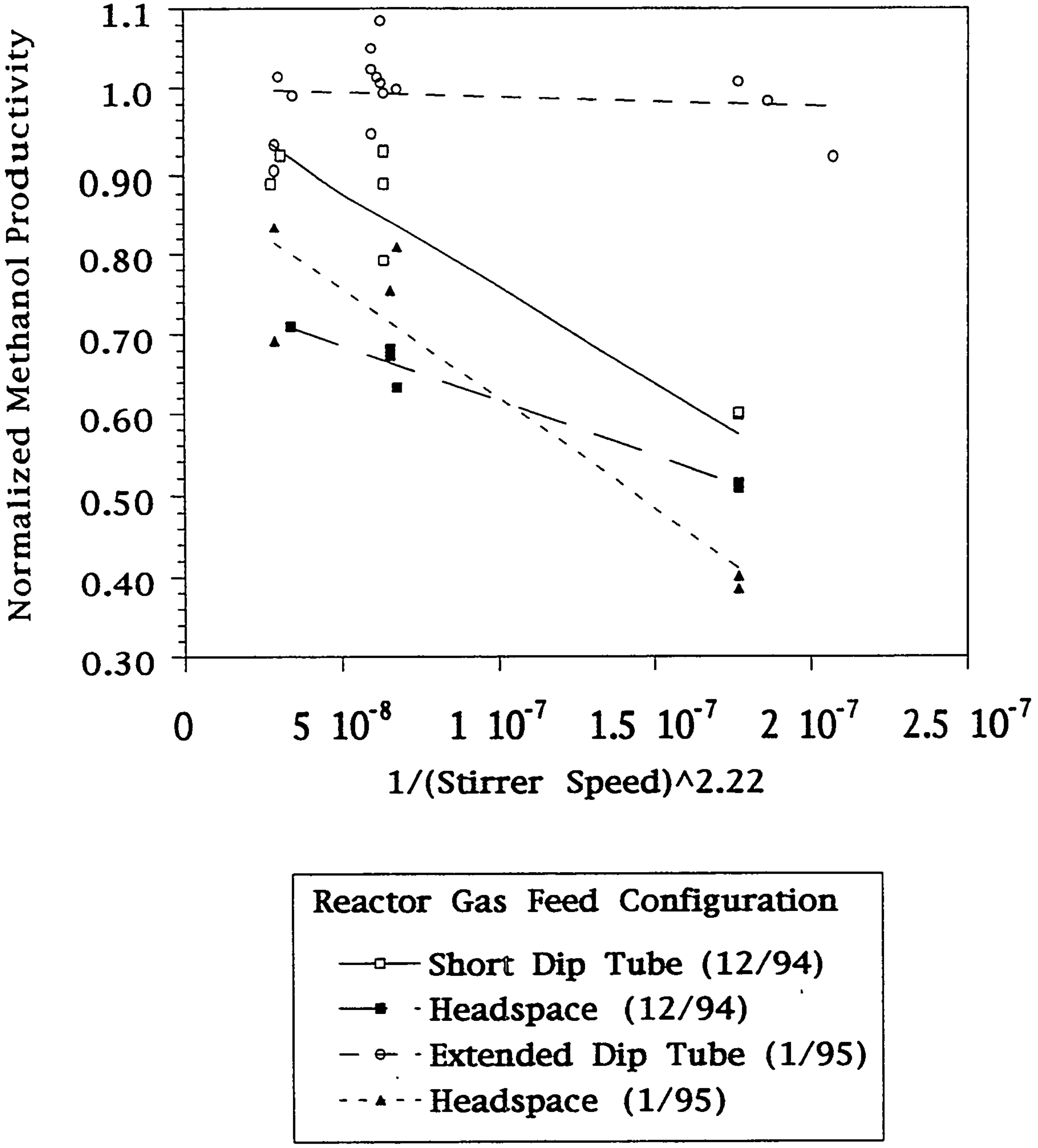

Figure 3

Effect of H_2/CO Ratio on Product Distribution
(5000 GHSV, 68 atm, 375°C)

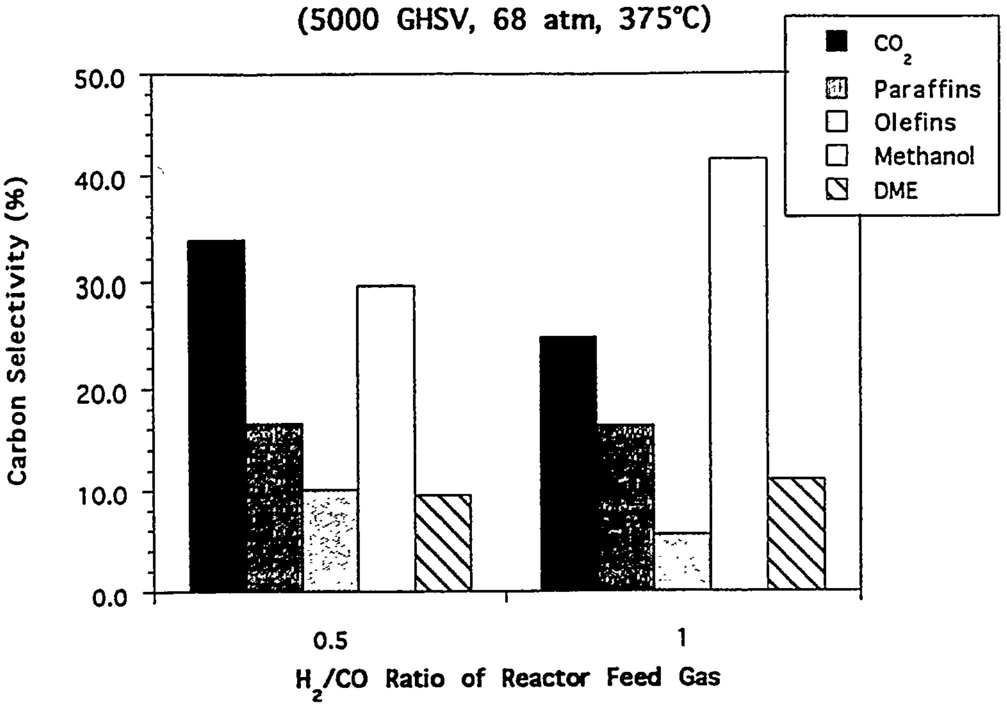

Figure 4

Product Distribution for ZnCrO Catalyst
(1500 GHSV, 375°C, 68 atm, H_2/CO = 1)

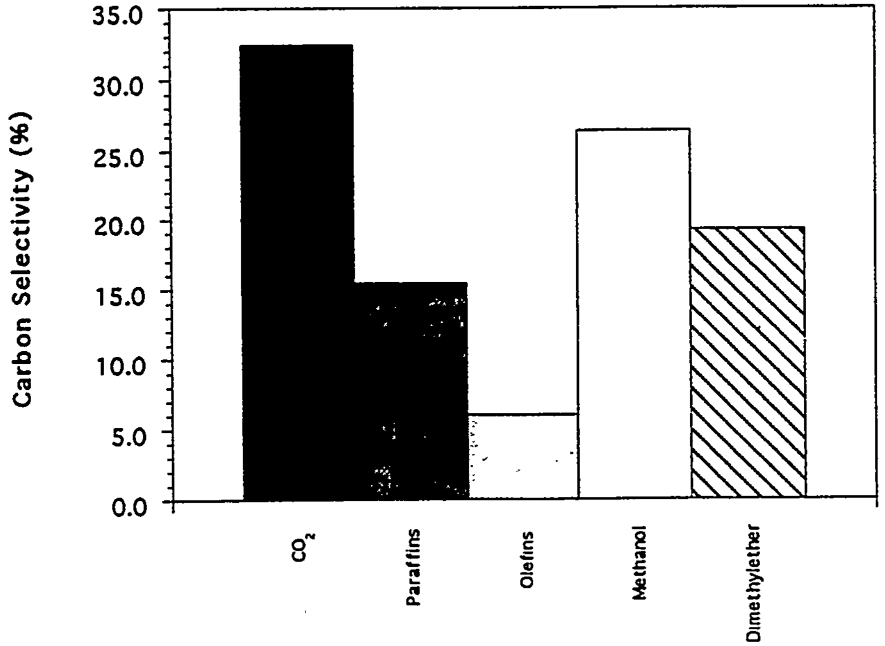

Figure 5

Effect of Temperature on Product Distribution (5000 GHSV, 68 atm, $H_2/CO = 0.5$)

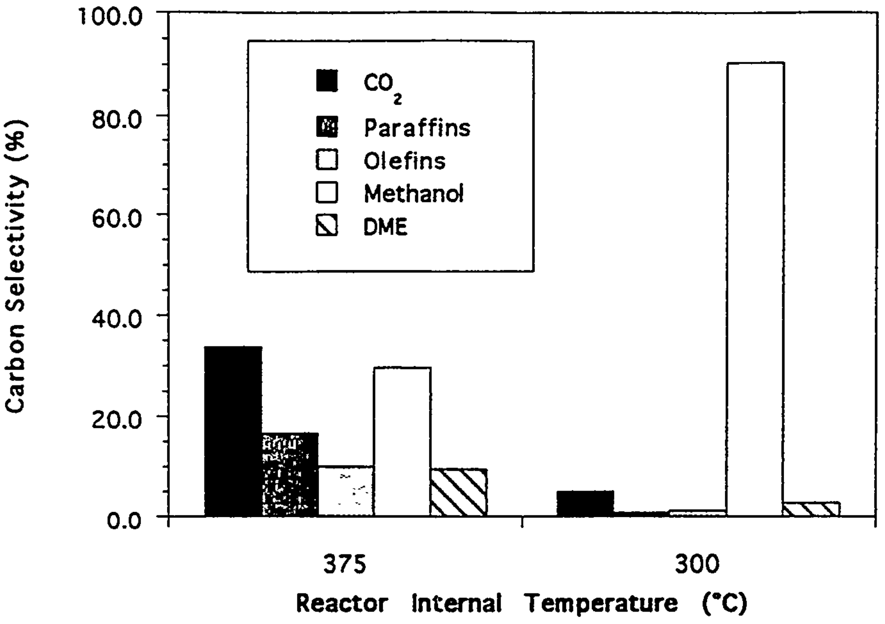

Figure 6

Effect of Temperature on Methanol Production (5000 GHSV, 68 atm, $H_2/CO = 0.5$)

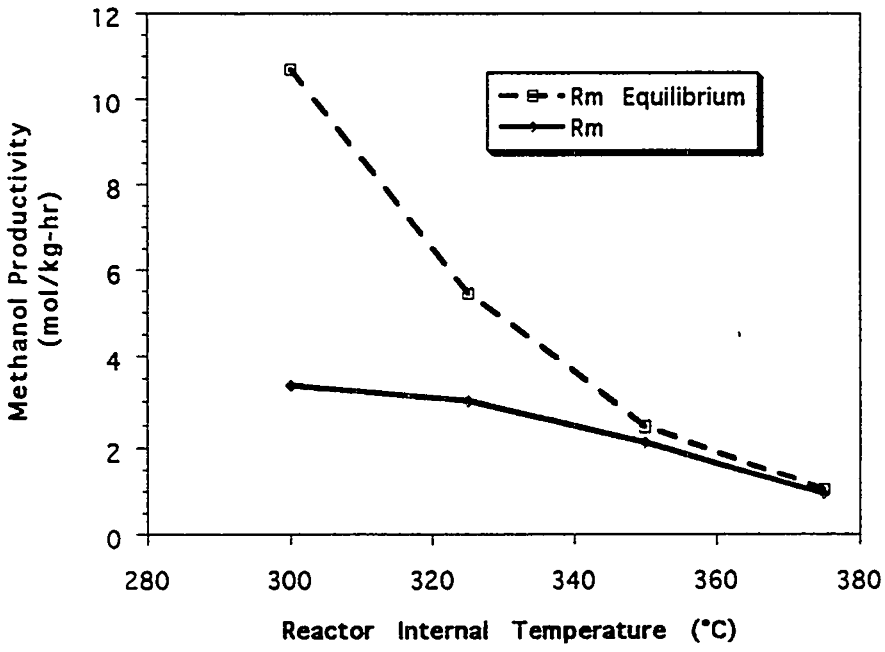

Figure 7

Effect of GHSV, H_2/CO Ratio on Methanol Production (300°C, 68 atm)

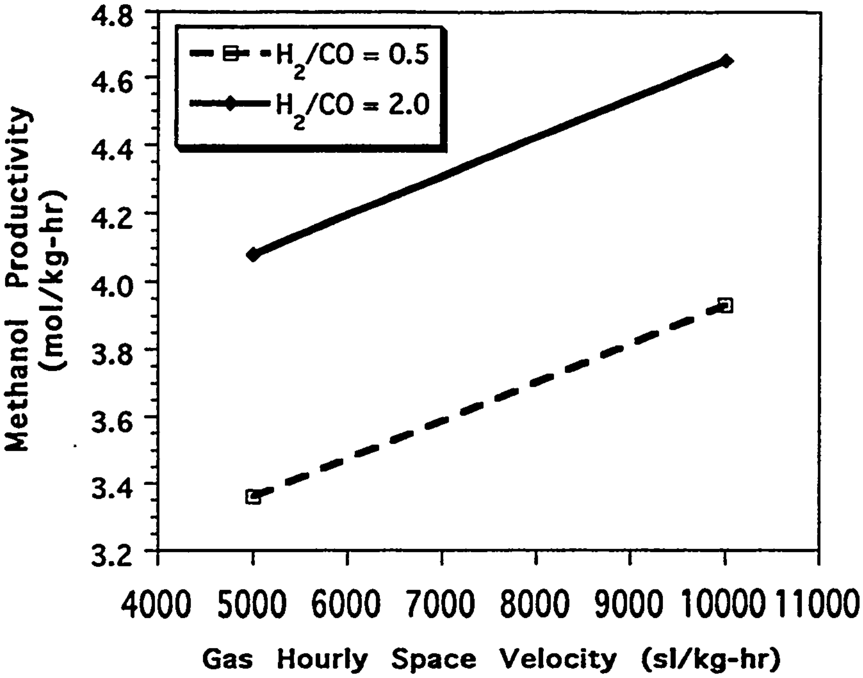

Figure 8

Catalyst Activity Versus Run Time (375°C, 5000 GHSV, H_2/CO = 1)