CONSTRUCTION AND DEMONSTRATION OF A REACTOR SYSTEM FOR TESTING METHANOL SYNTHESIS CATALYSTS

by

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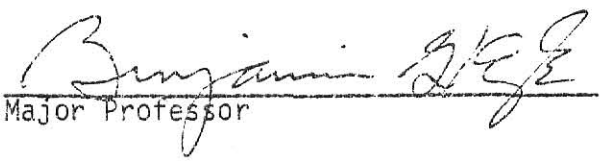

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INTRODUCTION

Methanol is an important chemical feedstock. About 3.7 million tons were produced in the United States in 1979 (41), almost half of which went for production of formaldehyde for manufacture of synthetic resins, plastics, and adhesives (39). Because it may be synthesized from a wide variety of material and energy sources, and is very clean burning, it may find increasing application in the future as motor vehicle and boiler fuel.

Methanol was originally obtained from destructive distillation of wood. This was inefficient, yielding only about 6 gal./ton for hardwoods (38). Synthesis by hydrogenation of carbon monoxide was proposed in 1905 by the French chemist Paul Sabatier, and first commercialized by the Badische Company in Leunawerke, Germany, in 1923. For this reaction to proceed to any appreciable extent, a catalyst must be provided to give it a kinetic advantage over the thermodynamically favored production of aliphatic hydrocarbons. For both the hydrogenation of carbon monoxide and of carbon dioxide to methanol, the extent of reaction increases with increasing pressure and decreasing temperature. Early zinc chromite catalysts, however, required reaction temperatures of up to 400°C to produce an appreciable rate. At this temperature, it was necessary to use pressures of as much as 350 atm (40). Within the last twenty years, catalyst containing copper as well as zinc and chromium (or aluminum) and offering much better activity have come into commercial application. Although their higher sensitivity to poisons requires careful removal of chlorides and sulfur from the synthesis gas, their greater activity

provides sufficient rates at lower temperatures; this, in turn, allows lower pressures. The low pressure process typically operates at 225-250°C and 50 atm. pressure, reducing the very expensive compression power requirement almost by half (40). Most methanol plants currently use this sort of low pressure process, with feedstock obtained by steam reforming of natural gas or naphtha (38).

This project comprises the first step of an investigation proposed by Dr. Mufit Akinc, intending to study the performance and surface properties of $CuO/ZnO/Cr_2O_3$ catalysts. This project seeks to construct and demonstrate a reactor system, along with gas analysis techniques, to provide essential information on catalyst activity and selectivity.

REVIEW OF LITERATURE

The first comprehensive review of methanol synthesis kinetics was published by George Natta in 1955 (1). In this paper he reports on his own work with various catalysts, in addition to surveying previous literature on the subject. He concludes that only catalysts containing ZnO or CuO have real practical value. Promotion effects were attributed to Cr_2O_3 and Al_2O_3, with the former receiving the most attention. Both metallic iron and nickel are active catalysts for the competing reaction to methane, which is thermodynamically favored over methanol. Copper-based catalysts were found to be susceptible to poisoning by chlorides and by sulfur-containing compounds. Several other, less common poisons are also discussed.

Natta and his coworkers performed kinetic tests in a tubular reactor, which was specially designed to maintain isothermal conditions throughout the mass of catalyst. Results of experiments with catalysts of different composition and method of preparation were reported. Experimental conditions ranged from 200 to 300 atm. pressure, and temperatures from 260 to 360°C. Inlet gas composition was 90.9% H_2, 9.1% CO, in all the reported experiments. Although no CO_2 was used in the process gas, Natta reported that small quantities of CO_2 have a favorable effect on the conversion to methanol at high space velocity.

Two kinetic models are developed for comparison with experimental rate data, both of which assume the rates of the necessary diffusion, adsorption, and desorption processes are much higher than the rate of reaction between adsorbed species. The treatment applied was based on the

method described by Hougen and Watson (2). The first model assumes the surface reaction proceeds by way of two bimolecular reactions in series. The resulting expression is shown to be inconsistent with experimental isothermal rate curves, so the hypothesis is rejected. The second model proposed is based on a trimolecular mechanism for the surface reaction. This analysis yields an overall rate expression involving four empirical constants, which are functions of temperature only. Predictions of exit gas composition were obtained by integrating this expression, and were found to agree closely with experimental results. Values of the empirical constants over a range of temperatures are presented graphically, for two catalysts of different composition.

Very few new ideas appeared in the literature during the twenty years following Natta's comprehensive work. A number of articles reported results of kinetic studies at various conditions of temperature, pressure, and space velocity (3-8). Some papers have proposed mechanisms to explain the observed rate behavior, with conflicting results. Several Russian authors have accepted the adsorption of hydrogen as the rate limiting step (7, 9, 10). Other authors advance different proposals of the rate determining step, including trimolecular surface reaction (1), desorption of methanol (4), and reaction between hydrogen gas and the adsorbed CH_3O methanol precursor (11). On the subject of diffusion resistance, the agreement is better. Several authors (6, 8, 23, 26) have studied the effect of diffusion resistance both within the pellet, and between pellets and bulk gas. All report that diffusion resistance is negligible for pellets 5x5 mm or smaller, and linear gas velocities as small as 0.06 cm/sec.

During the 1960's, a number of reports were published which dealt with formulation and characterization of methanol synthesis catalysts, almost exclusively those containing copper, zinc, and chromium. One U.S. patent was filed on behalf of Imperial Chemical Industries, Ltd., of London (12), and two were filed for Japan Gas Chemical Company, Inc., of Tokyo (13, 14). All three specified means of preparation of ternary catalysts containing these three metals. Several authors have reported on different phases of catalyst preparation, including precipitation, thermal decomposition, and partial reduction (15-20, 29). Goroshko and co-workers (28) used electron microscopy to study the effect of preparation method and pelleting pressure on the pore structure of zinc-chromium catalysts. Mutual promotion of adsorption of CO and H_2 has been studied on ZnO (30, 31) and a $Cu/ZnO/Cr_2O_3$ catalyst (32). Parks and Dreiling (33) conducted electron spectroscopic studies of the adsorption of methanol on ZnO. Koreneuskaya et al. (34) reported on determination of ZnO surface area in ZnO/Cr_2O_3 catalysts by volumetric measurements of CO_2 chemisorption. Smith and Quets (35) used infrared spectroscopy to study the adsorption of CO on copper.

In 1979, an analysis of the low pressure methanol synthesis catalysts Cu/ZnO, $Cu/ZnO/Cr_2O_3$, and $Cu/ZnO/Al_2O_3$ was presented by Herman et al. (21). In their study, catalysts were prepared by coprecipitation of basic salts of the metals from hot (85 to 90°C) nitrate solutions by addition of sodium carbonate until the solution pH was 6.8 to 7.0. After drying overnight at 60 to 110°C, the samples were calcined in air by heating at 100°C/hr to 350°, where they were held for 3 hr. These samples (typically 3 ml.) were reduced in 2% H_2 in N_2 (1 atm.) at 250°C at a flow rate of approximately 4 liters/hr for 4-20 hrs. Samples prepared for measurements

such as X-ray diffraction and surface area determination were tested before use, and maintained in a nitrogen atmosphere to prevent oxidation. In this study, X-ray diffraction analysis was used to determine the phase composition of the precipitated basic salts. X-ray diffraction, along with XPS/Auger and optical reflectance spectroscopics were employed to follow the changes occurring in each phase during calcination and reduction. Surface areas and pore size distributions were determined by analysis of adsorption-desorption isotherms for argon at -195°C.

Herman and coworkers used a flow reactor to test the catalysts characterized in this manner for activity and selectivity. The process gas contained 70% H_2, 24 % CO, and 6% CO_2, at 75 atm. pressure, in the temperature range from 200 to 300°C. All catalysts tested were more than 99% selective to methanol with respect to carbon conversion. Kinetic results from varied compositions of Cu/ZnO catalysts, and comparison of Cu/ZnO, Cu/ZnO/Cr_2O_3, and Cu/ZnO/Al_2O_3 formulations demonstrate that active and selective low pressure catalysts require presence of both copper and zinc oxide, and that the effects of the trivalent cation are secondary. This activity is evidently related to strong modification of ZnO valence-to-conduction band transitions by the presence of partially reduced CuO dissolved in the ZnO lattice. This interaction is evidenced by a new strong near-infrared-visible absorption spectrum (ca. 560 nm) of Cu/ZnO catalysts, which is unlike that of CuO, Cu_2O, Cu metal, or Cu(II) ions in ZnO. This spectrum is assigned to Cu(I) ions dissolved in ZnO. It was the most pronounced in the 30/70 Cu/ZnO catalyst, which was also the most active in methanol synthesis of all the binary formulations. Testing a 60/30/10 Cu/ZnO/Al_2O_3 catalyst in CO_2-free synthesis gas (H_2/CO = 76/24) revealed normal initial activity, but rapid and

irreversible deactivation of the catalyst was observed. Examination of the catalyst by optical spectroscopy revealed that the near-infrared-visible absorption disappeared during catalyst deactivation. This was taken to indicate that the role of CO_2 in the synthesis gas is to prevent complete reduction of Cu(I) in the ZnO lattice.

Although the catalytic activity is explained independently of any trivalent cation, a possible explanation for the observed promotion effects of Cr(III) and Al(III) is hypothesized. The extent of Cu(I) solubility is limited by the requirement of electroneutrality upon substitution of Cu(I) for some Zn(II). This substitution requires oxygen vacancies, interstitial cations, or simultaneous dissolution of trivalent cations. The role of Cr(III) or Al(III), then, is to enhance the formation of the catalytically active Cu(I)/ZnO solution.

The mechanism of the catalytic function of the Cu(I)/ZnO solution may be hypothesized, based on the known properties of zinc oxide and univalent copper. Zinc oxide is a good hydrogenation catalyst that activates hydrogen by heteropolar splitting, forming ZnH and OH groups on the ZnO surface. Cu(I), on the other hand, is shown to be a good candidate for chemisorption of CO. From this basis, Herman and coworkers proceed to detail a proposed mechanism, of which the rate limiting step is the hydrogenolysis of the $Cu-CH_2OH$ bond. Effects of poisons and oxidizing gases are also discussed.

In a later continuation of the foregoing study (22), the same workers reported on electron microscope studies of the crystal morphologies of Cu/ZnO and $Cu/ZnO/Cr_2O_3$ catalysts. Two distinct morphologies of zinc oxide were found: an interconnected network of thin crystallites at copper concentrations of 0-30%, and hexagonal platelets at higher copper

concentrations. Both were reported to be active and selective methanol synthesis catalysts. In accordance with their previous conclusion, the characteristic common to all active Cu/ZnO and Cu/ZnO/Cr_2O_3 catalysts is the high content of copper dissolved in ZnO.

Kagan and coworkers (23-25) investigated the mechanism of methanol synthesis from carbon dioxide and hydrogen over a copper-zinc-aluminum oxide catalyst. They dispute what they report to be the generally held view, that this reaction occurs by way of an intermediate of carbon monoxide formed by the reaction of CO_2 and H_2. When using synthesis gas containing only CO_2 and H_2, CO concentration increased with contact time to a peak before declining. This behavior is characteristic of an intermediate in series reactions. It was found, however, that the rate of methanol production was the highest at low contact times and that it declined continuously as CO_2 conversion increased. Using this and other kinetic arguments, the direct hydrogenation of CO_2 is inferred to be the only significant mechanism of methanol synthesis from CO_2 and H_2. The possibility of CO hydrogenation to methanol occurring is not ruled out, but is taken to be much slower and therefore insignificant in the system studied. Based on this indirect evidence, this team goes on to conclude that methanol synthesis from CO and H_2 proceeds by way of intermediate formation of CO_2, which is the species hydrogenated to methanol. The coproduced water undergoes the water-gas shift with CO to regenerate CO_2 and H_2. While other researchers have noted that CO_2 promotes methanol synthesis (1, 26, 27), none others suggest its direct involvement in the synthesis mechanism. This proposal is in apparent conflict with the previously mentioned observation reported by Herman et al. (21), that high rates were initially observed with feed gas containing only CO and H_2.

The role of CO_2 suggested by some researchers (1, 7, 21, 26) is to prevent complete oxidation of CuO, which is supposed to be important to catalytic activity.

DESCRIPTION OF PROJECT

This project is the first step in a plan to extensively research the properties and behavior of methanol synthesis catalysts, by Dr. Mufit Akinc of this department. The stated aim of Akinc's proposal (36) was to prepare and characterize a series of catalysts, and to compare the surface properties of each to its performance. This was to include studying the effects of preparation techniques on the ultimate properties of the catalyst, and searching for correlation between measurable surface properties and catalytic activity and selectivity.

A set of catalysts of identical composition was to be prepared by varying conditions such as starting materials, precipitating agents, calcination procedure, and reduction procedure. Preparation would be followed by the various characterization techniques such as X-ray diffraction, electron microscopy, surface area determination, and gravimetric adsorption measurements. A list of various techniques, and the information obtainable from each is provided in Table 1.

The scope of this project includes construction of a reactor system, development of necessary chemical analysis techniques for kinetic tests, and demonstration of each. Most of the testing for this project involved a commercially available catalyst, but a catalyst prepared by the experimenter was also tested for comparison.

Table 1: Catalyst Characterization Techniques

Technique	Information Obtainable
X-ray diffraction	Crystal structure, crystal size, lattice parameters, chemical composition
Reactor testing	Catalytic activity and selectivity
Thermal analysis (TGA and DTA)	Temperature dependence of chemical changes during calcination and reduction
Gravimetric adsorption measurements	Thermodynamics of gas-catalyst interaction, including measurement of active surface by H_2 and CO chemisorption
Electron microscopy	Surface topology, particle size, pore structure
Flow type BET measurements	Total surface area
Infrared spectroscopy	Nature of surface sites and intermediates

EXPERIMENTAL

The catalyst used for most of this study was supplied by United Catalyst, Inc., and identified as "C79 Methanol Synthesis Catalyst." This material is composed of CuO, ZnO, and Al_2O_3, and was supplied as tablets, 3/16 in. diameter by 3/16 in. long. Information on physical and chemical properties, as provided by the manufacturer, is listed in Table 2. The operating instructions for this catalyst include the recommended reduction procedure, along with a statement to the effect that the method and conditions of reduction are essential to the ultimate performance of the catalyst, and must be carefully controlled. The details of the laboratory scale reduction procedure are given in Table 3. The recommended reaction conditions are: 425-550°F (218-288°C), preferably as low as possible, and 500-2000 psig. Additionally, the operating instructions indicate the synthesis gas should contain a $CO:CO_2$ ratio less than 4:1.

In order to test the effect of reduction conditions on catalyst performance, several different preparatory procedures were applied to this catalyst, and the results compared. Reduction by synthesis gas (H_2:CO = 2:1) at synthesis conditions (300°C, 600 psig) produced a catalyst with no activity for methanol. Similarly, reduction with pure hydrogen at high pressure (600 psig) failed to produce any observable activity. Consequently, later tests were all planned to expose the catalyst to less vigorous reducing conditions for longer periods of time, and with more careful temperature control. The reduction reaction is very exothermic, and can generate enough heat in a large bed to cause thermal degradation

Table 2: Typical Chemical and Physical Properties for C79 Methanol Synthesis Catalyst
Source: United Catalyst, Inc.

I. Catalyst Type, Form and Size	
Catalyst Type	C79-4-01
Form	Tablets
Size: Diameter	3/16"
Length	3/16"
II. Chemical Composition	**Weight Percent**
A. Dry Basis	
CuO*	62-70
ZnO*	20-24
Al_2O_3*	10-12
Na*	<0.05
S*	<0.04
Cl*	<0.01
Fe*	<400 ppmw
Ni*	<100 ppmw
B. As Received	
C	2.0-3.0
CO_2	3.0-5.0
Loss on Ignition	8.0-14.0
III. Physical Properties	
A. Bulk Density, lbs./cu.ft.	78±5.0
B. Surface Area, m^2/g	75-125
C. Pore Volume, cc/g>29.2A	0.25-0.45
D. Attrition, wt.% Loss	
E. Crush Strength, lbs. (min. avg.)	15
F. Particle Size: Length, in.	.187
Diameter, in.	.187

* Properties normally measured by Quality Control on all shipments or lots.

Table 3: C79 Laboratory Reduction Procedure
(For Small Catalyst Volumes)
Laboratory Scale 100 cc's

I. Load 20 cc of catalyst

II. Purge with N_2

III. Switch to 2% H_2 in N_2--50 psig and approximately 3-4,000 v/v/hr.

IV. Heat from room temperature to 250°F (121°C)

- A. Hold at 250°F (121°C) 1 hour
- B. Hold at 350°F (177°C) 1 hour
- C. Hold at 400°F (204°C) 16 hours (4 hr. minimum)
- D. Hold at 450°F (232°C) 2 hours

V. Cool to 350°F (177°C)

VI. Switch to process gas

- A. Raise to 200 psig. hold 15 minutes
- B. Raise to 400 psig. hold 15 minutes
- C. Raise to 750 psig. hold 15 minutes

VII. Raise to operating temperature of 450° (232°C)

VIII. Raise space velocity to 13,000

(such as sintering) if sufficient means of heat transfer are not provided (27).

It was also desired to demonstrate an active catalyst prepared in the laboratory similar to those reported in the literature. A solution of nitrate salts (Cu:Zn:Cr = 46:36:19) was prepared, and heated to 50°C. Ammonium hydroxide was added to the stirred solution until the pH rose to 8.0. The total volume of solution and precipitate was 1.5 liters. The precipitate was vacuum filtered, and washed with dilute NH_4OH. This was a time consuming operation, because the precipitate formed a heavy, cohesive cake on the filter, causing slow passage. This precipitate was dried at 105°C overnight, and crushed to a fine powder. This material was tabletted by compressing a slurry at 4900 atm. pressure for 5 min. No binder material was added. The resulting pellets were 3/16 in. diameter, 3/16 to 5/16 in. long, and a density of about 2.1 g/cm^2 (after drying at 105°C). These pellets were calcined by heating at the rate of about 150°C/hr., to 650°; this temperature was held for 8 hrs. Gradual heating was necessary, because decomposition of the catalyst precursor in a 650°C oven was rapid enough to cause splattering of loose powder samples, and to crack preformed pellets. During calcination, the material was observed to change color from medium green to flat gray. About 15% reduction in size was also noted.

The reactor employed in this study was a 1 liter vessel manufactured by Autoclave Engineers, Inc., of Erie, Pennsylvania. A schematic diagram of the system is shown in Figure 1. The maximum working pressure of the vessel at 350°C was 3900 psi. The reactor's contents were stirred by a packless drive turbine. All parts of the reactor in contact with the working gas were constructed of 316 stainless steel. Pressure relief was

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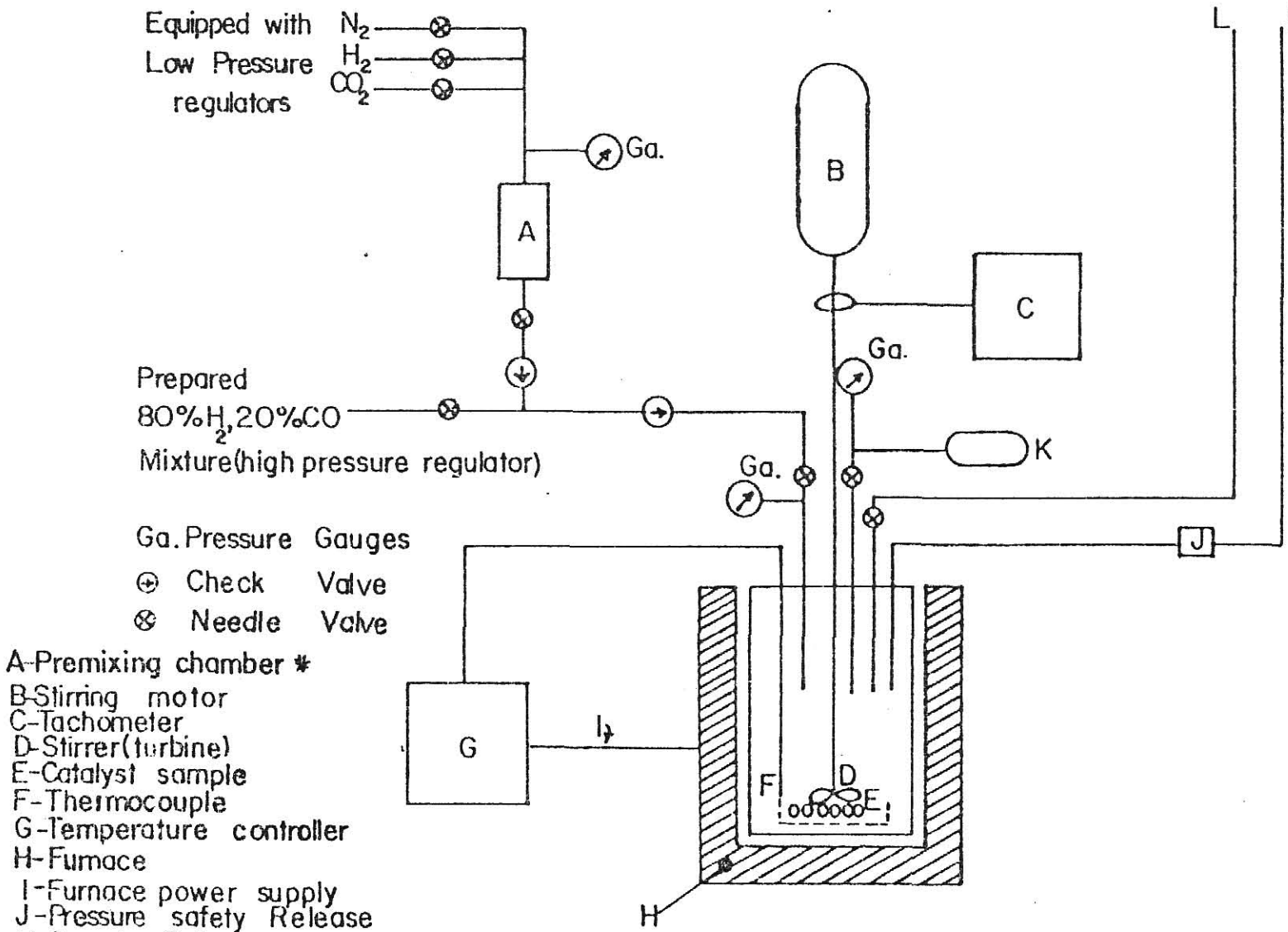


Figure 1: Reactor System for Methanol Synthesis

provided by a rupture disk calibrated for 1000 psi at 250°C. Handling of high pressure gases was entirely with 1/4 in. O.D. stainless steel hydraulic tubing (4200 psi rating), "Swagelok" tube fittings, and standard (NPT) stainless steel pipe fittings and valves. No means of compression or accurate blending of gas mixtures were available, so all high pressure gases were delivered from cylinders of prepared mixtures. Low pressure gases were handled in 1/8 in. O.C. copper tubing, all of which was protected from the high pressure parts of the system by a stainless steel check valve. A personnel shield made of transparent Lexan was placed around the reactor system during all high pressure (>50 psig) work.

The catalyst pellets to be tested were placed in an open-top stainless steel mesh basket, placed directly below the turbine. An iron-constantan thermocouple was contained in a sealed thermowell near the basket. The voltage signal from the thermocouple was connected to a time proportioning type temperature controller, which supplies power to the furnace surrounding the vessel. Continuous cooling was provided by a flow of compressed air (from building supply) through an internal cooling coil.

Samples of the reactor contents were analyzed with a Varian-Aerograph Series 200 gas chromatograph, with a thermal conductivity detector. An Aerograph model 600-D gas chromatograph with a flame ionization detector was tested and found unsuitable, due to lack of sensitivity for all non-flammable components and very low sensitivity to carbon monoxide. The complete analysis required two columns. A column packed with Molecular Sieve 5A material separated hydrogen, nitrogen, oxygen, methane, and carbon monoxide. Components such as carbon dioxide, water, and methanol were permanently adsorbed in the column; when previously analyzed samples were spiked with one of these materials, no change in the integrator output was

observed. A column packed with Poropak Q material separated carbon dioxide, methane, ethane, propane, water, and methanol, but hydrogen. nitrogen, oxygen, and carbon monoxide eluted as a single peak. Each sample taken, then, was analyzed with both columns. Combination of the results provided complete composition data.

Peak areas were calculated from the chromatograph output using an Autolab System I Computing Integrator for Chromatography, made by Spectra-Physics. The area of each peak was multiplied by a correction factor, referred to as KF, for the component it represented. The resulting corrected area of each peak was normalized by dividing by the total of all the corrected areas to find component concentration. Calibration for methanol and water was performed by injecting a carefully measured volume of liquid into a sample bulb of known volume containing a mixture of 20% CO and 80% H_2. The liquid was allowed to evaporate, and samples taken for injection into the instrument. The KF factor for methanol was observed to vary with concentration, as indicated in Figure 2. The averages are plotted in this figure, and individual observations reported in Appendix II. Calibration for all other components was by injection of available known mixtures, and is reported in Table 4. The thermal conductivity detector was decreasingly sensitive to hydrogen with increasing partial volume. Consistent results were obtainable when the partial volume of hydrogen was less than 0.1 ml. Accordingly, injections into the Molecular Sieve column were always 0.1 ml. in volume. Since hydrogen accounted for only about 5% of the multicomponent "Noncondensibles" (H_2, D_2, N_2, and CO) peak area on the Poropak column, the partial volume was not as critical. Based on confidence limits for calibration data calculated at the .05 level, the accuracy

Figure 2 : Calibration of Gas Chromatograph for Methanol

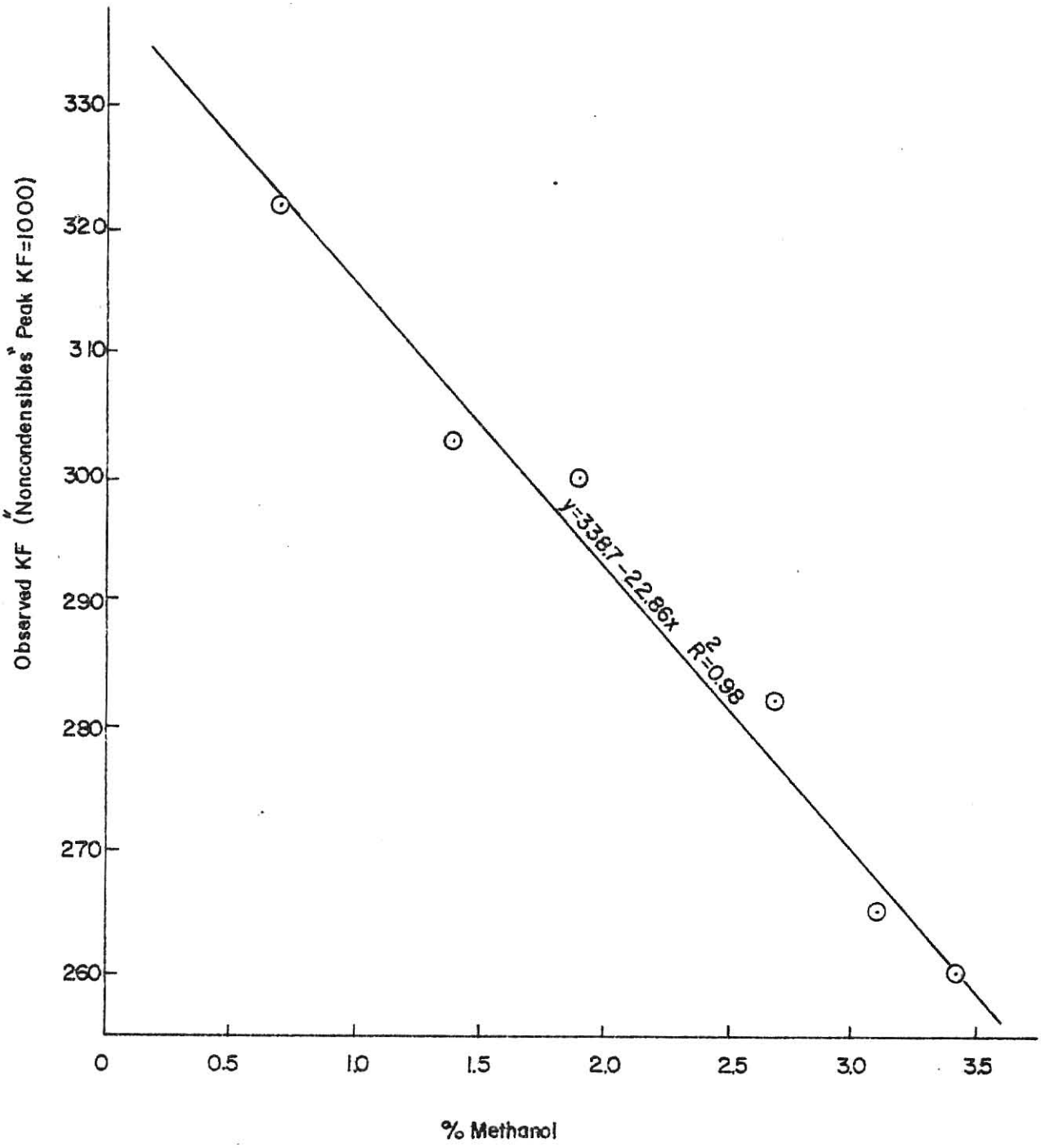


Table 4: Chromatograph Calibration

Poropak Column			Molecular Sieve Column		
Component	KF	Typical Retention Time	Component	KF	Typical Retention Time
Noncondensibles	1000	20 sec.	Hydrogen	57500	18 sec.
Methane	375	24	Oxygen	1087	24
Carbon Dioxide	172	30	Nitrogen	995	30
Ethane	235	42	Carbon Monoxide	1000	50
Propane	220	85			
Water	250	100			
Methanol	see Fig. 2	135			

Integrator Parameters			
Set	1	2	3
Peak Width	2 sec.	5 sec.	12 sec.
Slope Sensitivity	15	25	50
Initializing Time (T1)	0 sec.	30 sec.	80 sec.

of the analysis procedure was ±10% of the calculated concentrations. Calculations were performed by way of a FORTRAN program.

For each trial, a quantity of catalyst was weighed (typically 10 g.) and placed in the catalyst basket. Assembly of the reactor followed the manufacturer's instructions. After the cover screws were tightened to the specified torque, the vent connections completed, and the drive belt installed, the reactor contents were flushed with nitrogen. Reduction of the catalyst followed.

At first, the importance of the reduction procedure was not known. Similarly, nothing was known about the expected kinetics. Therefore, quantity and preparation were both subject to experiment.

Sample 1 (0.80 g. of C79 catalyst) was reduced with process gas (H_2:CO = 2:1) at 600 psig, 300°C. Sample 2 (0.89 g. of C79 catalyst) was reduced with hydrogen gas at 150°C and 600 psig pressure, for 16 hrs. Subsequent to these two attempts, a recommendation was received from Messrs. Okamoto and Hancock (27) to reduce the catalyst under more moderate conditions, especially with regards to control of temperature. It was later yet that the recommendations of UCI were received (37). As a result of this information, four reduction procedures were planned. Each involved slow reduction by hydrogen with careful control of temperature. It was desired to compare the effect of gas composition (specifically, 100% H_2 at atmospheric pressure vs. 2% H_2 in N_2 at 50 psig), as well as comparing flow reduction processes with static ones (both with mixing).

The activation procedure for Sample 3 consisted of a nonflow process intended to approximate the conditions of the UCI procedure (see Table 3). The sample was 7.87 g. of C79 catalyst. Mixing of the reduction gas was performed by filling a length of pipe of known volume with hydrogen to

a predetermined pressure. This quantity of gas, which was sufficient to produce a hydrogen concentration of 2% in the reactor vessel, was delivered by flushing with nitrogen to 50 psig. The specified time and temperature steps were followed, with replacement gas being introduced every half hour during the one and two hour periods, and four times during the sixteen hour period. Sample 4 was treated with 100% hydrogen at atmospheric pressure in a static process. The pressure was maintained at atmospheric throughout. The temperature was held at 150°C for 120 hrs., with replacement gas flushed through the vessel every 24 hrs. This was concluded by 24 hrs. at 250°C. Sample 5 was reduced with flowing hydrogen at atmospheric pressure, at a flow rate of 4 liters/hr. Sample size was 10.01 g. (C79 catalyst), which produced a bed volume of about 8 cc. The time and temperature levels used were those specified by UCI. Sample 6 (9.97 g. of C79) was prepared with 2% H_2, 98% N_2 gas mixture supplied by Matheson. Flow rate was 2 liters/hr., and pressure 50 psig. The temperature was maintained at 150°C for 100 hrs., 200°C for 24 hrs., then 225°C for 24 hrs.

The last experimental run made tested the catalyst formulated in the laboratory, as described previously. This sample, designated Sample 7, consisted of 12.8 g. reduced under UCI conditions. Three trials were made: two at 250°C, and one at 300°C. A summary of all sample sizes and reduction procedures is provided in Table 5.

After the specified reduction procedure for each sample preparation was continued by stepwise introduction of process gas. First, the reactor and contents were cooled to 177°C, and process gas (79.4% H_2, 20.6% CO) introduced to raise the reactor pressure to 200 psig. After a 15 min. holding period, the pressure was increased to 400 psig for another 15 minute period. The pressure was then raised to 600 psig, and after a

Table 5: Sample Preparation

Sample	Date of First Test	Mass g.	Temperature °C	Time hr.	Pressure psia.	Gas Composition H_2 %	N_2 %	CO %	Flow Rate liter/hr.
1	11/26/79	0.80	300	1	615	67	0	33	None
2	12/28/79	0.890	150	16	615	100	0	0	None
3	2/7/80	7.87	121 177 204 232	1 1 16 2	65 same ↓	2 same ↓	98	0	None
4	1/29/80	7.61	150 250	120 24	14.7	100	0	0	None
5	2/29/80	10.01	121 177 204 232	1 1 16 2	14.7	100	0	0	4
6	3/19/80	9.97	150 200 225	100 24 24	65	2	98	0	2
7	3/24/80	12.82	121 177 204 232	1 1 16 2	65	2	98	0	4

Note: The catalyst used for samples 1-6 was United Catalyst Inc. C79 Methanol Synthesis catalyst. Sample 7 consisted of 46/36/19 $CuO/ZnO/Cr_2O_3$ catalyst prepared in the laboratory.

third 15 minute period the temperature was raised from 177°C to the operating temperature of 250°C. This concluded the catalyst preparation procedure.

For the purpose of testing the kinetics of the catalysts, it was desired to have a small concentration of CO_2 (less than 5%) present with the reactants. The process gas mixture available did not contain CO_2, however, so gas for experimental runs was mixed in the reactor. First, the reactor contents were vented to atmospheric pressure, and flushed with CO_2. The outlet valves were closed to trap CO_2 at 18.5 psig, and the prepared mixture (H_2:CO = 5.1) rapidly (<5 sec.) charged to a pressure of 600 psig. This yielded operating process gas with a composition of 77.0% H_2, 20.0% CO, and 3.0% CO_2. No preheating was required, as the temperature of the incoming gas quickly reached thermal equilibrium with the reactor vessel. Mixer speed was constant at 1500 rpm.

A timer was started when the reactor pressure reached 600 psig. Samples were drawn periodically into evacuated glass sample bulbs equipped with a septum for sampling. Makeup gas was supplied as necessary to maintain constant pressure. Six or eight samples were taken from each run and analyzed promptly, as experience from the calibration procedure indicated a significant decrease in hydrogen concentration was observable after 8 hrs. of sample storage. Between different runs with the same catalyst sample, reactor temperature and reducing atmosphere were maintained to avoid any changes in the catalyst surface.

RESULTS AND DISCUSSION

Sample 1, reduced with process gas at 600 psig and 300°C, was tested at 300°C with synthesis gas of composition 67% H_2, 33% CO. The results of this and all other trials are tabulated in Appendix 1. As previously noted, no methanol was observed at any time from this sample. This could not be due to the absence of carbon dioxide, however. Although no CO_2 was introduced with the process gas, a quantity (0.63 to 2.05%) was observed in each sample. This may have been due to disproportionation of CO to CO_2 and solid carbon, or due to further reduction of the catalyst. Sampling at t = 100 min. (contact time = 80 g. min./liter) indicated that 13.7% of the CO had been converted, with the principal product being methane. Mass balances calculated from the gas analysis indicated no significant decrease in the atomic fraction of carbon in the gas phase, but carbon was observed to have been deposited on the interior surfaces of the reactor. At equilibrium, a small amount of carbon would be deposited under these process conditions (37). The observed deposition may have occurred during cooling, however, as the reactor remained pressurized during the cooling cycle. At equilibrium, the amount of carbon deposited would increase with decreasing temperature. On the basis of this observation of carbon, it was decided to increase the H_2:CO ratio from 2:1 to 4:1.

Sample 2, reduced with H_2 at 600 psig and 150°C, was tested at 250°C with synthesis gas of composition 79% H_2 and 21% CO. No methanol was produced, but as before, CO_2 was observed in each sample. Carbon monoxide conversion was 18.1%, with the principal product being CO_2. No methane

was detected, but traces (less than 1%) of ethane, propane, and water were present. On the basis of these two trials, it was concluded that rapid, severe reduction could not produce active catalyst.

Sample 3, as detailed previously, was reduced by static treatment with dilute hydrogen. This would be an effective treatment only if the hydrogen concentration was not substantially depleted during the long (16 hr.) exposure at 204°C. This appears, however, to have happened. According to the approximate analysis of this catalyst supplied by the manufacturer, the weight percent of copper (II) oxide is 62-70. In the 7.87 g. quantity taken for sample 3 this constitutes 0.062-0.069 moles. At 204°C, 50 psig, 2% hydrogen constitutes only 0.0022 moles of reducing agent in each charging. For complete reduction of the copper oxide, at least 30 fillings of the vessel would have to be completely depleted of hydrogen. This number is greater than the number of times the reactor was refilled. During pretreatment, then, the catalyst was only partially reduced. Introduction of high pressure process gas completed the reduction very rapidly, which in part defeated the original purpose of attaining a slower reduction rate. Results of testing this sample show that after 2 hrs. of reaction, the carbon monoxide was completely converted. Methanol accounted for only 9.9% of the carbon monoxide conversion; carbon dioxide accounts for 33.7%, methane 33.9%, and ethane and propane together 22.5%. This sample was aged 11 days at room temperature under a reducing atmosphere (80% H_2, 20% CO at 1 atm. pressure) and retested. Both activity and selectivity to methanol were diminished approximately 50%.

Sample 4, treated with static hydrogen at atmospheric pressure, did not suffer this same limitation. Two reactor volumes would have been required to effect complete reduction, with six being supplied. Testing

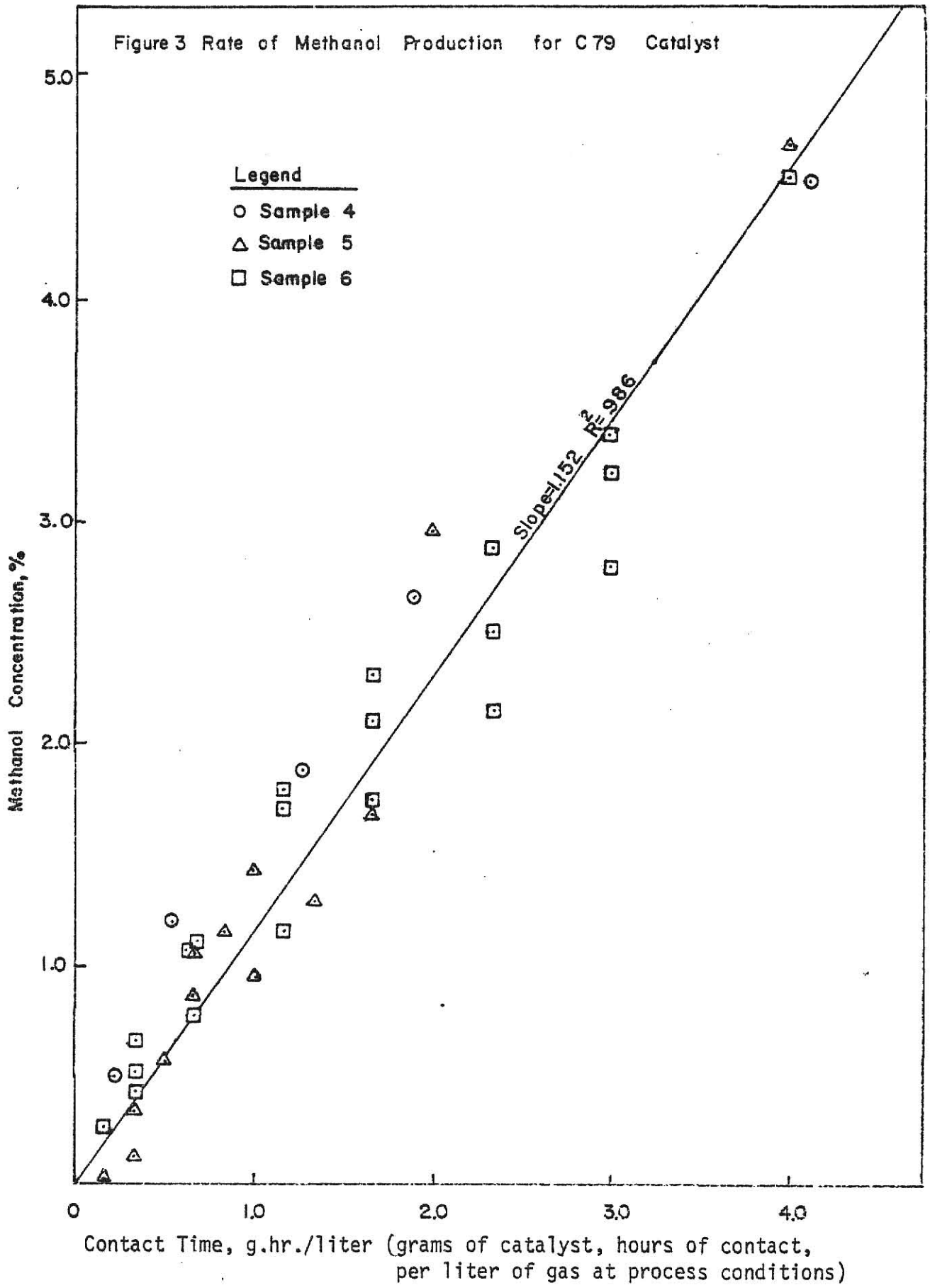
of this catalyst revealed much better activity, and very good selectivity at short contact times. After 15 min. of reaction the total carbon conversion (CO and CO_2 combined) was 12.8%, of which conversion to methanol was 79.8%. Other products were ethane and propane. No methane was observed until the fifth sample, which was taken after 32 1/2 min.

Three trials were run using sample 5, which was treated with flowing hydrogen at atmospheric pressure. The results of the first trial was very different from the second and third. The rate of methanol production in the first trial was approximately 1/6 that of the two subsequent trials. The selectivity of the first was very poor--methanol accounted for only 11% of the total carbon conversion. The average selectivity calculated from each sample taken during the second and third trials was 97%. No experimental observation was made which would indicate the reason for this disparity. It is possible that the reduction of the catalyst was not completed during pretreatment, changing its behavior for the first trial. The atomic fraction of oxygen did rise during this trial, but not to an extent significantly different from random variability.

As with sample 5, three trials were run using sample 6. This sample was prepared by reduction with flowing gas of composition 2% H_2, 98% N_2, at 50 psig. All three trials provide comparable results, with the observed activity very similar to that of sample 4, and the last two trials of sample 5. The combined results of these six trials are reported in Figure 3. The average selectivity of all the analyses taken from sample 6 was 77%.

Sample 7 consisted of catalyst formulated in the laboratory, as described previously, and reduced in accordance with the procedure recommended by UCI. Selectivity to methanol was very low--in every analysis less than 5%. The major product was methane. The rate of production of

Figure 3 Rate of Methanol Production for C 79 Catalyst



methanol is reported in Figure 4. Table 6 summarizes the results for each sample.

Figure 4: Rate Of Methanol Formation for 46:36:19 (Cu:Zn:Cr) Oxide Catalyst

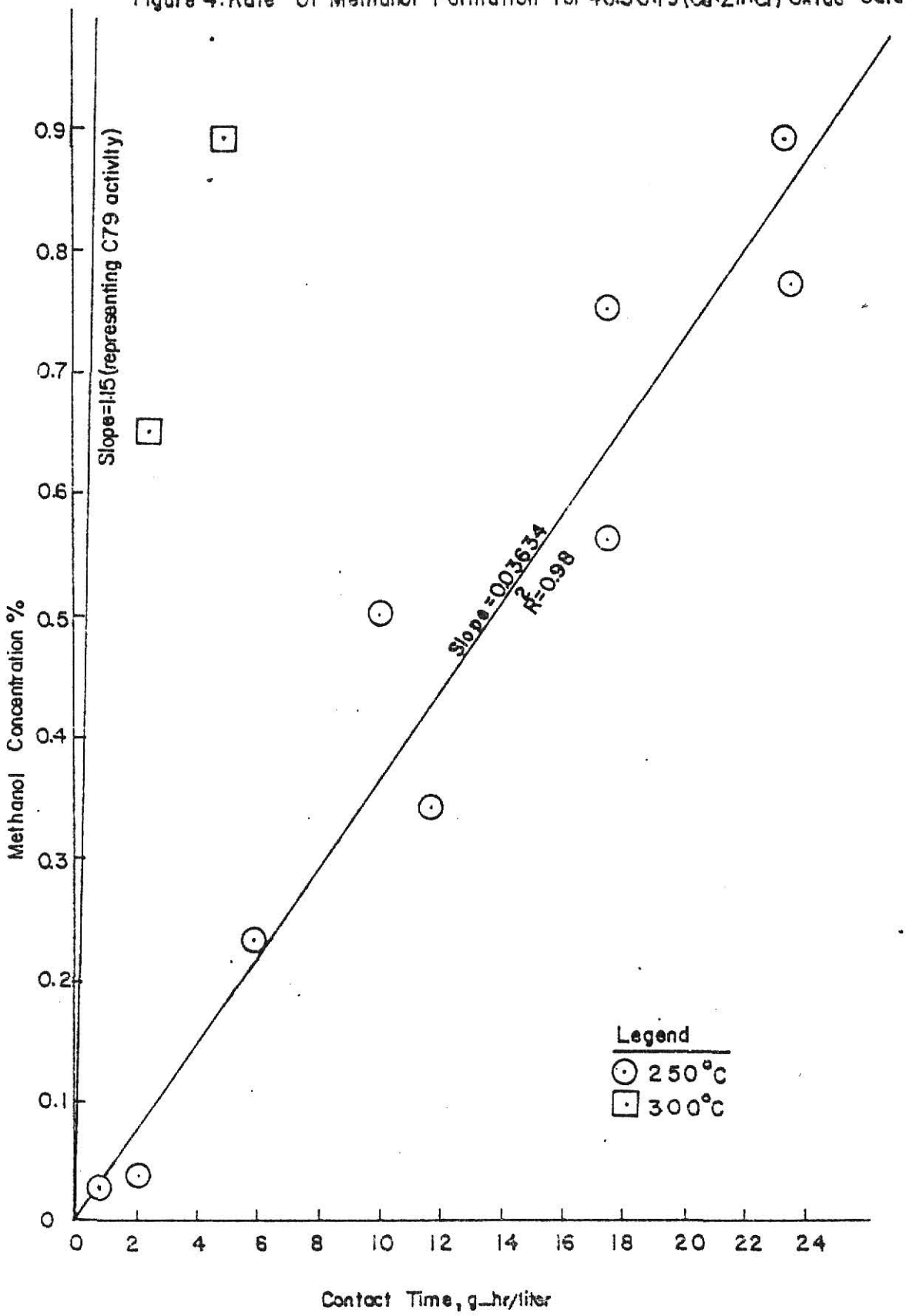


Table 6: Summary of Results

Sample	Observations
1	No activity for methanol. Major product was CH_4, with some CO_2 present also.
2	No activity for methanol. CO_2, C_2H_6, and C_3H_8 observed.
3	Reduction procedure insufficient. Selectivity to methanol 9.9%, to CO_2 33.7%, to CH_4 33.9%. After 11 days storage at reduced temperature and pressure, 50% reduction in activity and selectivity was observed.
4	After 15 minutes, carbon conversion was 12.8%, with selectivity to methanol 79.8%. Other products were ethane and propane.
5	First trial inconsistent with second and third trials. Average selectivity for trials #2 and 3 was 97%. (Only results of last two trials are reported in Figure 3.)
6	Activity comparable to samples 4 and 5 (see Figure 3). Average selectivity for three trials 77%.
7	Very low selectivity to methanol (<5%), major product was methane. Activity was about 1/25 that observed for C79 catalyst.

CONCLUSIONS

The fundamental purpose of this project was to construct and demonstrate a system for testing the activity and selectivity of low pressure methanol synthesis catalysts. The previously described system has been tested, and shown to provide reproducible results in comparing different catalyst preparations. No standard or accepted value was available for comparison for this catalyst from an outside source.

It was also desired to investigate the effect of reduction conditions on catalytic activity. It was found that rapid reduction under process conditions and comparably strong reducing conditions does not produce active catalyst. In order to produce active catalyst, the reduction conditions must be moderate, at temperatures typically from 150-200°C, and hydrogen partial pressures from 1.3-15 psia. Reduction must be completed under these conditions before the catalyst is exposed to higher temperatures and hydrogen partial pressures associated with process conditions.

It was also found that storage of active catalyst at reduced temperature and pressure can cause changes in the catalyst which have large detrimental effects on its activity. This would indicate that future studies involving various characterization techniques should involve careful handling of activated catalyst. In some cases, in situ reduction may be possible, albeit time consuming, in order to ensure that the surface under examination has all the characteristics of surfaces known to possess catalytic activity. It is unknown what changes might occur during transfer if a sample is reduced in one apparatus, then transported and tested

under different conditions of temperature, pressure, and atmosphere.

Finally, catalyst precipitated and calcined in the laboratory has been shown slight activity for methanol synthesis. The selectivity of this formulation is very poor, however, and its activity more than an order of magnitude ($X \frac{1}{25}$) less than the commercial catalyst tested. The experimenter's opinion is that better performance is attainable with further research.

The objective of future work should be to examine the effect of: catalyst composition, precipitating conditions, and precipitating agent on ultimate activity. Also, thermogravimetric analysis in a neutral atmosphere can supply information on temperature dependence of changes occurring during calcination; in a reducing atmosphere, similar information on catalyst reduction. The present investigation made no attempt to elucidate the role of carbon dioxide in the synthesis gas, which may also be of interest to future studies.

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Appendix I: Table of Results

Appendix 1: Table of Results

Sample	Contact Time g.hr./liter	Methanol %	Hydrogen %	Carbon Monoxide %	Carbon Dioxide %	Water %	Methane %	Ethane %	Propane %
1	0.0133	0.00	66.85	32.17	0.62	0.00	0.00	0.12	0.24
	0.133	0.00	64.98	33.30	0.84	0.00	0.00	0.41	0.47
	0.407	0.00	62.13	32.15	1.01	0.00	3.40	0.57	0.74
	0.733	0.00	60.56	31.99	1.36	0.00	4.39	0.75	0.94
	1.33	0.00	61.80	28.77	2.04	0.00	5.29	0.96	1.13
2	0.0370	0.00	72.98	18.64	0.18	1.17	0.00	0.03	0.00
	0.0750	0.00	80.34	18.22	0.36	0.93	0.00	0.15	0.00
	0.148	0.00	80.26	18.13	0.49	0.53	0.00	0.28	0.31
	0.297	0.00	80.11	17.60	0.89	0.79	0.00	0.48	0.13
	0.667	0.00	79.40	16.39	2.31	0.51	0.00	0.97	0.41
3	0.262	0.59	75.97	20.41	2.47	0.03	0.00	0.12	0.41
	0.657	0.00	76.38	19.21	2.50	1.85	0.00	0.06	0.00
	1.38	0.00	78.43	17.82	2.90	0.65	0.00	0.13	0.07
	2.23	1.90	76.94	16.95	3.27	0.62	0.00	0.20	0.11
	3.94	3.44	74.56	12.29	5.55	0.47	2.93	0.94	0.32
	7.87	5.59	66.83	7.63	10.37	0.98	6.69	1.12	0.74
	11.81	3.65	61.86	6.52	13.47	1.51	10.15	1.79	1.04
	15.74	4.61	54.50	0.50	18.77	1.81	15.87	2.81	1.63
3	0.230	0.00	76.59	19.51	3.68	0.10	0.00	0.12	0.00
	0.722	0.00	75.68	19.03	4.37	0.52	0.00	0.30	0.09
	1.31	0.00	75.69	16.66	6.25	0.63	0.00	0.55	0.22
	1.97	0.43	76.08	15.61	6.49	0.52	0.00	0.61	0.26
	3.94	0.97	75.62	13.72	7.96	0.62	0.00	0.75	0.35
	8.00	3.44	62.85	9.06	12.79	0.94	8.69	1.50	0.72

Appendix 1 (cont'd)

Sample	Contact Time g.hr./liter	Methanol %	Hydrogen %	Carbon Monoxide %	Carbon Dioxide %	Water %	Methane %	Ethane %	Propane %
4	0.222	0.49	76.53	20.32	2.51	0.15	0.00	0.00	0.00
	0.633	1.20	76.73	19.44	2.51	0.00	0.00	0.09	0.03
	1.27	1.87	77.53	17.22	3.13	0.05	0.00	0.11	0.09
	1.90	2.65	76.77	16.37	3.69	0.24	0.00	0.17	0.11
	4.12	4.53	74.49	13.19	5.06	0.20	2.08	0.30	0.15
	6.98	8.06	67.98	11.87	7.14	0.52	3.53	0.54	0.35
	12.05	11.29	64.77	6.87	9.35	0.73	5.67	0.89	0.48
	15.22	5.62	65.27	5.87	12.28	0.60	8.37	1.25	0.77
5	0.333	0.57	76.03	16.64	4.21	0.49	1.69	0.21	0.17
	0.833	0.63	75.26	13.07	5.70	0.49	4.01	0.49	0.35
	1.67	1.25	70.76	11.27	8.36	0.69	6.34	0.80	0.53
	2.50	1.42	73.07	9.66	6.32	0.62	7.49	0.80	0.62
	3.34	1.59	69.46	8.78	10.00	0.48	8.14	0.96	0.59
	5.01	2.19	63.57	6.54	11.91	0.71	13.07	1.22	0.79
	7.51	2.14	61.30	6.08	14.26	0.95	12.58	1.70	1.00
	11.18	2.58	55.97	5.17	16.96	0.00	16.18	1.83	1.30
5	0.167	0.00	78.03	19.53	2.35	0.09	0.00	0.00	0.00
	0.333	0.12	78.37	19.17	2.11	0.23	0.00	0.00	0.00
	0.500	0.56	78.49	17.85	2.87	0.22	0.00	0.00	0.00
	0.667	1.06	78.59	17.87	2.25	0.25	0.00	0.01	0.00
	0.833	1.14	78.23	17.99	2.36	0.28	0.00	0.00	0.00
	1.00	1.42	82.91	12.59	2.71	0.33	0.00	0.03	0.00
5	0.333	0.33	79.06	18.41	2.10	0.10	0.00	0.00	0.00
	0.667	0.85	79.07	17.95	1.97	0.15	0.00	0.02	0.00
	1.00	0.94	78.96	17.91	2.10	0.00	0.00	0.04	0.06
	1.33	1.28	78.96	17.36	2.29	0.04	0.00	0.06	0.02
	1.67	1.67	78.62	16.66	2.76	0.06	0.00	0.04	0.00
	2.00	2.96	77.93	15.96	2.73	0.27	0.00	0.10	0.04

Appendix 1 (cont'd)

Sample	Contact Time g.hr./liter	Methanol %	Hydrogen %	Carbon Monoxide %	Carbon Dioxide %	Water %	Methane %	Ethane %	Propane %
6	0.332	0.51	77.67	18.40	3.17	0.22	0.00	0.02	0.00
	0.665	1.08	78.62	17.23	2.61	0.36	0.00	0.07	0.00
	1.16	1.65	78.45	15.92	3.33	0.35	0.00	0.16	0.13
	1.66	2.10	78.99	14.60	3.58	0.34	0.00	0.21	0.17
	2.33	2.88	83.40	6.72	5.38	0.41	0.56	0.34	0.30
	2.99	3.39	76.13	11.11	6.01	0.50	2.04	0.45	0.36
6	0.167	0.26	77.55	19.13	2.74	0.32	0.00	0.00	0.00
	0.332	0.41	78.46	18.66	2.15	0.28	0.00	0.04	0.00
	0.665	0.76	78.58	17.88	2.39	0.27	0.00	0.10	0.02
	1.16	1.14	79.08	16.27	2.93	0.28	0.00	0.18	0.11
	1.66	1.74	78.67	15.47	3.41	0.34	0.00	0.22	0.15
	2.33	2.14	77.73	14.87	4.45	0.30	0.00	0.31	0.20
	2.99	2.79	78.62	12.96	4.72	0.33	0.00	0.33	0.24
	3.99	4.70	76.59	11.46	5.47	0.36	0.74	0.4	0.28
6	0.167	0.25	77.76	19.22	2.55	0.20	0.00	0.00	0.01
	0.332	0.65	78.52	18.65	1.97	0.22	0.00	0.00	0.00
	0.665	1.07	78.73	17.84	2.05	0.29	0.00	0.04	0.00
	1.16	1.78	78.64	16.36	2.85	0.27	0.00	0.08	0.00
	1.66	2.30	78.46	15.18	3.50	0.24	0.00	0.18	0.13
	2.33	2.50	79.08	13.92	3.85	0.28	0.00	0.21	0.16
	2.99	3.22	78.57	13.21	4.30	0.23	0.00	0.25	0.21
	3.99	4.56	77.80	11.35	5.25	0.43	0.00	0.34	0.27
7	10.04	0.50	65.86	16.71	7.47	1.19	6.72	1.06	0.51
	17.52	0.75	60.63	10.88	9.46	0.76	14.26	2.14	1.13
	23.28	0.89	57.05	9.80	10.54	0.93	17.15	2.39	1.25

Appendix 1 (cont'd)

Sample	Contact Time g.hr./liter	Methanol %	Hydrogen %	Carbon Monoxide %	Carbon Dioxide %	Water %	Methane %	Ethane %	Propane %
7	0.855	0.02	73.02	20.75	1.80	0.55	3.63	0.13	0.09
	2.14	0.03	74.75	19.79	1.88	0.61	2.51	0.26	0.17
	5.98	0.23	72.61	17.67	3.04	0.76	4.72	0.60	0.37
	11.75	0.34	77.05	11.99	3.39	0.65	5.40	0.72	0.45
	17.52	0.56	67.35	13.32	6.26	0.79	9.63	1.32	0.78
	23.50	0.77	63.04	10.78	8.31	1.31	12.85	1.96	0.98
7	2.56	0.65	60.70	10.70	9.82	0.72	14.18	2.07	1.17
(300°C)	4.92	0.89	56.06	9.79	10.88	1.03	17.54	2.43	1.39

Appendix II. Chromatograph Calibration for Methanol

Appendix II: Chromatograph Calibration for Methanol

Bulb Volume ml.	Liquid Methanol Volume µl.	Resulting Methanol Concentration %	Mean KF	Observed KF Values					Standard Deviation	90% Confidence Interval	C.I. as Percentage of Mean %
172.1	2.0	0.702	322	308	336	323			14.0	±17.4	±5.4
177.5	4.0	1.41	303	302	299	310	277	327	18.2	17.4	5.7
171.5	6.0	1.93	300	299	277	315	309	299	14.5	13.8	4.6
184.8	8.0	2.57	282	270	284	306	277	271	14.7	14.0	5.0
170.6	9.0	3.11	265	255	272	254	269	273	9.3	8.9	3.3
185.5	10.0	3.42	260	255	269	252	262	261	6.6	6.3	2.4

CONSTRUCTION AND DEMONSTRATION OF A REACTOR SYSTEM FOR TESTING METHANOL SYNTHESIS CATALYSTS

by

DOUGLAS JAMES LITTLE

B.S., Kansas State University, 1978

AN ABSTRACT OF A MASTER'S THESIS

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1980

ABSTRACT

This report deals with construction and demonstration of a reactor system and gas analysis techniques, for testing the performance of methanol synthesis catalysts. Using a catalyst containing copper, zinc, and aluminum oxides obtained from United Catalysts, Inc., four different reduction procedures were compared. These involved both flow and nonflow processes, and diluted hydrogen (2% in nitrogen) at 50 psig pressure and undiluted hydrogen at atmospheric pressure. Very similar results were obtained for three of four procedures. Also, a catalyst containing copper, zinc, and chromium oxides was prepared and tested.