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**CATALYTIC CONVERSION OF OXYGENATED COMPOUNDS TO
LOW MOLECULAR WEIGHT OLEFINS**

Annual Report for January 1–December 31, 1978

By
Rayford G. Anthony

MASTER

January 1979

Work Performed Under Contract No. EW-78-S-02-4717

Texas A&M University
Department of Chemical Engineering
College Station, Texas

U. S. DEPARTMENT OF ENERGY

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ABSTRACT

The conversion of methanol or synthesis gas is an attractive route for producing ethylene and propylene from coal. Utilizing a chabazite ion exchanged with ammonium and rare earth chlorides, methanol is converted to ethylene, propylene and propane with carbon yields of 70 to 90% at reaction temperatures of 360 to 450°C and pressures from 1 to 18 atmospheres. Carbon disulfide in the feed at concentrations less than 2000 ppm increases the operating time between regenerations from four hours to twenty hours. At carbon disulfide concentrations of 3000 ppm or greater, the catalyst goes through three stages. The first is that of a dehydrogenation catalyst that produces carbon monoxide and hydrogen. The second stage produces ethylene and propylene, and finally, the third stage is a dehydration catalyst that produces dimethyl ether. Water has no detrimental effect on the catalyst, and appears to enhance its activity. Increase in pressure increases the production of propylene and propane at the expense of ethylene. X-ray diffraction studies show the formation of an ultrastable zeolite. No permanent deactivation was observed even though the catalyst was overheated once, and had been deactivated and regenerated for as many as 21 times. Ethylene yields increase as the temperature increases from 360°C to 450°C.

When synthesis gas is passed over the catalyst at pressures equal to or less than 500 psi, methane and carbon dioxide are produced.

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I. OBJECTIVE

The objective of this investigation was to study the reaction kinetics of converting methanol to low molecular weight olefins utilizing a chabazite catalyst ion exchanged with a mixture of rare earth chlorides and ammonium chloride. This study, therefore, included the effect of pressure, temperature, space velocity, water vapor, carbon disulfide, and dimethyl ether on the yields of ethylene and propylene, on the conversion of methanol, and on the rate of catalyst deactivation. The activity of the catalyst for converting carbon monoxide and hydrogen to methanol and subsequently to ethylene was, also, to be evaluated.

II. SUMMARY AND CONCLUSIONS

Two experimental reactor systems were used in this investigation. One system utilized a nonisothermal tubular reactor and the other system utilized a Berty® recycle reactor. The tubular reactor system was used to assess the activity of a chabazite catalyst ion exchanged with a mixture of rare earth chlorides for converting carbon monoxide and hydrogen to olefins. The Berty® reactor was used in studies on the reaction kinetics of converting methanol to ethylene and propylene.

A. Conversion of Synthesis Gas to Olefins: When carbon monoxide and hydrogen were passed over the catalyst methane, carbon dioxide and carbon were produced for feed mixtures of 1:1 and 1:9 carbon monoxide and hydrogen. Temperatures of 346°C to 456°C and pressures from 25 to 500 psi were utilized. Hence, neither the chabazite ion exchanged with rare earth chloride, nor chabazite ion exchanged with rare earth chlorides and ammonium chloride have any activity for converting synthesis gas to methanol or olefins in the range of pressures and temperatures investigated. The presence of carbon disulfide in the feed gas appeared to have no effect on the product distribution.

B. Conversion of Methanol to Ethylene and Propylene: The catalyst utilized in our experiments is a chabazite ion exchanged with a mixture of rare earth chlorides and ammonium chloride. Initially the catalyst was placed in the Berty® reactor using the inserts such that the bed depth was approximately 3½ inches. During these experiments a temperature gradient of approximately 10°C existed across the bed. Later, the inserts were not used and the catalyst bed depth was one-half inch. Even though a temperature gradient still existed between the top and bottom thermocouples, the bed temperature was approximately equal to the temperature indicated by the bottom thermocouple. Subsequently, the temperature gradient was decreased to less than 1°C by separately controlling the reactor heaters.

The feeding of carbon disulfide with methanol at concentrations of 1000 to 6000 ppm changed the character of the catalyst. At 6000 ppm only the de-

hydrogenation of methanol to carbon monoxide and hydrogen was observed. Reduction of the carbon disulfide to 1000 ppm restored the activity to produce ethylene and propylene. The presence of carbon disulfide at a concentration of 2000 ppm was fed in the majority of the experiments.

When a mixture of 36% (m) methanol and 64% (mole%) water was fed, the yield of ethylene increased from the range of 30 to 40% to 60 to 80%. When the pressure was increased from 2.7 atmospheres to 18 atmospheres the yield of ethylene decreased from 40% to 20% while the yield of propylene and propane increased from 30% to 80%.

When a mixture of methanol, dimethyl ether and water were fed to the reactor, the yields of olefins dropped substantially. For conversion of dimethyl ether to olefins higher temperatures are required than when feeding only methanol.

The yield of ethylene and propylene increases with an increase in temperature and increases with a decrease in liquid hourly space velocity. The rate of temporary deactivation appears to be independent of space velocity and a function only of temperature and time-on-stream. No permanent loss of activity has been observed. One catalyst charge was deactivated and regenerated 21 times with no loss in activity. X-ray diffraction studies indicate the formation of an ultrastable zeolite. These zeolites are very stable in the presence of water and can be used at high temperatures without destroying the crystal structure.

III. PERSONNEL (Other than P.I.)

Mr. Balaji B. Singh, a Ph.D. candidate in Chemical Engineering, is responsible for all of the methanol studies which are reported and some of the synthesis gas experiments.

Mr. Craig Hill, a Master of Science student in Chemical Engineering conducted the CO and H₂ experiments in the tubular reactor system.

IV. HISTORICAL

In 1974, we initiated a program to study the catalytic decomposition of methanol. The initial study examined the decomposition reactions over zinc chromite and γ -alumina catalyst. As expected, the zinc chromite, a methanol synthesis catalyst, catalyzed the decomposition of methanol to carbon monoxide and hydrogen. About 1% carbon dioxide was also produced. The γ -alumina catalyzed the conversion of methanol to dimethyl ether and water. This program was funded for two years beginning October 1, 1975, by NSF-RANN with the stated objective of converting coal-based methanol to a gaseous fuel and ethylene.

Approximately fifty catalyst which had properties similar to the catalyst used in the late thirties to convert ethanol to butadiene were evaluated to assess their potential for converting methanol to ethylene. In the fall of 1976, we found that tungsten oxide on various ratios of silica alumina catalyzed the conversion of methanol to carbon monoxide, methane, carbon dioxide, ethylene, ethane, propylene, propane, butane, dimethyl ether, and water. A considerable number of experiments were conducted with a Harshaw catalyst, W-0801. From these experiments, we concluded that the ethylene was probably being formed by adsorbed methanol dehydrogenating to an adsorbed formaldehyde specie which in turn polymerized to dimer. Even though the yields over this catalyst were

encouraging, we identified a precipitate in the reactor effluent as tungsten carbonyl. We tried sulfiding the catalyst, however, its activity was lost for converting methanol to hydrocarbon species.

At the beginning of our study in 1975, we were aware that Mobil Oil Company was studying the conversion of methanol to gasoline by use of zeolite catalysts. Venuto and Landis (1968) reported that the decomposition of methanol over a Na-Y zeolite yielded a hydrocarbon mixture of low molecular weight olefins. Since we wished to produce primarily ethylene, we reasoned that a small pore zeolite such as Linde 4A, 5A, and AW500 might convert methanol to ethylene with significant yields. These catalyst were tested and in particular the chabazite, Linde AW500, when exchanged with a mixture of rare earth chlorides and ammonium chloride converted methanol to ethylene and propylene with significant yields. In several cases, 30% of methanol was converted to ethylene, 30% to propylene, and 18% to propane, [i.e. conversion of methanol to component $i = (\text{mole percent of } i) \times (\text{number of carbon atoms in } i) / (\text{sum of mole percent of } i \text{ times number of carbon atoms in } i)]$. This catalyst was, also, effective in converting dimethyl ether to ethylene and propylene. Figures 1, 2, and 3 illustrate results obtained by Lin *et al.* (1977) in the tubular reactor system. Figure 1, illustrates yields using chabazite ion exchanged with rare earth and ammonium chlorides. Figures 2 and 3 illustrate results obtained with chabazite ion exchanged with only rare earth chlorides.

We postulated (Lin, Chao, and Anthony, 1977) that the mechanism was as follows:

Venuto and Landis (1968) suggested an α -elimination for the production of hydrocarbons from methanol. Their proposed mechanism suggests that dehydration of methanol is a rate controlling step. Chang and Silvestri (1977) suggests an insertion reaction for the production of hydrocarbons from methanol. Salvado and Kladnig (1977) in a study on surface reactivity of Type H-Y and Na-Y zeolites with methanol propose the formation of a methoxy specie SiOCH_3 which is formed by

The methoxy specie then decomposes by the reaction

This mechanism has also been proposed by Topchieva, et al. (1957) for Al_2O_3 . The carbene specie then polymerizes to produce the olefin. The alkanes are postulated to occur by hydrogen exchange which occurs when coke is produced.

We have found that carbon disulfide in the feed increases the active life of the rare earth ion exchanged chabazite. The carbon disulfide appears to retard coke formation by some unknown mechanism.

The current project to examine the potential of the AW500-RE for conversion of synthesis gas to low molecular weight olefins and gasoline components and to continue the studies with methanol was funded by DOE-PETC, January 1, 1978.

V. CATALYST

Commercial chabazite zeolite Linde AW500, lot #579038 in 1/8" pellets was obtained from Union Carbide Corporation. Properties of chabazite have been reported for composition, structure, x-ray pattern, thermal stability, intrinsic diffusivity, cation exchange and catalyst properties by Breck (1974). The unit cell contents of dehydrated chabazite were reported as 1.6 Na^+ , 4.4 Ca^{++} (10.4 AlO_2 25.6 SiO_2). The modified forms of chabazite were prepared by ion-exchange.

Based on the results obtained in this laboratory in a tubular reactor system, by F.N. Lin et al. (1977), a catalyst ion exchange with ammonia and rare earth chlorides has been used in this project. The extent of exchange based on the replacement of Na and Ca has been found to be 37%. The catalyst has been subjected to x-ray studies. The results are presented in a separate section.

All of the data reported in Table I were obtained with samples taken from the one preparation. Three fresh charges were used in these studies.

VI. EXPERIMENTAL APPARATUS

A schematic of the apparatus used in this investigation is shown in Figure 4. High purity methanol, reagent grade supplied by Fisher Chemical Co., is pumped from the reservoir with the metering pump, Lapp model MLS-10. Methanol is vaporized in a stainless steel tube preheater packed with stainless steel turnings. The vaporized methanol is passed over the catalyst bed contained in a Berty® reactor, purchased from Autoclave Engineers and developed by Union Carbide. The temperatures measured at top and bottom of the catalyst bed using strategically placed thermocouples were initially controlled using a Thermoline temperature controller. Separate control of the heaters was ultimately used.

Two procedures have been used to analyze the reactor effluent and obtain material balances. The best procedure is described as follows. The reactor effluent is passed through a condenser and trap to remove methanol and water so they would not affect the gas chromatograph further down the line. The undensified gases are then passed through the GC for analysis and the bubble meter for flow measurement. The liquid sample is weighed and analyzed. All the lines

starting from the reactor to the bubble meter are heated and insulated using heating tapes and asbestos cloth tapes to prevent any condensation of liquids. Keeping the lines clear of any liquid condensation is important for the material balances. The gas flow measurement is sometimes found to be pulsating and irregular. There could be two reasons for this. One is the Lapp pump being used is of positive displacement type and imparts a certain amount of pulsations to the flow, which become significant in the range of flow rates involved. This problem has been reduced to a great extent by use of a damper. The large capacity of the system also tends to dampen the gas flow. Secondly, any condensation of liquid on lines and the method used for condensing liquid shows its effects on the gas flow rate. This can be greatly reduced by carefully designing the condensor and the connecting lines.

The other procedure which was used was to remove condensibles after analysis with the gas chromatograph. This latter procedure is described in detail in progress report COO-4717-1, July 1978. A considerable amount of difficulty was encountered in closing material balances with this procedure.

The tubular reaction system used for the majority of the CO and H₂ feed experiments has been described by Lin, Chao and Anthony (1977) and in DOE progress report COO-4717-1. Its operation is similar to the Berty[®] Reaction System.

VII. EXPERIMENTAL PROCEDURE

For the first twenty one runs the inserts for the Berty[®] reactor were used and the catalyst bed depth was 3.5 inches. The temperature drop across the bed was approximately 10°C. Reported temperatures are, therefore, average temperatures. For runs 22 and 23 the inserts were not used and the bed depth for the same volume of catalyst was 0.5 inches. A temperature gradient still existed between the top and bottom thermocouples which are located approximately 3.5 inches apart. However, the temperature drop across the bed was estimated to be less than 1°C. Therefore, for these two runs the temperature is within 1°C of the true temperature. After run 23, the bottom heater in the autoclave was put on separate manual control. By adjusting the power to the bottom heater the two thermocouples indicated the same temperatures within 1°C. Hence, runs 24 to 34 are correct to $\pm 0.5^\circ\text{C}$.

The catalyst is placed in the basket inside the reactor, and the system is checked for any leaks. The reactor is heated under nitrogen atmosphere and kept under nitrogen atmosphere when not in use. Just prior to starting the run, nitrogen gas is passed at 40 to 60 ml/min for 1 hour and then the reactants are fed into the reactor. At the end of a series of experiments, if regeneration is not needed, the system is flushed with nitrogen and then kept under nitrogen atmosphere. Regeneration of catalyst is conducted for 10 to 12 hours at 800 to 1000°F using dry air at 40 ml/min. The last four runs were regenerated at 906°F for 10 to 11 hours.

The GOWMAC thermal conductivity detector gas chromatograph, a porapak Q column, a helium flowrate of 25 ml/min, an oven temperature of 50 to 150°C were used to analyze the reactor effluent. The products in order of their appearance on the chromatograph are CO, CH₄, CO₂, C₂H₄, C₂H₆, H₂O, C₃H₆, C₃H₈, DME, MeOH, C₄, C₅... Hydrogen produced cannot be determined using a parapak Q column. Hence, hydrogen is determined using three methods, a Carle gas chromatograph with multiple columns, hydrogen balances over the reactor and oxygen balances over the reactor. Carle analyses and oxygen balances are more accurate than using hydrogen balances because of the hydrogen in the coke accumulated on the

catalyst. A CRS104 digital integrator and a recorder are used with the gas chromatograph to obtain quantitative information. A computer program has been written to calculate compositions and material balances. A sample output is shown in appendix B.

VIII. EXPERIMENTAL RESULTS AND DISCUSSION

The experimental study consists of three phases. The initial set of experiments were designed to investigate the catalyst life, temporary decay, and the effect of water, pressure and carbon disulfide on ethylene yields. The result of these experiments indicated very little loss of ethylene selectivity with time-on-stream. A second set of experiments were conducted to obtain kinetic data. However, examination of these data showed decay was affecting the results. Therefore, a third set of experiments was conducted. The liquid hourly space velocity was different for each run. Each run was conducted at essentially the same temperature and pressure. In this manner time-on-stream data were obtained for several space velocities.

These data are discussed in the sequence in which they were taken and are presented in Table I, Appendix C.

A. Initial Experiments: A difficulty with the catalyst prepared and tested by Lin *et al.* (1977) was the short time between regenerations. In the latter part of this work, Lin observed that 100 ppm of carbon disulfide appeared to restore the catalyst activity. Therefore, CS₂ was fed with the methanol to determine its effect on the rate of temporary decay of the catalyst and on the catalyst selectivity. Concentrations in the range of 1000 to 6000 ppm CS₂ were utilized.

Figure 5 illustrates the rapid decay of the catalyst when pure methanol is fed. Results similar to those reported by Lin (Figures 1, 2, and 3) were obtained. Figure 6 illustrates the effect of feeding methanol with 6000 ppm of CS₂. Initially only dehydrogenation of methanol to CO and H₂ is observed. After the CS₂ concentration is decreased to 1000 ppm ethylene, propylene and propane are produced. These data are, also, presented in Table I runs IF-2-1 to IF-2-7.

In a study of methanol decomposition over a copper catalyst, Baksi and Gosh (1926) report that CS₂ in methanol feed stabilizes the formaldehyde intermediate. The reactions

were postulated to occur. The velocity constant for the first reaction decreases slightly while that of the second reaction is almost halved. Above a level of 4112 ppm CS₂ the copper catalyst was completely deactivated.

Froment *et al.* (1976) report the use of CS₂ with cracking catalyst to maintain catalyst activity and to prevent coking.

To determine the effect of water on the catalyst activity and selectivity a mixture composed of 64% (mole %) water and 36% CH₃OH was passed over the cata-

lyst. As illustrated in Figure 7, ethylene yields were as high as 60%. Hence, water enhances the catalyst selectivity substantially. If CS_2 is not included in the feed the catalyst decays as fast as when only methanol is fed. Run II-6, Table I illustrates this effect. Givens *et al.* (1978) have also found that water enhances the selectivity to ethylene.

The effect of pressure on the selectivity of producing ethylene is shown in Figure 8 and in Table I, Runs II-15 through II-18. These data illustrate that increasing the pressure increases the yields of propylene and propane at the expense of producing ethylene. The effect of decreasing yields of ethylene with increasing pressure suggests that the increased ethylene yields obtained when cofeeding water is due to the reduction of partial pressures of the methanol and hydrocarbon products. Topchieva *et al.* (1968) in a study of Cumene cracking on zeolites observed a two fold increase in catalyst activity due to the presence of water. They postulated that the presence of water increased the number of active centers. Jacobs *et al.* (1977) suggest increased catalyst activity was due to partial pressure. Additional experiments at low partial pressures would have to be conducted to determine whether water is increasing the number of sites or whether increased selectivity is only a partial pressure effect.

The effect of feeding an equilibrium mixture of methanol, dimethylether and water was investigated. Methanol was passed over a γ -alumina catalyst and the reaction product was then passed over the chabazite catalyst. As illustrated in Runs 19 and 20 ethylene yields were low. Comparison of these results with those shown in Figure 3 seem to be contradictory. In Figure 3, pure dimethyl ether was fed and the reaction temperature was 450°C instead of 397°C as in these experiments. Obviously more work is needed when feeding mixtures across the catalyst.

In the majority of the experiments conducted in this set, methanol conversions were high. Where the space velocity was varied erratic results were obtained. Conversions were not correlating with change in the space velocity. This behavior was traced to a faulty pump. Even though the pump was not working properly, it appeared from examination of the data in Figures 5, 6, 7, and 8 that the catalyst activity was essentially constant for eight to ten hours. Therefore, the next set of experiments were planned to obtain kinetic data.

B. Second set of Runs II-21 through II-30: Since the catalyst activity appeared to be constant, a set of runs were conducted where space velocity was changed during a run. Run 21 was conducted at 396°C and then the catalyst was accidentally heated to 1300°F . Even though the catalyst had not been damaged as indicated by a comparison of product distributions, (x-ray diffraction studies also showed no change in the catalyst structure), a fresh batch of catalyst was charged to the reactor. Runs 21 through 30 constitute this set. Run 24 and 25 were conducted at 420°C and 416°C and at 1/LHSV of 12.82 and 6.67, respectively. Examination of the data in these experiments shown in Table I indicated the catalyst activity and selectivity was changing substantially over a run time of 10 to 12 hours. Corrections for Runs 21, 22, 23, 26, 27, 28, 29, and 30 to zero run time would be significant. These data uncorrected for catalyst decay are shown in Figure 9.

The time-on-stream for each run at high reciprocal LHSV (liquid hourly space velocities) and high conversions was less than 2 hours. In each run the maximum conversion is 90 to 94 percent. This seems to suggest some type of limit on conversion at least for this type of reactor. Figure 9, also, illustrates

that space velocities of 0.1 to 10 should be used to collect kinetic data.

Figure 10 illustrates the changes in selectivity at constant LHSV. The major change occurs in the ethylene yield which decreased from 40 to 30% over a 10 hour period.

Figure 11 illustrates that ethylene and propylene yields increase with increasing temperature.

C. Third Set of Experiments: Runs 31 through 34 constitute this third set of experiments. The LHSV and temperature were held constant for each run. The catalyst was regenerated at approximately 482°C for 10 to 12 hours, between each run. The conversion as a function of space velocity and time-on-stream is shown in Figure 12. Runs 24 and 31 illustrate that no permanent loss in catalyst activity has occurred. The fact that these curves are nearly parallel suggests that the decay is independent of space velocity. Similar results have been reported by Weekman (1968) for the decay of cracking catalysts. These curves are substantially different than those reported by Cobb et al. (1978).

Figures 13, 14, and 15 illustrate the effect of space velocity on selectivity. Data illustrated in these figures could indicate that dimethyl ether is formed by a primary reaction and lost by a secondary reaction. The olefins and paraffins are formed by secondary reactions. Similar curves can also be obtained in a parallel net work. This concept is discussed in greater detail in the section on mechanism and stoichiometry. Carbon dioxide and carbon monoxide appear to be participating in both primary and secondary reactions depending on the length of time-on-stream. Interpretation of graphs of this type are discussed by Holland and Anthony (1979). More data are needed to firmly establish the trends indicated by these figures. However, the trends indicated by the data in Figures 13, 14 and 15 are similar to those reported by Chang and Silvestri (1977) for the conversion of methanol to gasoline on a ZSM-5 zeolite.

D. X-ray Diffraction Studies: The crystal structure of AW500 Zeolite has been studied using Co-K (Alpha) radiation in a x-ray spectrometer in an effort to understand the effects of modifications due to the ion exchange processing on the catalyst and to get an understanding of the effect of crystal structure on the deactivation characteristics of the catalyst. The studies indicate that the ion-exchange does not have any effect on the crystal structure compared to a catalyst that has not been exchanged. The heat treatment of the catalyst changes the crystal structure to some extent compared to the catalyst that has never been subjected to heat treatment. X-ray studies on a catalyst that is deactivated indicates presence of some external substance (carbon) on the surface. From the comparison of experiments conducted, it can be concluded that after about 21 regenerations and 3 months of use, catalyst could be regenerated and returned to initial activity. These observations coupled with the x-ray analysis suggest that no permanent deactivations occurred for the 3 month period and the deactivation that is occurring is predominantly due to the coke formation and is only a temporary effect.

X-ray diffraction data for chabazite has been reported by A.P. Grude and R.A. Sheppard, Amer Mineral 51;909 (1966), who used powder photography. From the data the most significant peaks with reasonable intensities, have been selected to identify and compare the x-ray results. Intensities from the x-ray diffraction graphs are used to compare the various x-ray studies as follows. The x-ray patterns are presented in Appendix A. The characteristic x-ray peaks for

chabazite crystal are

hkl	d(A)	I	2θ
101	9.351	50	9.42
003	5.021	30	17.67
211	4.32	76	20.55
212	3.870	28	22.97
401	2.925	100	30.55
214	2.890	30	30.95

The above peaks are identified for each of the x-ray determinations.

Sample #6 is an x-ray diffraction for pure AW500 without any ion exchange and heat treatment. The structure complies with the significant peaks as suggested by Grude and Sheppard.

Samples #1,2 and 3 represent the samples of AW500 exchanged within ammonia and RECl_3 , RECl_3 only and ammonia only. These peaks also conform to the original chabazite structure, indicating very little change in crystal structure due to ion exchange. The x-ray patterns were obtained, on samples that had not been exposed to the reactants or the reaction temperature.

Sample #8 is an x-ray pattern for the catalyst used in the study, AW500 exchanged within ammonia and rare earth chloride after subjecting it to the reaction temperature 400°C for 35 hours with a nitrogen blanket. Compared to Sample #1 the structure shows noticeable modifications in the peak intensities, indicating that exposure to heat does modify the structure slightly.

Sample #4 is an x-ray pattern for the AW500 RECl_3 Amm catalyst after 3 months of use and 21 regenerations. The catalyst was temporarily deactivated. Clearly the deactivation does have an effect on the structure.

Sample #5 is an x-ray pattern for the above catalyst after regeneration. The regenerated catalyst has properties similar to the catalyst that has been subjected to 400°C for 35 hours. By comparing it to Sample #8, we can conclude that the deactivation changes the crystal structure in certain planes due to coking and returns to normal condition after regeneration.

Sample #7 is an x-ray pattern for the AW500 RECl_3 Amm catalyst, accidentally overheated to 1300°F , and there seems to be no damage to the crystal structure.

In the studies conducted by Cobb *et al.* (1978) at the University of Pittsburgh, the following observations were reported.

"The initial activity was the same throughout the first three D-R (deactivation-regeneration cycles). After the fourth D-R cycle, the initial activity was less. During 10th D-R cycle the conversion to olefin nearly disappeared."

"The x-ray diffraction showed no peaks at all except for two very weak, broad peaks diffracted by the 211 and 401 planes. It was estimated qualitatively that about 80% of the crystallinity had been destroyed."

The conclusions drawn by Cobb *et al.* from these results were "that carbon laydown is the cause of short-term deactivation and that structure degradation is the cause of long-term activity loss."

In our study x-ray diffraction patterns were obtained for the catalyst which we used. The x-ray pattern for a catalyst after 21 D-R cycles shows a modification in the intensities due to defects introduced, but it still retains the basic crystal structure intact. The experiments conducted using pure methanol indicated that the catalyst is active in producing olefins. Hence, it is concluded that the short term deactivation is due to carbon formation or coking. There is no long term deactivation for this catalyst at least in the time the experiments were conducted, 3 months.

The differences in the results of the two sets of investigations needs further study. The basic difference between the two studies is the type of exchange used for the initial catalyst. In the studies conducted at Pittsburgh, they used the catalyst reported by us in the early stages of our investigation, (i.e., exchange with La). Since then, the catalyst has been improved significantly using different procedures for ion exchange. The catalyst used in the present study is exchanged with ammonia and rare earth chlorides.

In our work we also report that presence of water increases the activity of the catalyst toward forming olefins. Now, the effect of ammonia and water vapor in combination on a zeolite is very complex. The reaction temperatures involved and the water formed during olefin formation have a distinct effect on forming an ultrastable zeolite. The concept of ultrastable zeolite was first conceived by Barrer and Bratt, Phys. Chem. Solids 12:130 (1960), [Breck (1974)]. This has been defined as "ultrastable" zeolite. The crystal structure of ultrastable zeolite Y is retained after heating to temperatures in excess of 1000°C compared to zeolite Y which has structural changes if exposed to a temperature of 600°C.

For Y type zeolites, it was reported that the thermal stability is a function of the degree of ammonium exchange. Based on the x-ray powder diffraction analysis, the zeolite crystal structure was retained until the breakdown temperature. The atmosphere surrounding the ammonium exchanged zeolite is very important. The hydrogen form of zeolite Y dehydroxylates rapidly when heated to 650°C in an inert gas. If water is removed by heating in vacuum, the resulting zeolite has relatively poor thermal stability. If the zeolite is calcined in presence of water vapor, the thermal stability is retained at 1000°C. Hence, in the present work we have prepared an ultrastable zeolite as evidenced by the fact that the catalyst is active even after 21 D-R cycles.

B. Mathematical Model Development: The existence of catalyst decay in the treatment of kinetic data increases the difficulty of developing rate equations to describe the reaction system. In the absence of significant resistance to pore and film diffusion, the rate is a function of temperature, composition, and catalyst activity. This can be expressed as

$$r_A = f(T, p_i, \alpha(T, p_i, t)) \quad (1)$$

where

T=temperature
 p_i =partial pressure of component i
 α =measure of catalyst activity
 t=time-on-stream
 r_A =rate of disappearance of methanol

Treatment of the decay function is simplified if the intrinsic kinetics and the activity can be treated separately as

$$r_A = \alpha(T, p_i, t) f(T, p_i) \quad (2)$$

For a perfectly mixed flow reactor the rate can be expressed as

$$r_A = \rho_A S_\ell x \quad (3)$$

where

ρ_A = molar concentration of methanol in the liquid phase. For pure methanol feed ρ_A is the molar density of methanol.
 S_ℓ = is the liquid hourly space velocity defined as the volumetric feed rate divided by the volume of catalyst. The abbreviation LHSV is used in the other parts of this report.
 x = conversion of methanol.

The flow patterns in the Berty^(R) reactor are such that it is appropriate to use Eq. (3) to calculate the rate.

Elimination of r_A from Equations (2) and (3) yields

$$x = \frac{1}{\rho_A S_\ell} \alpha(T, p_i, t) f(T, p_i) \quad (4)$$

Pachovsky et al. (1973) have shown for coking on cracking catalyst that the activity function α may be represented as a function of time-on-stream where

$$\begin{aligned} n &= \text{order of deactivation} \\ \alpha &= (1 + Gt)^{-N} \\ N &= nM \\ M &= 1/m - 1 \\ G &= (m-1)k_d \\ m &= \text{order of decay reaction, } \frac{d\alpha}{dt} = -k_d \alpha^m \\ k_d &= \text{rate constant, } k_d \text{ is a function of } T. \end{aligned} \quad (5)$$

If we assume that $f(T, p_i)$ can be represented as a power-law function then

$$f(p_i, T) = k_p \prod_{i=1}^c p_i^{\beta_i} \quad (6)$$

where k_p = velocity constant, and a function of temperature
 c = number of components in the system
 β_i = order of reaction for component i

By restricting this function to be dependent only on the partial pressure of methanol, we get

$$f(p_A, T) = k_p p_A^\beta$$

terms of conversion

$$f(p_A, T) = k_p \left[\frac{p_A^\circ (1-x)}{(1+\epsilon x)} \right]^\beta \quad (7)$$

where p_A° = partial pressure of methanol at the entrance to the reactor at the temperature and pressure of the reaction
 ϵ = expansion coefficient for unequal molar reaction. Holland and Anthony (1979). ϵ varies between 1.3 and 1.5 for our data.
 This factor is calculated for each experiment as follows:

$$\epsilon = \frac{\text{moles product/time} - \text{moles of feed/time}}{\text{moles of feed/time}}$$

and conversion, x , is calculated as

$$x = \frac{\text{moles of methanol reacted}}{\text{mole of methanol fed}}$$

Elimination of α and f in Equation (4) with their equivalent expression from Equations (5) and (7) and rearranging yields.

$$\left[\frac{[p_A^\circ (1-x)]^\beta}{p_A S_L x [1+\epsilon x]^\beta} \right]^{1/N} = a + b t \quad (8)$$

where $a = k_p^{-1/N}$

$$b = \left[k_p^{-1/N} \right] G$$

Cobb et al. correlated the catalyst decay in their experiments with an expression of this type. They used $N=1, \beta=2, \epsilon=0$, and obtained b as a function of space velocity. However as discussed previously, the catalyst they used and the method of operation is different from ours.

Table II shows the lack of fit of Equation (8) for simple orders for runs 24,25,31 through 34. Additional work is needed to develop an equation which describe both the rate of reaction and temporary catalyst deactivation.

The modelling of the selectivity distribution represents an additional degree of complexity. Future work should deal with modelling product distributions.

F. Mechanism and Stoichiometry: The stoichiometric equations for the formation of CO, CO₂, dimethyl ether, olefins and paraffins may be represented as follows:

The above set of reactions are not all independent. Reactions (5) and (7) indicate that the ratio of paraffins to CO and to CO₂ should be 2:1 or 3:1. Examination of the data in Table I, shows that in every case more paraffins are produced than indicated by these two ratios. The additional paraffins may come from consideration of Reactions (8) and (9). The curves in Figures 13,14, and 15 can be generated by a sequential or a parallel set of reactions, i.e.

The fact that the olefin yields dropped substantially when feeding an equilibrium mixture of DME, water and methanol and the fact that higher temperatures are required to obtain a reasonable yield of olefins, suggest that reactions (10), (11) and (12) are the predominant reactions. Therefore, it appears that two reaction sites are occurring on the catalyst. One which promotes the reaction of dimethyl ether and the second which promotes the formation of olefins. As the catalyst deactivates the second site becomes totally inactive or is converted to the first site for producing dimethyl ether.

G. Results of CO + H₂ Experiment: A preliminary exploratory experiment on feeding CO and H₂ simultaneously on the zeolite catalyst was conducted on Run #35 in the Berty reactor. CO and H₂ mixture in the ratio 1:9 was fed at an average temperature of 350°C and 320 psig pressure in the reactor. The feed also had about 7000 ppm CS₂ in vapor phase.

The reactor effluent had only CO, H₂ and traces of CH₄, CO₂ and water. A trace of H₂S was also observed. Residence times of 29.33 min, 10.32 min and 4.68 min were used to study the reaction. After 4 hours of operation, CO and H₂ mixture was stopped. To make sure the catalyst was okay pure methanol with 2000 ppm at LHSV of 0.089 was run and the ethylene yield of 26.4% based on GC analysis was noted.

The basic objective in conducting the above experiment was to explore the possibilities of using CO and H₂ as the starting material instead of methanol by itself. The idea is that in our previous runs methanol in the presence of excessive amounts of CS₂ dehydrogenated completely forming CO and H₂. The attempt has been made to see if it would be possible to reverse the reaction to produce methanol and subsequently ethylene from CO and H₂. Experiments were also conducted in our tubular reactor system at temperatures of 346°C 356°C and 424°C and pressures of 6, 9 and 20 atmospheres. Methane, CO₂ and carbon were the only reaction products.

Even though equilibrium calculations as shown in Table III for the reaction

indicate low conversions and low concentrations at low reaction pressures and temperatures, it was felt that the secondary reaction of forming ethylene would act as a pump in promoting the methanol synthesis reaction. It now appears that experiments need to be conducted at pressures of at least 1000 psi and preferably at 2000 to 3000 psi. Additional equipment is needed to operate our reactor system at these higher pressures.

IX. TRAVEL AND VISITORS

During the contract period, I attended the Fifth Annual DOE /Fossil Energy Conference on University Coal Research, August 23-24, 1978, in Lexington, Kentucky and presented a summary of our research accomplishments. I also attended with my students the spring semi-annual catalysts symposium sponsored by the Southwest Catalyst Society. Discussions pertinent to this research occurred.

I was invited to attend the NSF-sponsored workshop on "Research Needs and Instrumental Requirements in Catalysis" on June 22,23, 1978. Prior commitments prevented me from attending, however, I did receive the proceedings from the conference.

Dr. Richard Diffenbach visited our facilities and reviewed the progress of our research effort. Several of his recommendations have been implemented.

X. RECOMMENDATIONS FOR FUTURE STUDIES

1. Collect conversion and yield data at 375°C and 475°C as a function of time-on-stream at several space velocities. Increase the range of space velocities 20 to 0.09. These data would be collected in the same manner as Runs 24,25 and 31 through 34. The data would be used in developing a mathematical model for estimating yields and conversions for larger systems.
2. The catalyst has been regenerated at 905°F for 10 to 12 hours. A series of experiments should be conducted utilizing different regeneration temperatures and times. For example utilizing the experiments at 417°C as standards, the catalyst would be regenerated at 1000°F, 950°F and 850°F at air flows of 50 ml/min for 10 hours. The catalyst activity would be tested using methanol feed with 0.1 liquid hourly space velocity and reaction temperature of 417°C. These experiments would then be used as a basis to optimize the regeneration cycle. The variables would be regeneration temperature, regeneration time, and air flow rate.
3. Each of the products should be passed over the catalyst at reaction conditions with and without methanol, these experiments would aid in developing the mathematical model (ie. rate functions) and at the same time increase our understanding of how the products affect the catalyst and reaction mechanism.
4. Compounds other than CS₂ should be investigated for stabilizing the catalyst activity and preventing coking reactions.
5. Additional experiments should be conducted at pressures of 100 to 2000 psi. The co-feeding of methanol with water and with inert gas should be further studied. Both of these types of experiments would increase our understanding of the reaction mechanism.
6. Efforts should be continued to produce ethylene and propylene from synthesis gas. Future experiments should be conducted at pressures of 1000 psi or greater. The incorporation of a methanol synthesis catalysts into the zeolite should be investigated. The effect of feeding reactor effluents from a methanol synthesis reactor directly into the reactor for producing olefins should be investigated. This reactor configuration should increase the overall efficiency for producing olefins from synthesis gas.

7. X-ray diffraction studies should be continued to determine if structural changes in the catalyst occur with any of the above experiments. Electron microscope pictures of the catalyst should also be taken and examined.

8. Evaluate the use of erionite as a catalyst. This zeolite should be ion exchanged with ammonium and rare earth chlorides, rare earth chlorides, and ammonium chloride, and evaluated for catalyst activity and stability. Chang, Lang, and Silvestri (1977) obtained higher yields with an erionite catalyst as compared to a chabazite catalyst. However, we have obtained yields on chabazite comparable to those reported by Chang et al. for erionite, therefore, this catalyst needs further evaluation.

9. The effect of diffusional resistances on selectivities should be investigated. The experimental work to date has been with 1/16" x 1/8" cylindrical pellets.

10. The use of a fluid bed reactor should be evaluated. The catalyst could be withdrawn, regenerated and recycled in this type of reactor, thereby maintaining a constant activity of the catalyst inside the reactor.

XI. ACKNOWLEDGEMENT

The support of the Department of Chemical Engineering and the Texas Engineering Experiment Station is appreciated. In particular, the discussions with Professor Jack Lunsford in the Department of Chemistry on zeolites and in regard to interpretation of the X-Ray diffraction data is appreciated. Special thanks are due Dr. Deepak Thakur and Professor Abraham Clearfield for obtaining the X-Ray diffraction data.

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Appendix A

X-Ray Diffraction Data

Appendix B

1. Typical Results of Material Balance Calculations
2. Determination of Hydrogen Using Material Balances in Absence of Hydrogen Analysis

RUN#31

SAMPLE # 1.00
TIME 9.25
TEMPERATURES : TOP. BOTTOM. AVERAGE 417.75 418.33 418.04 C
REACTOR PRESSURE 25.00 PSIG
LIQUID HOURLY SPACE VELOCITY = 0.0820 1/HRS
GAS HOURLY SPACE VELOCITY = 42.6418 1/HRS
RESIDENCE TIME 1.4071 MIN

HYDROGEN FREE GAS ANALYSIS BASED ON GC RESPONSES

PRODUCTS	AREA	AREA	MPCT	MPCT	PERCENTAGE OF HYDROCARBONS
CO	108.0	420.0	2.67	10.36	CH4
CH4	248.0	1604.0	5.37	36.31	C2H4
C2H4	223.0	207.0	5.11	4.70	C2H6
C2H6	4.89	0.00	0.00	0.00	H2O
H2O	26.27	24.30	18.22	5.32	DME
DME	20.64	18.94	11.70	5.13	CA
CA	0.00	0.00	0.00	0.00	C5
C5	0.00	0.00	0.00	0.00	OTHR
OTHR	0.00	0.00	0.00	0.00	MEOH
MEOH	3.06	124.0	3.06	0.00	WATER
WATER	0.00	0.00	0.00	0.00	

TOTAL MATERIAL BALANCES

GAS FLOW RATE 2612.00ML/HR LIQUID COLLECTED 2.8900GRAMS TIME OF COLLECTION 1.0000HRS
AMOUNT OF FEED = 6.32 GRAMS

PRODUCT DISTRIBUTIONS BY FORMING H2 BALANCE

PRODUCT DISTRIBUTIONS

PRODUCTS	MOLE IN	MOLE OUT	PRODUCTS	MOLE IN	MOLE OUT
CO	0.000	0.003	CH4	0.000	0.010
CH4	0.000	0.005	C2H4	0.000	0.035
C2H4	0.000	0.004	H2O	0.000	0.141
H2O	0.000	0.015	C3H8	0.000	0.011
C3H8	0.000	0.008	DME	0.000	0.000
DME	0.000	0.000	CA	0.000	0.000
CA	0.000	0.000	C5	0.000	0.000
C5	0.000	0.000	OTHR	0.000	0.012
OTHR	0.000	0.000	MEOH	0.000	0.015
MEOH	0.000	0.000	WATER	0.000	0.000
WATER	0.000	0.000			

TOTAL FEED BALANCE

GRAMS OF LIQUID	2.89	GRAMS OF GAS	3.11	GRAMS OF	FEED	6.32	BALANCE	=	94.8635					
PRODUCT YIELD % BY WEIGHT														
YLR	1.268	2.818	4.014	17.279	2.398	45.414	11.131	8.747	6.380	0.000	0.000	0.000	0.000	0.551

MOLES OF PRODUCT %CN PER MOLE OF METHANOL REACTED

PRODUCTS	CO	CH4	CO2	C2H4	C2H6	H2O	C3H6	C3H8	DME	C4	C5	OTHR	MEOH	H2
YLR	0.014	0.053	0.028	0.372	0.048	0.000	0.290	0.180	0.084	0.000	0.000	0.000	0.000	0.000

NORMALIZED CARBON YIELDS

YLR	0.013	0.052	0.027	0.366	0.047	0.000	0.236	0.177	0.082	0.000	0.000	0.000	0.000	0.000
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MEOH REACTED ACTUAL = 0.1857 MEOH ESTIMATED == 0.1891 PERCENT DEVIATION = 1.8093

PERCENTAGE OF HYDROCARBONS IN EXIT INCLUDING UNREACTED REACTANTS BY WEIGHT 39.705

PRODUCT DISTRIBUTIONS BY WEIGHT AMONG HYDROCARBONS

WCT	0.00	6.65	0.00	40.73	5.66	0.00	26.27	20.64	0.00	0.00	0.00	0.00	0.00	0.00
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INDIVIDUAL MATERIAL BALANCES

CARBON BALANCE	CARBON IN = 0.20	CARBON OUT 0.20	MOLES BALANCE -1.70 %
HYDROGEN BALANCE	HYDROGEN IN = 0.79	HYDROGEN OUT = 0.79	MOLES BALANCE -0.00 %
OXYGEN BALANCE	OXYGEN IN 0.20	OXYGEN OUT 0.17	MOLES BALANCE 12.09 %

CARBON/HYDROGEN IN = 0.2500	CARBON/HYDROGEN OUT = 0.2543
HYDROGEN/OXYGEN IN = 4.0000	HYDROGEN/OXYGEN OUT = 4.5500
OVERALL CONVERSION OF METHANOL = 94.44	

OVERALL RATE OF REACTION = 0.1673E-02 MOLES/HR.GR OF CATALYST

INDIVIDUAL RATES MOLES/HR.GM OF CAT
 RATE BASED ON CO = 0.1231E-03
 RATE BASED ON CH4 = 0.4786E-03

RATE BASED ON CO2 =0.2479E-03
 RATE BASED ON C2H4 =0.1677E-02
 RATE BASED ON C2H6 =0.2172E-03
 RATE BASED ON H2O =0.6955E-02
 RATE BASED ON C2H6 =0.7201E-03
 RATE BASED ON C2H6 =0.5402E-03
 RATE BASED ON DME =0.3768E-03
 RATE BASED ON C4 =-0.0000E+00
 RATE BASED ON C5 =-0.0000E+00
 RATE BASED ON OTHR =-0.0000E+00
 RATE BASED ON MECH =-0.0000E+00
 RATE BASED ON H2 =0.7488E-03

PRODUCT DISTRIBUTION BY FORCING O BALANCE

NEGATIVE VALUE FOR MOLES OF H2 FORCED TO ZERO

PRODUCT DISTRIBUTIONS *****

PRODUCTS	CO	CH4	CO2	C2H4	C2H6	H2O	C3H6	C3H8	DME	C4	C5	OTHR	MECH	H2
MOLE IN	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.197	0.000
MOLE OUT	0.003	0.011	0.006	0.040	0.005	0.142	0.017	0.013	0.009	0.000	0.000	0.000	0.012	0.000

TOTAL MASS BALANCE *****

GRAMS OF LIQUID	2.89	GRAMS OF GAS	3.57	GRAMS OF	FEED	6.32	BALANCE	=	102.2697					
PRODUCT YIELD % BY WEIGHT														
YLR	1.264	3.030	4.316	18.980	2.578	42.253	11.969	9.406	6.504	0.000	0.000	0.000	0.000	0.000

MOLES OF PRODUCT #CN PER MOLE OF METHANOL REACTED

PRODUCTS	CO	CH4	CO2	C2H4	C2H6	H2O	C3H6	C3H8	DME	C4	C5	OTHR	MECH	H2
YLR	0.016	0.062	0.032	0.434	0.056	0.000	0.279	0.210	0.092	0.000	0.000	0.000	0.000	0.000

NORMALIZED CARBON YIELDS														
YLR	0.013	0.052	0.027	0.367	0.048	0.000	0.237	0.177	0.078	0.000	0.000	0.000	0.000	0.000

MECH REACTED ACTUAL = 0.1853 MECH ESTIMATED = 0.2188 PERCENT DEVIATION = 18.1156

PERCENTAGE OF HYDROCARBONS IN EXIT INCLUDING UNREACTED REACTANTS BY WEIGHT 42.796

PRODUCT DISTRIBUTIONS BY WEIGHT AMONG HYDROCARBONS														
HPCT	0.00	6.65	0.00	40.78	5.66	0.00	26.27	20.64	0.00	0.00	0.00	0.00	0.00	0.00

INDIVIDUAL MATERIAL BALANCES

 CARBON BALANCE CARBON IN = 0.20 CARBON OUT 0.23 MOLES BALANCE -16.99 %
 HYDROGEN BALANCE HYDROGEN IN = 0.79 HYDROGEN OUT = 0.83 MOLES BALANCE -4.99 %
 OXYGEN BALANCE OXYGEN IN 0.20 OXYGEN OUT 0.19 MOLES BALANCE 10.00 %

CARBON/HYDROGEN IN = 0.2500 CARBON/HYDROGEN OUT = 0.2786
 HYDROGEN/OXYGEN IN = 4.0000 HYDROGEN/OXYGEN OUT = 4.6662
 OVERALL CONVERSION OF METHANOL = 93.80

OVERALL RATE OF REACTION = 0.1669E-02 MOLES/HR.GR OF CATALYST

INDIVIDUAL RATES MOLES/HR.GR OF CAT

RATE BASED ON CO = 0.1434E-03
 RATE BASED ON CH4 = 0.5576E-03
 RATE BASED ON CO2 = 0.2388E-03
 RATE BASED ON C2H4 = 0.1954E-02
 RATE BASED ON C2H6 = 0.2520E-03
 RATE BASED ON H2O = 0.6911E-02
 RATE BASED ON C3H6 = 0.9390E-03
 RATE BASED ON C3H8 = 0.6294E-03
 RATE BASED ON IHE = 0.4163E-03
 RATE BASED ON C4 = 0.0000E 00
 RATE BASED ON C5 = 0.0000E 00
 RATE BASED ON C6+H2 = 0.0000E 00
 RATE BASED ON MECH = 0.0000E 00
 RATE BASED ON H2 = 0.0000E 00

Determination of Hydrogen Using Material Balances in Absence of Hydrogen Analysis

Preliminary analysis indicate that the product contains small amounts of hydrogen. Analyzing for hydrogen is a complicated procedure, because of its thermal conductivity and the requirement of carrier gas different than helium. Hydrogen is determined from the material balances using different procedures to force the material balances. The method used for forcing also gives a fairly good idea on the closure of material balances. The difference in the values for yields based on two methods of material balances define the error bands on these estimations.

The arrangement of analytical equipment which gives excellent closure on material balances is as follows.

The products coming out of the reactor are passed through a cold trap made of 200 ml conical flasks submerged in an ice bath. Water, methanol and some dimethyl ether are condensed in the cold trap. Apart from aiding in material balances, the cold traps keep the gas chromatograph from being overloaded. Gas containing the products is then passed through the same loop of the gas chromatograph to analyze for CO, CH₄, CO₂, C₂H₄, C₂H₆, H₂O, C₃H₆, C₃H₈, C₄, MeOH and dimethyl ether. The flow rate of the gas leaving the sample loop of the gas chromatograph is measured using the bubblemeter.

Let

- n_T = Total moles of gas exiting from reactor
- W_L = weight of liquid product collected
- m_i = molecular weight of each component
- n_i = moles of component i, $i = 1, 14$
- n_G = moles of gas
- n_{HFG} = moles of hydrogen free gas
- n_{H_2} = moles of hydrogen produced
- n_L = moles of liquid

Using Oxygen Balance to Determine H₂ and Material Balances.

$$n_T = n_{H_2} + n_{HFG} + n_L = n_G + n_L \quad (1)$$

$$\text{oxygen}_{IN} = \left(\sum_{i=1}^{14} n_i \text{ON}_i \right)_{IN} \quad (2)$$

where ON_i = moles of oxygen per mole of component i

$$\text{oxygen OUT} = n_{HFG} \sum_{i=1}^{14} Y_{iG} ON_i + n_L \sum_{i=1}^{14} Y_{iL} ON_i \quad (3)$$

Y_{iG} = mole fraction obtained from the GC analysis on H_2 -free basis for gas

Y_{iL} = mole fraction obtained from the GC analysis of liquid product.

Forcing an oxygen balance, we obtain

$$\left(\sum_{i=1}^{14} n_i ON_i \right)_{IN} = n_{HFG} \left(\sum_{i=1}^{14} Y_{iG} ON_i \right)_{OUT} + n_L \left(\sum_{i=1}^{14} Y_{iL} ON_i \right)_{liquid}$$

$$\sum n_i ON_i = n_{HFG} (\sum Y_{iG} ON_i) + n_L (\sum Y_{iL} ON_i) \quad (4)$$

$$n_{HFG} = \frac{(\sum n_i ON_i)_{IN} - n_L (\sum Y_{iL} ON_i)}{(\sum Y_{iG} ON_i)_{OUT}} \quad (5)$$

From Equation 1 we obtain

$$n_{H_2} = n_G - n_{HFG}$$

The moles of hydrogen obtained can be used in the overall material balances and used in calculating yield percents.

Forced Hydrogen Balance

$$\text{Hydrogen IN} = (\sum n_i HN_i)_{IN} \quad (6)$$

$$\text{Hydrogen OUT} = n_{H_2} + n_{HFG} \sum Y_{iG} HN_i + n_L \sum Y_{iL} HN_i \quad (7)$$

HN_i = moles of Hydrogen per mole of component i

From Equation 1

$$n_{H_2} = n_G - n_{HFG}$$

∴ From Equation 7

$$\text{Hydrogen OUT} = n_T + n_{HFG} (\sum Y_{iG} HN_i - 1) + n_L (\sum Y_{iL} HN_i - 1)$$

Forcing a hydrogen balance, we obtain,

$$(\sum n_i \text{HN}_i)_{\text{IN}} = n_T + n_{\text{HFG}} (\sum Y_{iG} \text{HN}_i - 1) + n_L (\sum Y_{iL} \text{HN}_i - 1) \quad (8)$$

$$n_{\text{HFG}} = \frac{(\sum n_i \text{HN}_i)_{\text{IN}} - n_T - n_L (\sum Y_{iL} \text{HN}_i - 1)}{(\sum Y_{iG} \text{HN}_i - 1)} \quad (9)$$

and
$$n_{\text{H}_2} = n_T - n_{\text{HFG}} - n_L = n_G - n_{\text{HFG}}$$

The assumption used in conducting the material balances using the above procedure is that there is no accumulation of oxygen or hydrogen in the reactor. The oxygen balance is expected to yield the best estimate of hydrogen because of the method of analysis involved. Apart from that it is possible that the coke formation on the catalyst may be a hydrocarbon, which may give errors in hydrogen balance. The two values can define the range of values for the estimated variables.

Appendix C

DATA

Tables I through III

Figures 1 through 15

TABLE I. EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR SYSTEM

Date: 5/19/78

Catalyst: AW500 Exchanged with Ammonia and Rare Earth Chloride - Preparation A.

Feed: Pure Methanol + 3000 ppm carbon disulfide

Reactor Pressure: 100 psig

Room Temp: 76°F Barometric pressure: 29.9 in

Previous History: On Stream for 10 hrs., Regenerated for 13 hrs.

RUN #	TIME ON STREAM HRS.	REACTOR TEMP °C			PRODUCT YIELD* %								CONVERSION MeOH	SPACE TIME MINUTES
		TOP	BOTTOM	AVERAGE	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME		
I-1-1	1.5	418	381	400	90.44	1.33	0.24	0.00	0.00	0.00	0.00	7.98	74.2	4.80
I-1-2	1.58	427	420	423	76.88	8.72	3.48	6.29	3.24	0.00	0.00	1.40	93.10	4.62
I-1-3	1.83	427	418	423	70.18	7.00	6.23	10.03	6.56	0.00	0.00	0.00	91.4	4.86
I-1-4	2.25	428	421	424	25.86	14.62	10.34	31.51	12.61	2.60	0.00	2.37	83.0	4.88
I-1-5	3.00	430	421	426	0.21	19.30	4.51	54.87	18.67	0.00	0.00	2.44	39.0	4.64
I-1-6	4.00	431	423	427	1.57	31.63	0.48	5.32	2.03	2.65	0.00	40.63	13.8	4.83
I-1-7	4.50	432	423	427	0.76	8.24	0.54	0.4	1.48	0.00	0.00	88.59	34.63	4.81
I-1-8	5.00	432	421	426	0.01	0.62	0.18	0.00	0.08	0.00	0.00	99.10	38.86	4.80
I-1-9	6.00	442	433	438	3.34	24.22	2.70	0.94	3.59	0.00	0.00	65.21	61.44	4.86
I-1-10	7.00	446	439	443	5.91	34.20	1.33	8.21	2.03	0.00	0.00	48.32	80.15	4.89

Stopped running on the catalyst.

Changed catalyst.

Date: 5/26/78

Catalyst: A Fresh Charge of Catalyst Loaded into Reactor AW500 Amm. & ReCl₂. II.

Feed: Pure MeOH with 6000 ppm CS₂ for 4.50 hrs., then CS₂ reduced to 1000 ppm.

Reactor Pressure: 100 psig

Room Temp: 76°F Barometric pressure: 29.80 in

Previous History: Fresh Charge Prep. A.

* Experimental procedures are discussed in Appendix B. Space time is volume of catalyst divided by feed rate at reaction conditions. Product yield is equal to moles of i times number of carbon atoms divided by the sum of moles of i times number of carbon atoms. Yield and methanol conversion are calculated using the gas chromatograph analysis, only for Run 1 through 20. After run #20, all results are based on material balance calculations.

TABLE I. EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR SYSTEM
CONT'D.

RUN #	TIME ON STREAM HRS.	REACTOR TEMP °C			PRODUCT YIELD %								CONVERSION	SPACE TIME MINUTES
		TOP	BOTTOM	AVERAGE	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME	MeOH	
II-2-1	1.25	405	396	400	97.03	2.07	0.00	0.00	0.00	0.00	0.00	0.00	98.43	3.66
II-2-2	1.50	403	394	398	98.12	1.88	0.00	0.00	0.00	0.00	0.00	0.00	94.67	6.31
II-2-3	2.25	398	387	392	98.42	1.58	0.00	0.00	0.00	0.00	0.00	0.00	91.79	6.37
II-2-4	6.25	405	391	398	96.00	2.92	0.58	0.50	0.00	0.00	0.00	0.00	100.0	5.05
II-2-5	6.75	393	388	391	48.8	5.37	0.37	3.49	0.00	14.32	27.66	0.00	82.20	5.14
II-2-6	7.25	392	286	389	32.9	9.19	0.95	9.23	0.00	22.5	25.48	0.00	78.00	5.34
II-2-7	7.75	392	384	388	29.53	12.47	1.70	14.5	0.00	36.24	5.58	0.00	74.56	5.12
II-2-8	8.25	392	385	389	12.87	9.01	1.34	11.93	0.42	33.49	5.93	0.00	83.70	5.13
II-2-9	9.00	388	383	386	25.86	29.12	2.40	35.30	0.97	0.00	0.00	6.34	77.83	5.42
II-2-10	9.75	388	382	385	19.67	17.41	0.67	18.62	0.00	43.63	21.25	0.00	56.00	4.57
II-2-11	10.75	387	379	383	14.06	17.59	1.99	20.12	0.40	45.42	0.42	0.00	29.00	5.17
II-2-12	11.75	386	381	384	15.24	14.54	1.93	18.38	0.32	47.77	1.83	0.00	80.00	5.28
II-2-13	12.25	388	382	384	11.64	11.89	1.61	15.12	0.50	15.32	43.92	0.00	82.15	5.34
II-2-14	12.75	388	382	385	8.93	12.84	1.78	14.94	0.75	18.77	41.99	0.00	82.88	5.39
II-2-15	13.75	389	383	386	9.92	14.25	1.92	16.03	1.46	24.50	31.92	0.00	74.88	4.57
II-2-16	14.75	389	383	385	16.08	32.53	2.17	22.03	4.65	20.61	1.93	0.00	78.63	5.14
II-2-17	15.75	389	383	386	14.17	20.45	2.40	25.22	1.20	29.88	6.68	0.00	79.78	5.34
II-2-18	17.00	390	383	387	18.81	17.60	2.81	28.12	0.81	24.75	7.09	0.00	39.25	5.26
II-2-19	18.25	392	385	389	16.80	20.70	1.68	22.94	1.39	30.20	6.29	0.00	81.17	5.32
II-2-20	19.00	392	385	388	10.71	12.83	2.00	16.06	1.52	24.71	32.18	0.00	78.29	5.42

Date: 5/31/78

Catalyst: Catalyst Charged on 26th May.

Feed: Pure MeOH with 6000 ppm CS₂

Reactor Pressure: 100 psig.

Room Temp: 75°F Barometric pressure: 29.82 in

Previous History: Regenerated with air at 450°C with about 60 ml/min air for 42 hours and then kept under a static Nitrogen blanket.

TABLE I. EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR SYSTEM
CONT'D.

RUN #	TIME ON STREAM HRS.	REACTOR TEMP °C			PRODUCT YIELD %								CONVERSION MeOH	SPACE TIME MINUTES
		TOP	BOTTOM	AVERAGE	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME		
II-3-1	1.25	385	385	382	99.04	0.96	0.00	0.00	0.00	0.00	0.00	0.00	92.28	5.17
II-3-2	1.50	386	379	383	91.81	4.00	3.10	1.09	0.00	0.00	0.00	0.00	73.2	5.11
II-3-3	1.75	387	379	383	44.85	13.75	7.05	9.36	4.71	19.15	1.15	0.00	82.17	5.09
II-3-4	2.75	386	381	383	29.43	14.92	9.92	16.78	7.01	20.65	1.29	0.00	81.17	5.18
II-3-5	3.42	392	385	388	25.77	19.91	8.93	28.18	5.78	9.96	1.47	0.00	75.06	5.12
II-3-6	4.42	405	398	402	24.51	17.44	10.19	25.31	5.27	15.41	2.88	0.00	94.12	5.08
II-3-7	5.42	397	392	395	62.17	4.18	3.46	5.01	2.97	9.52	1.48	11.19	92.11	4.57

Date: 6/2/78

Catalyst: Catalyst Charged on 26th May.

Feed: Pure MeOH, No CS₂

Reactor Pressure: 100 psig

Room Temp: 73°F Barometric pressure: 29.88 in

Previous History: Regenerated with air at 800°F with 40 ml/min air for 21 hours.

RUN #	TIME ON STREAM HRS.	REACTOR TEMP C			PRODUCT YIELD %								CONVERSION MeOH	SPACE TIME MINUTES
		TOP	BOTTOM	AVERAGE	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME		
II-4-1	1.32	405	393	399	33.96	3.48	0.07	0.09	0.00	0.00	0.00	62.40	99.23	1.92
II-4-2	3.58	407	394	401	43.92	10.28	0.14	0.15	0.32	0.00	0.00	45.20	94.59	1.81
II-4-3	4.58	405	393	399	37.24	18.25	0.80	1.52	2.79	0.00	0.00	38.69	95.19	1.79

Regenerated with air at 828°F for 27 hours and kept at the same temperature under N₂ blanket.

TABLE I. EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR SYSTEM
CONT'D.

Date: 6/8/78
Catalyst: Charged on 26th May
Feed: Pure MeOH, No CS₂
Reactor Pressure: 100 psig
Room Temp: 74°F Barometric pressure: 29.85 in
Previous History: Regenerated and kept under N₂ blanket.

RUN #	TIME ON STREAM HRS.	REACTOR TEMP °C			PRODUCT YIELD %								CONVERSION MeOH	SPACE TIME MINUTES
		TOP	BOTTOM	AVERAGE	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME		
II-5-1	2.50	413	395	404	40.60	17.42	17.82	3.84	1.03	0.00	0.00	19.28	87.41	5.13
II-5-2	3.83	409	396	403	17.21	9.16	6.54	8.18	4.04	0.00	0.00	54.87	62.5	5.21
II-5-3	4.33	410	397	403	18.51	13.36	7.52	10.84	0.00	0.00	0.00	49.8	89.75	5.13
II-5-4	6.03	406	398	402	58.66	6.85	4.73	6.30	4.72	0.00	0.00	18.75	89.92	5.16
II-5-5	8.53	411	391	401	0.00	0.10	0.18	0.00	20.00	0.00	0.00	79.73	39.27	5.04
II-5-6	9.53	411	391	402	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100.00	80.00	4.46

Date: 6/9/78
Catalyst: Charged on 26th May
Feed: 64% Water, 36% MeOH mole %, No CS₂
Reactor Pressure: 25 psig
Room Temp: 75°F Barometric pressure: 29.78 in
Previous History: Regenerated overnight.

RUN #	TIME ON STREAM HRS.	REACTOR TEMP °C			PRODUCT YIELD %								CONVERSION MeOH	SPACE TIME MINUTES
		TOP	BOTTOM	AVERAGE	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME		
II-6-1	3.25	412	390	401	1.38	1.06	1.42	44.93	4.19	46.23	0.00	0.79	46.2	1.93
II-6-2	4.25	413	392	402	0.52	0.01	2.13	0.21	0.00	0.00	0.00	97.04	97.9	1.49
II-6-3	6.25	415	393	404	1.77	0.01	3.19	6.93	1.13	0.00	0.00	86.96	98.52	1.36

Catalyst is completely deactivated. Therefore stopped the run.

TABLE I. EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR SYSTEM
CONT'D.

Date: 6/19/78

Catalyst: Charged on 26th May

Feed: 64% Water, 36% MeOH and 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temp: 73°F Barometric pressure: 29.9 in

Previous History: The Catalyst has been regenerated and kept under Nitrogen.

RUN #	TIME ON STREAM HRS.	REACTOR TEMP °C			PRODUCT YIELD %								CONVERSION MeOH	SPACE TIME MINUTES
		TOP	BOTTOM	AVERAGE	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME		
II-7-1	1.15	427	399	413	0.02	8.03	0.43	32.43	0.61	49.09	9.34	0.00	48.54	1.4412
II-7-2	1.72	426	401	413	0.00	5.07	0.07	37.73	0.00	29.83	27.31	0.00	13.23	0.29
II-7-3	3.06	426	401	413	0.00	4.95	0.17	49.91	0.69	44.29	0.00	0.00	84.92	0.4977
II-7-4	4.31	426	400	413	0.23	4.50	0.51	36.27	1.84	51.22	0.00	5.43	86.58	0.3219
II-7-5	6.06	425	401	413	0.02	1.04	0.08	86.78	0.52	10.71	0.00	0.85	97.09	1.8663
II-7-6	10.12	423	398	411	0.00	7.66	0.00	59.87	1.42	24.38	0.00	20.96	54.78	1.8731

Date: 6/20/78

Catalyst: Charged on 26th May

Feed: 64% Water, 36% MeOH by mole and 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temp: 74°F Barometric Pressure 29.92 in

Previous History: Regenerated Overnight

RUN #	TIME ON STREAM HRS.	REACTOR TEMP °C			PRODUCT YIELD %								CONVERSION MeOH	SPACE TIME MINUTES
		TOP	BOTTOM	AVERAGE	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME		
II-8-1	0.50	412	401	407	0.27	5.58	0.38	29.29	0.55	44.34	19.21	0.38	51.08	0.545
II-8-2	2.06	412	400	406	0.09	3.01	2.06	24.35	0.62	36.40	33.00	0.46	90.08	2.18
II-8-3	3.06	414	400	407	0.23	0.66	1.08	52.07	0.57	19.72	20.31	5.37	90.61	0.793

Stopped because of leak in the system.

TABLE I. EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR SYSTEM
CONT'D.

Date: 6/23/78
Catalyst: Charged on 26th May
Feed: 64% Water, 36% MeOH by mole and 2000 ppm CS₂
Reactor Pressure: 25 psig
Room Temp: 74°F Barometric pressure: 29.92 in
Previous History: Kept under N₂, no regeneration.

RUN #	TIME ON STREAM HRS	REACTOR TEMP °C			PRODUCT YIELD %								CONVERSION MeOH	SPACE TIME MINUTES
		TOP	BOTTOM	AVERAGE	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME		
II-9-1	0.25	399	382	391	0.12	1.57	0.33	6.82	1.48	3.59	3.81	82.28	65.48	0.1654
II-9-2	0.50	407	383	395	0.09	1.18	0.25	5.06	1.09	2.66	38.09	51.58	21.24	0.1709
II-9-3	1.25	396	383	390	0.21	11.42	1.11	58.79	5.48	13.00	1.25	8.74	87.8	0.251
II-9-4	1.75	397	384	390	0.04	1.97	0.19	16.11	0.36	4.68	0.00	76.65	45.39	0.218
II-9-5	2.25	396	384	390	0.21	9.54	0.85	67.90	5.62	7.99	0.94	6.95	90.70	0.322

Continued the run for another 4 hours. The data were not good because of too much liquid product.

Date: 6/26/78
Catalyst: Charged on 26th May
Feed: Pure MeOH and 2000 ppm CS₂
Reactor Pressure: 100 psig
Room Temp: 74°F Barometric pressure: 29.80 in
Previous History: Regenerated from 23rd 5:30 PM to 24th 11:45 PM then put on N₂.

RUN #	TIME ON STREAM HRS.	REACTOR TEMP °C			PRODUCT YIELD %								CONVERSION MeOH	SPACE TIME MINUTES
		TOP	BOTTOM	AVERAGE	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME		
II-10-1	0.50	407	391	399	2.15	6.01	0.62	60.30	0.00	14.67	16.32	0.00	75.00	3.96
II-10-2	1.75	407	392	400	14.07	17.60	1.99	20.14	0.40	45.38	0.42	0.00	60.19	3.21
II-10-3	3.47	404	395	400	7.54	10.52	15.43	14.62	0.62	15.78	35.48	0.00	75.74	4.403
II-10-4	5.25	404	394	399	5.80	7.78	12.82	11.62	10.82	20.19	13.29	17.69	100.00	3.26

TABLE I. EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR SYSTEM
CONT'D.

RUN #	TIME ON STREAM HRS.	REACTOR TEMP °C			PRODUCT YIELD %								CONVERSION MeOH	SPACE TIME MINUTES
		TOP	BOTTOM	AVERAGE	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME		
II-10-5	6.50	402	392	398	3.83	6.88	7.89	21.63	2.41	17.81	39.55	14.32	34.8	2.15
II-10-6	7.25	401	394	398	1.03	2.22	3.10	7.57	8.29	67.15	9.44	1.20	38.7	3.36
II-10-7	8.40	408	401	405	25.94	6.90	6.79	24.24	3.64	28.18	3.76	0.53	78.31	2.5212

Date: 6/27/78

Catalyst: Charged on 26th May

Feed: Pure MeOH with 2000 ppm

Reactor Pressure: 100 psig

Room Temp: 74°F Barometric pressure: 29.86 in

Previous History: Regenerated overnight.

RUN #	TIME ON STREAM HRS.	REACTOR TEMP °C			PRODUCT YIELD %								CONVERSION MeOH	SPACE TIME MINUTES
		TOP	BOTTOM	AVERAGE	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	CME		
II-11-1	2.50	403	398	401	68.20	2.35	3.40	9.28	0.87	10.21	4.55	1.14	56.76	1.209
II-11-2	2.90	402	393	398	28.05	6.04	11.18	19.72	4.77	13.64	15.72	0.88	74.83	1.053
II-11-3	3.90	403	391	397	13.83	6.74	9.32	36.22	9.61	21.72	10.01	2.56	74.49	1.053
II-11-4	4.90	409	395	402	9.20	65.4	3.82	9.50	1.98	5.78	0.72	3.52	96.43	1.72
II-11-5	6.40	406	400	403	6.41	10.95	0.00	40.73	5.30	24.31	16.25	0.00	84.32	3.71
II-11-6	9.50	409	401	405	0.80	14.36	0.54	44.09	7.09	28.56	1.39	3.16	81.5	4.09

Date: 6/28/78

Reactor Pressure: 100 psig

Room Temp: 73°F Barometric pressure: 29.72 in

Regenerated for 10 hrs.

TABLE I. EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR SYSTEM
CONT'D.

RUN #	TIME ON STREAM HRS.	REACTOR TEMP °C			PRODUCT YIELD %								CONVERSION MeOH	SPACE TIME MINUTES
		TOP	BOTTOM	AVERAGE	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME		
II-12-1	1.75	378	367	373	0.00	56.84	0.00	23.29	10.58	7.59	1.69	0.00	92.39	5.04
II-12-2	2.50	377	368	373	1.18	17.14	0.56	42.06	5.90	16.58	9.86	6.72	94.07	0.8187
II-12-3	4.5	381	370	375	0.81	12.94	0.50	39.87	5.31	23.49	11.75	5.33	94.57	2.13
II-12-4	5.5	382	372	377	0.74	13.13	0.48	40.35	6.16	25.77	8.86	4.51	96.62	5.0613
II-12-5	6.65	383	373	378	1.16	11.79	0.30	36.06	5.06	28.79	12.26	4.58	96.02	4.95
II-12-6	7.15	387	374	380	1.32	13.4	0.51	37.08	9.47	26.11	7.48	4.03	97.8	7.25
II-12-7	9.25	391	383	386	1.29	14.69	0.91	37.99	5.77	24.05	7.52	7.77	96.	5.2
II-12-8	10.25	391	383	386	0.87	15.68	0.86	36.10	6.71	19.12	0.00	12.34	93.1	4.72

There is no run 13. Next run is #14 as shown

Run #14

Date: 8/8 AW500 Exchanged units ammonia and rare earth chloride - Prep. A. Charge II.

Feed: 64% H₂O, 36% MeOH + 2000 ppm CS₂

Reactor Pressure: 100 psig

Room Temperature 73°F Barometric Pressure: 29.9 in

Previous History: Left unregenerated on 3rd, regenerated on 4th till 4:30PM, N₂ blanket

Run #	Time, hr	Temp, °C	1/LHSV	X%*	PRODUCT YIELD %						
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ & C ₃	DME
II-14- 1	0.75	386	7.07	—	0.02	0.02	0.01	0.03	0.03	0.00	0.00
II-14- 2	1.50	386	6.25	85.8	0.25	4.02	0.46	35.06	1.57	53.86	4.78
II-14- 3	2.42	386	6.25	85.4	0.23	3.28	0.32	30.43	1.30	60.05	4.39
II-14- 4	3.75	386	5.80	84.5	0.13	6.05	0.47	49.64	1.42	37.02	5.27
II-14- 5	4.08	385	5.32	85.4	0.12	6.50	3.76	34.89	1.11	47.21	6.41
II-14- 6	4.91	385	2.16	77.2	0.72	5.84	12.96	40.60	0.66	27.37	11.84
II-14- 7	5.43	384	2.2	73.8	0.54	4.07	16.21	39.18	0.90	26.76	12.33
II-14- 8	6.16	383	2.32	83.22	0.76	2.79	9.23	17.04	0.65	21.46	48.07
II-14- 9	6.58	383	2.34	83.8	0.53	3.57	7.66	14.93	0.65	21.92	50.74
II-14-10	8.83	385	2.32	75.48	0.85	9.97	5.16	26.14	1.01	45.25	11.63

* X% is the percent conversion of methanol. LHSV=volumetric flow rate of liquid methanol by volume catalyst.

*In Runs #14 through #20 difficulties were encountered in separating the C₃⁼ and C₃. Therefore where reported separately, the sum is more accurate.

TABLE I. EXPERIMENTAL DATA OBTAINED WITH BERTY® REACTOR SYSTEM

CONT'D.

Run #15

Date: 8/14 AW500 Recl Amm - II

Feed: Pure methanol with 2000 ppm CS₂

Room Temperature: 72°F, Barometric Pressure: 29.80 in

Previous History: Regenerated for 38 hrs. 120 ml/min air at 856°F and then under N₂
Ran out of air in the middle

Run #	Time, hrs	Temp °C	1/LHSV	X%	Product Yield %							Press, psig
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ ⁼ & C ₃	DME	
II-15-1	2.15	383	4.59	88.52	4.21	3.72	1.03	21.85	0.00	68.76	0.43	250
II-15-2	2.85	380	4.59	88.0	2.31	3.34	1.06	21.13	0.08	71.70	0.38	245
II-15-3	3.93	381	4.59	87.9	3.02	3.21	1.09	21.73	0.74	69.6	0.60	160
II-15-4	5.68	382	4.59	76.8	0.95	3.11	0.48	31.79	0.23	62.26	1.18	250
II-15-5	6.25	383	1.92	28.96	1.82	11.70	0.02	9.33	0.05	25.12	51.96	255

Run #16

Date: 8/16 AW500 Recl Amm - II

Feed: Pure Methanol with 2000 ppm CS₂

Room Temperature: 74°F, Barometric Pressure: 29.96 in

Previous History: Regenerated for 13 hrs. at 792°F flow 100 ml/min

Run #	Time, hrs	Temp °C	1/LHSV	X%	Product Yield %							Press, psig
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ ⁼ & C ₃	DME	
II-16-1	1.58	406	2.70	77.3	6.14	4.74	1.28	26.18	1.44	59.80	0.42	180
II-16-2	1.99	403	2.69	43.0	4.07	6.08	2.49	18.93	5.01	61.35	2.07	122
II-16-3	2.99	408	2.67	48.0	9.29	2.53	2.71	22.57	1.51	57.31	4.07	220
II-16-4	9.21	387	3.24	67.3	6.70	4.90	1.43	17.64	2.52	60.60	6.22	245
II-16-5	12.62	386	3.24	67.4	5.99	4.67	1.92	10.97	1.87	68.72	5.86	255

TABLE I. EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR
SYSTEM - CONT'D.

Run #17

Date: 8/20 AW500 Recl Amm II

Feed: Pure Methanol with 2000 ppm CS₂

Room Temperature: 69°F Barometric Pressure: 29.84 in

Previous History: Regenerated for 20 hrs at 786°F Flowrate

Run #	Time hr	Temp °C	1/LHSV	X %	PRODUCT YIELD, %								Pressure
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME	
II-17- 1	0.50	398	2.71	59	6.92	5.48	3.83	11.24	2.34	32.16	12.98	0.00	120
II-17- 2	0.75	394	2.70	87	7.42	3.89	2.94	10.94	4.86	28.48	10.46	0.00	120
II-17- 3	1.05	395	12.10	86	6.94	5.46	4.23	9.89	5.32	33.62	9.29	0.00	140
II-17- 4	1.30	393	12.1	96	5.91	4.05	2.74	8.38	1.14	43.53	34.24	0.02	150
II-17- 5	2.05	393	12.2	96	7.49	5.35	3.52	12.42	1.65	59.86	9.71	0.00	150
II-17- 6	3.63	393	12.1	96	4.06	3.16	1.29	7.42	1.26	46.56	36.26	0.00	150
II-17- 7	4.88	393	12.2	97	8.89	7.19	5.36	15.27	1.81	53.71	7.76	0.00	155
II-17- 8	6.38	393	12.3	97	3.90	5.66	3.46	20.70	2.77	53.69	9.82	0.00	150
II-17- 9	7.13	392	12.1	96	7.69	6.75	4.37	21.19	2.95	48.35	8.68	0.00	150
II-17-10	7.63	392	12.1	96	7.18	5.13	3.58	20.68	2.20	50.45	10.79	0.00	155
II-17-11	8.13	393	12.1	96	6.31	4.18	3.53	19.84	2.42	51.15	12.58	0.00	155

Run #18

Date: 8/22 AW500 Recl Amm II

Feed: Pure methanol with 2000 ppm CS₂

Room Temperature: 69°F, Barometric Pressure: 29.84 in,

Previous History: No regeneration, kept under N₂ at 393°C

Run #	Time hr	Temp. °C	1/LHSV	X %	PRODUCT YIELD, %								Pressure
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME	
II-18-1	0.50	398	2.03	96.8	6.99	7.02	2.82	22.83	1.37	55.90	0.53	2.53	255
II-18-2	0.76	398	2.03	90.3	2.45	4.98	1.03	16.31	1.40	39.60	31.44	2.78	250
II-18-3	1.56	398	6.25	93.2	5.21	4.93	1.40	20.25	0.85	44.00	20.86	2.52	255
II-18-4	2.39	398	6.25	92.0	4.80	4.31	1.07	16.34	8.14	41.73	21.58	2.03	240
II-18-5	3.39	399	6.28	93.0	4.71	2.49	1.32	19.06	1.00	46.59	22.29	2.54	245
II-18-6	4.72	401	12.74	93.8	4.13	3.51	1.96	12.07	0.97	50.14	22.60	4.63	250
II-18-7	5.78	401	12.72	86.5	0.19	0.38	0.02	0.18	0.01	0.14	0.00	99.09	180

TABLE I. EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR SYSTEM
COND'T

Run #19 AW500 Recl Amm - II Date 8/24

Feed: Pure methanol with 2000 ppm CS₂ through 45 grams of γ -Alumina then into Berty[®] Reactor.

Room Temp: 72°F, Barometric pressure 29.88 Reactor pr: 25 psig

Previous History: Regenerated at 880°F for 22 hrs at 52 ml/min.

Run #	Time, hrs	Temp °C	1/LHSV	X%	Product Yield %						
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ ⁼ & C ₃	DME
II-19-1	0.51	397	1.71	89.01	0.00	0.29	0.00	1.67	0.00	1.93	96.11
II-19-2	0.76	398	1.71	85.03	0.00	0.30	0.00	2.50	0.00	0.00	97.20
II-19-3	1.66	406	1.71	80.84	0.00	0.00	0.00	0.00	0.00	0.00	100.00

Run # 20 AW500 Recl Amm - II Date 8/28

Feed: Pure Methanol with 2000 ppm CS₂ through 45 grams of γ -Alumina then into Berty[®] Reactor

Room Temp: 72°F, Barometric pressure 29.85 in., Reactor Pressure: 25 psig

Previous History: No Regeneration after Run II-19-3 on 8/24, kept under Nitrogen.

II-20-1	1.30	397	16.26	49.6	0.00	0.14	0.00	1.06	0.00	1.85	96.94
II-20-2	1.76	397	16.28	62.4	0.00	0.77	0.00	5.37	0.11	11.73	82.02
II-20-3	2.52	396	16.20	71.41	0.01	0.74	0.02	5.61	0.30	10.02	83.30
II-20-4	3.02	395	16.20	67.58	0.00	0.34	0.00	2.91	0.06	16.61	80.08
II-20-5	4.52	395	13.00	59.68	0.00	0.51	0.00	3.96	0.21	3.52	91.80
II-20-6	5.18	395	13.04	58.20	0.04	0.88	0.05	4.34	0.55	63.20	87.20

For the Runs # 1 through #20 material balances are not available. The reported yields are based on the GC output. The temperature gradient across the catalyst bed was 10°C. Temperature above the bed is T_{ave} +5 and the temperature below the bed is T_{ave} -5. Runs 14 through 20 have propylene and propane reported together in most cases.

Beginning with Run #21 all results are based on material balance calculations. In most cases closures were within 10%.

TABLE-EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR
SYSTEM-CONT'D.

Run #21

Date: 9/18 AW500 Recl Amm - II

Feed: Pure MeOH + 2000 ppm CS₂

Room Temperature: 73°F, Barometric Pressure 29.50 in

Reactor Pressure: 25 psig

Previous History: Regenerated at 857°F, 40 ml/min for 10.15 hours

Run #	Time hr	Temp °C	1/LHSV	X %	PRODUCT YIELD, %							
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
II-21-1	1.75	396	11.68	92.5	1.1	5.6	7.	33.	1.1	31.4	23.5	3.6
	1.75	396	11.68	92.25	1.1	5.6	7.	33.	1.1	31.6	23.6	3.3
II-21-2	4.5	396	6.94	69.84	1.8	6.6	7.	29.2	1.0	32.5	24.3	3.9
	4.5	396	6.94	69.51	1.9	6.6	7.	29.3	1.0	32.6	24.4	3.4
II-21-3	8.6	392	5.00	80.04	2.3	15.9	1.0	26.6	5.2	11.4	19.2	18.5
	8.6	392	5.00	81.62	2.0	14.2	.9	23.7	4.6	10.2	17.2	27.2
II-21-4	11.08	396	3.84	62.28	1.9	12.5	.8	20.1	3.1	8.6	5.1	47.9
	11.08	396	3.84	64.76	1.4	8.8	.6	14.1	2.2	6.0	3.5	63.4
II-21-5	12.33	395	2.5	29.76	2.0	1.1	0.0	0.0	0.0	0.0	0.0	98.6
	12.33	395	2.5	29.81	0.0	2.	0.0	0.0	0.0	0.0	0.0	99.8

The bed height was changed on 9/25 from 3.5" to 0.5". With 0.5" bed depth, temperature is accurate to a $\pm 1.0^\circ\text{C}$. The data reported in Runs 2 through 21 were obtained on the catalyst charged May 26, 1978. After Run 21 the catalyst was accidentally heated to 1380°F. Therefore, a fresh charge from batch preparation A was placed in the reactor.

TABLE I-EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR
SYSTEM-CONT'D.

Run #22 AW500 Recl Amm - III Date 10/25

Feed: MeOH + 2000 ppm CS₂

Room Temp: 74°F, Br. Pr. 29.50 in, Reactor Pressure 25 psig.

Previous History: Fresh Sample of catalyst charged on 10/20.

Run #	Time hr	Temp °C	1/LHSV	X, %	PRODUCT YIELD %							
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
III-22-1	1.92	363	12.19	88.37	1.8	12	1.1	28.7	1.2	26.1	22.5	6.6
	1.92	363	12.19	88.22	1.8	12	1.1	28.8	1.2	26.2	22.6	6.4
III-22-2	6.72	362	5.45	66.83	1.9	14.1	0.9	25.7	3.1	7.2	11.9	35
	6.72	362	5.45	69.02	1.5	10.9	.7	19.9	2.4	5.6	9.2	49.8

Run #23 AW500 Recl Amm - III Date 11/13

Feed: MeOH + 2000 ppm CS₂

Room Temp: 74 Br. Pr. 29.56 in, Reactor Pressure 25 psig

Previous History: Regenerated at 892°F for 14.5 hrs. at 46 ml/hr.

Run #	Time hr	Temp °C	1/LHSV	X %	PRODUCT YIELD %							
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
III-23-1	1.25	423	13.88	94.5	1.6	7.0	1.7	33.5	1.7	23.5	27.0	4
	1.25	423	13.88	94.3	1.6	7.1	1.8	33.5	1.7	23.5	27.	3.8
III-23-2	4.67	423	9.60	83.0	1.5	4.5	1.1	40.2	2.1	23.7	17.9	9.0
	4.67	423	9.60	83.	1.5	4.5	1.1	40.2	2.1	23.7	17.9	9.
III-23-3	6.42	422	5.0	65.10	2.1	4.0	1.5	29.7	3.5	19	21.6	18.5
	6.42	422	5.0	71.00	1.9	3.7	1.4	27.3	3.2	17.5	19.9	25.
III-23-4	8.58	423	2.81	38.34	1.3	6.4	1.0	14.4	3.8	10.1	10.9	52.1
	8.58	423	2.81	38.34	1.1	5.6	.9	12.6	3.3	8.9	9.5	58.1

TABLE I-EXPERIMENTAL DATA OBTAINED WITH BERTY REACTOR
SYSTEM-CONT'D.

Run #24

Date: 11/15 AW500 Recl Amm - III

Feed: MeOH + 2000 ppm CS₂

Room Temperature: 73°F Barometric Pressure: 29.56 in, Reactor Pressure 25 psig

Previous History: Regenerated at 960°F for 10 hrs, air 54 ml/hr

Run #	Time hr	Temp °C	1/LHSV	X %	PRODUCT YIELD %							
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
IIF-24-1	2.00	421	12.82	94.5	1.6	7.0	1.7	33.5	1.7	23.5	27.	4.00
	2.00	421	12.82	94.3	1.6	7.1	1.8	33.5	1.7	23.5	27.	3.80
IIF-24-2	5.00	421	12.82	90.88	1.3	7.3	1.4	33.4	2.0	23.4	25.6	5.70
	5.00	421	12.82	90.50	1.2	7.4	1.6	35.8	2.3	24.6	21.3	5.9
IIF-24-3	7.00	420	12.82	83.8	2.8	8.1	2.4	24.2	1.7	24.9	27.5	8.4
	7.00	420	12.82	85.15	2.8	8.0	2.4	23.8	1.7	24.5	27.1	9.8
IIF-24-4	10.20	421	12.82	82.3	6.0	4.7	3.3	18.4	3.1	17.8	30.8	15.9
	10.20	421	12.82	82.57	5.6	4.4	3.1	17.4	3.0	16.8	29.0	20.7
IIF-24-5	11.60	421	12.82	76.8	6.2	4.8	3.2	16.4	3.0	16.8	22.0	21.8
	11.60	421	12.82	76.4	6.1	4.6	3.2	16.4	3.0	17.2	26.8	22.6

Run #25 AW500 Recl Amm - III Date 11/28

Feed: Methanol + 2000 ppm CS₂

Room Temp: 73°F Br Pr 29.50 in, Reactor Pressure 25 psig

Previous History: Regenerated at 856°F for 12.5 hours air 50 ml/min.

Run #	Time hr	Temp °C	1/LHSV	X %	PRODUCT YIELD %							
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
III-25-1	2.33	416	6.67	87.24	1.6	4.6	1.7	39.1	6.4	21.2	20.0	5.5
	2.33	416	6.67	87.07	1.6	4.6	1.7	39.2	6.4	21.2	20.0	5.3
III-25-2	5.08	416	6.67	83.56	1.7	5.5	2.7	32.2	6.8	26.8	18.3	6.1
	5.08	416	6.67	83.56	1.7	5.5	2.7	32.3	6.8	26.9	18.3	6.1
III-25-3	8.67	416	6.67	76.45	2.2	6.6	3.2	30.0	8.6	19.7	21.0	8.7
	8.67	416	6.67	76.31	2.2	6.6	3.2	30.0	8.6	19.8	21.0	8.6
III-25-4	10.92	416	6.67	71.65	1.9	3.4	4.2	27.1	7.9	22.4	21.6	11.6
	10.92	416	6.67	71.65	1.9	3.4	4.2	27.1	7.9	22.4	21.6	11.6
III-25-5	12.42	416	6.67	52.35	1.3	2.9	1.0	7.7	2.6	1.6	1.6	61.7
	12.42	416	6.67	52.16	1.3	2.9	1.0	9.7	3.3	2.1	2.1	77.6

TABLE I. EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR SYSTEM
CONT'D.

Run #26 Date 12/11

Feed: Methanol + 2000 ppm CS₂

Room Temp: 73°F Barometric Pressure 29.50 in Reactor Pressure: 25 psig

Previous History: Regenerated at 864°F for 11.5 hours air 53 ml/min.

Run #	Time hrs	Temp °C	1/LHSV	X%	Product Yield %							
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
III-26-1	0.67	438	13.16	94.28	1.5	4.0	1.1	32.4	3.0	29.6	22.9	5.6
	0.67	438	13.16	94.28	1.5	4.0	1.1	32.4	3.1	31.1	24.1	5.9
III-26-2	1.58	438	8.20	88.08	1.1	5.1	0.6	30.5	1.9	31.0	23.2	6.5
	1.58	438	8.20	87.91	1.1	5.1	0.6	30.6	1.9	31.1	23.3	6.2
III-26-3	2.00	438	5.49	81.49	1.2	3.4	2.1	27.5	4.3	30.8	22.8	7.9
	2.00	438	5.49	81.49	1.2	3.5	2.2	29.0	4.5	32.5	24.1	8.3
III-26-4	3.50	438	2.58	55.57	0.9	5.8	2.4	20.4	6.5	18.7	14.4	18.9
	3.50	438	2.58	55.87	1.0	6.6	2.7	23.1	7.4	21.2	16.3	21.7
III-26-5	6.25	437	1.72	32.30	1.3	4.8	2.4	1.2	1.2	1.8	1.7	85.4
	6.25	437	1.72	32.33	1.3	4.9	2.3	1.2	1.2	1.8	1.7	85.4

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Run #27 Date 11/31

Feed: Methanol + 2000 ppm CS₂

Room Temp: 73°F Barometric Pr 29.85 in. Reactor Pressure: 25 psig

Previous History: Regenerated 12 hrs. air 50 ml/min 875°F.

Run #	Time hrs	Temp °C	1/LHSV	X %	Product Yield %							
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
III-27-1	1.3	415	11.63	91.77	1.1	5.2	0.6	30.7	1.9	29.9	21.9	6.6
	1.3	415	11.63	91.57	1.1	5.3	0.7	31.5	2.0	30.7	22.5	6.3
III-27-2	2.65	415	6.09	85.14	1.1	4.2	2.8	29.6	4.2	28.0	23.8	6.9
	2.65	415	6.09	85.20	1.2	4.3	2.6	29.6	4.1	28.0	23.9	7.0
III-27-3	4.18	415	3.29	65.07	1.2	5.9	4.9	21.8	9.5	24.0	21.7	11.60
	4.18	415	3.29	65.10	1.2	5.8	4.7	21.6	9.7	24.2	21.7	11.60
III-27-4	8.5	415	2.34	51.66	1.0	7.0	3.4	24.1	6.8	20.5	14.7	22.4
	8.5	415	2.34	52.39	1.0	5.9	3.4	23.9	6.8	20.3	14.6	23.1
III-27-5	10.1	415	1.87	35.72	0.7	4.5	2.5	9.89	3.2	8.4	5.6	65.21
	10.1	415	1.87	35.84	0.8	4.6	2.3	9.89	3.2	8.4	5.7	65.3

TABLE I. EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR SYSTEM
CONT'D

Run #28 Date 12/6

Feed: Methanol + 2000 ppm CS₂

Room Temp: 72°F Br. Pr. 29.82 Re Pr. 25 psig

Previous History: Regenerated at 925°F for 16 hours air 38 ml/min.

Run #	Time hrs	Temp °C	1/LHSV	X%	Product Yield %							
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
III-28-1	1.92	384	16.13	91.39	1.7	5.1	1.4	26.4	5.4	32.1	18.9	9.1
	1.92	384	16.13	91.28	1.7	5.1	1.4	26.4	5.4	32.1	18.9	8.9
III-28-2	3.27	384	7.937	75.25	2.3	6.7	1.7	27.4	3.7	30.3	17.6	10.1
	3.27	384	7.937	74.90	2.3	6.8	1.7	27.6	3.7	30.5	17.7	9.7
III-28-3	4.27	384	5.682	70.82	1.4	6.7	1.5	23.2	4.1	27.5	22.8	12.7
	4.27	384	5.682	70.82	1.5	6.6	1.6	23.4	4.3	27.6	22.7	12.8
III-28-4	5.19	385	3.94	69.61	1.8	6.9	1.5	23.9	4.0	27.2	21.2	13.5
	5.19	385	3.94	68.75	1.8	7.0	1.6	24.3	4.0	27.6	21.6	12.1
III-28-5	5.86	385	3.01	59.32	2.9	7.0	1.3	24.3	5.5	22.8	18.5	17.70
	5.86	385	3.01	58.93	2.9	7.1	1.2	24.3	5.8	22.8	18.2	17.70
III-28-6	6.94	385	2.23	28.54	2.7	8.6	9.5	11.80	4.6	13.6	9.2	40.00
	6.94	385	2.23	28.76	2.5	8.7	9.5	11.81	4.6	13.6	9.2	40.00

Run #29 Date 12/8

Feed: Methanol + 2000 ppm CS₂

Room Temp: 70°F Br. Pr: 29.70

Previous History: Regenerated at 911°F for 10 hours air 46 ml/min.

Run #	Time hrs	Temp °C	1/LHSV	X%	Product Yield %							
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
III-29-1	1.17	361	12.05	86.59	1.70	2.8	1.8	26.2	5.4	29.5	23.1	9.5
	1.17	361	12.05	86.59	1.70	2.8	1.8	26.2	5.4	29.5	23.1	9.5
III-29-2	2.67	361	6.58	80.29	2.10	3.0	2.1	27.0	4.6	28.1	23.2	9.9
	2.67	361	6.58	80.25	2.10	3.0	2.1	27.0	4.6	28.1	23.1	9.9
III-29-3	3.92	362	3.52	54.91	4.20	3.9	6.4	29.6	5.2	20.4	19.8	10.50
	3.92	362	3.52	54.83	4.20	3.9	6.4	29.6	5.2	20.4	19.8	10.50
III-29-4	4.84	362	2.76	46.11	1.9	4.8	3.9	24.5	5.4	16.4	12.8	30.30
	4.84	362	2.76	45.95	2.1	3.9	4.2	24.8	5.2	16.5	12.8	30.30
III-29-5	5.92	359	2.46	28.33	0.9	3.6	4.3	17.6	8.7	12.1	11.9	40.90
	5.92	359	2.46	28.01	0.9	3.6	4.3	17.6	8.7	12.1	11.9	40.90

TABLE I. EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR SYSTEM
CONT'D.

Run #30 Date 12/18

Feed: Methanol + 2000 ppm CS₂

Room Temp: 70°F Br. Pr. 30.80 Reactor Pressure: 25 psig

Previous History: Regenerated at 906°F for 11.75 hours at 42 ml/min air.

Run #	Time hrs	Temp °C	1/LHSV	X%	Product Yield %							
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
III-30-1	0.58	450	19.23	91.50	1.2	6.2	0.8	33.4	3.9	35.1	14.9	4.5
	0.58	450	19.23	90.40	1.2	6.2	0.8	33.6	3.9	35.3	17.9	4.7
III-30-2	2.25	451	10.75	93.79	1.8	5.6	1.0	32.9	5.5	35.1	16.3	4.3
	2.25	451	10.75	93.62	1.9	5.6	1.1	32.9	5.5	35.1	16.3	4.3
III-30-3	3.08	451	6.13	83.84	2.7	6.2	1.8	29.2	6.0	31.2	19.0	3.90
	3.08	451	6.13	83.60	2.8	6.2	1.7	29.2	6.1	31.2	18.9	3.90
III-30-4	3.66	449	4.39	90.82	3.6	8.8	4.8	25.0	6.2	27.1	13.2	11.3
	3.66	449	4.39	90.82	3.8	8.8	4.6	25.4	6.2	26.9	12.0	11.3
III-30-5	4.74	450	3.50	73.59	1.9	5.3	7.3	23.4	5.6	23.4	18.8	15.4
	4.74	450	3.50	73.64	1.9	5.4	7.4	23.5	5.8	23.2	18.7	14.10
III-30-6	6.07	450	2.69	56.62	2.3	5.8	0.8	23.8	6.5	27.9	23.1	10.5
	6.07	450	2.69	56.62	2.3	5.8	0.8	23.7	6.6	27.9	23.1	10.6
III-30-7	6.74	449	2.37	46.36	2.1	6.0	1.1	24.2	8.8	22.3	18.8	18.78

TABLE I-EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR SYSTEM
CONT'D.

Run #31 AW500 Recl Amm - III Date 12/21

Feed: Methanol + 2000 ppm CS₂

Room Temp: 72 Br. Pr. 30.80, Reactor Pressure 25 psig

Previous History: Regenerated at 906°F 10.4 hrs. air 42 ml/min.

Run #	Time hr	Temp °C	1/LHSV	X %	PRODUCT YIELDS %							
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
III-31-1	1.25	415	12.19	94.04	1.3	5.2	2.7	36.6	4.7	23.6	17.7	8.2
	1.25	415	12.19	93.80	1.3	5.2	2.7	36.7	4.8	23.7	17.7	7.8
III-31-2	4.67	416	12.19	90.66	1.4	6.9	3.5	30.2	5.7	23.5	19.5	9.3
	4.67	416	12.19	90.14	1.4	6.9	3.5	30.4	5.7	23.7	19.7	8.5
III-31-3	7.08	417	12.19	84.95	1.3	2.3	1.4	14.2	3.6	11.7	6.9	58.6
	7.08	417	12.19	83.66	2.0	3.5	2.1	21.7	5.6	18.0	10.5	36.6
III-31-4	10.4	416	12.19	76.87	3.5	5.6	3.5	30.7	8.0	18.2	15.5	15.0
	10.4	416	12.19	76.87	3.5	5.6	3.5	30.9	8.1	18.3	15.7	14.4

Run #32 AW500 Recl Amm III Date 12/25

Feed: Methanol + 2000 ppm CS₂

Room Temp: 72 Br. Pr. 29.8

Previous History: Regenerated at 910°F 10.85 hrs. air 40 ml/min.

III-32-1	1.83	419	3.98	75.28	2.90	5.1	2.8	25.1	9.7	23.8	15.8	14.6
	1.83	419	3.98	74.16	3.0	5.3	2.9	25.8	10.00	24.5	16.2	12.4
III-32-2	4.10	419	3.98	76.62	2.5	4.5	5.0	24.6	9.5	24.2	15.2	14.6
	4.10	419	3.98	76.21	2.5	4.5	5.1	24.9	9.6	24.5	15.4	13.7
III-32-3	6.33	421	3.98	72.39	3.7	5.6	3.7	21.8	10.9	19.9	18.9	15.5
	6.33	421	3.98	72.08	3.7	5.6	3.7	22.0	11.0	20.1	19.0	14.8
III-32-4	9.75	421	3.98	63.70	3.1	6.8	5.5	19.2	9.2	19.7	17.7	18.8
	9.75	421	3.98	63.30	3.2	6.8	5.6	19.4	9.3	20.0	18.0	17.7
III-32-5	11.66	422	3.98	57.88	3.7	7.5	6.1	18.3	7.8	18.9	18.0	19.5
	11.66	422	3.98	57.39	4.0	7.7	6.2	18.6	7.9	19.3	18.3	18.1

TABLE I. EXPERIMENTAL DATA OBTAINED WITH BERTY[®] REACTOR SYSTEM
CONT'D.

Run # 33

Date: 12/26 AW500 Recl Amm - III

Feed: Methanol + 2000 ppm CS₂

Room Temperature: 73°F Barometric Pressure: 30.50

Reactor Pressure: 25 psig

Previous History: Regenerated 908°F 11.5 hrs air 40 ml/min

Run #	Temp °C	Time hrs	X%	1/LHSV	Product Yield %							
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
III-33-1	418	1.67	59.56	3.125	4.8	4.3	3.1	25.6	10.9	19.2	17.4	14.8
	418	1.67	58.74	3.125	5.0	4.4	3.2	26.2	11.1	19.6	17.8	12.7
III-33-2	417	3.50	55.05	3.125	5.8	4.3	3.7	24.1	9.8	22.4	12.9	17.0
	417	3.50	53.99	3.125	6.0	4.5	3.8	25.1	10.2	23.3	13.4	13.7
III-33-3	417	6.50	52.97	3.125	6.3	3.6	2.7	23.2	10.5	20.2	17.2	16.3
	417	6.50	52.43	3.125	6.4	3.7	2.7	23.7	10.7	20.6	17.6	14.7
III-33-4	417	7.33	55.48	3.125	6.9	4.0	3.7	19.3	7.9	21.4	14.5	22.4
	417	7.33	54.82	3.125	7.0	4.0	3.8	19.8	8.1	21.9	14.9	20.6
III-33-5	418	9.66	50.90	3.125	6.6	4.7	4.2	19.2	4.6	23.1	15.9	21.6
	418	9.66	50.33	3.125	6.7	4.7	4.3	19.5	4.7	23.5	16.1	20.6
III-33-6	419	11.33	41.57	3.125	6.2	5.1	4.2	14.7	5.6	24.6	17.4	22.3
	419	11.33	40.73	3.125	6.4	5.2	4.3	15.1	5.8	25.2	17.9	20.1

Run # 34

Date: 12/28 AW500 Recl Amm - III

Feed: Methanol + 2000 ppm CS₂

Room Temperature: 72°F Barometric Pressure: 30.66

Reactor Pressure: 25 psig

Previous History: Regenerated 906°F 12.8 hrs air 40 ml/min

Run #	Temp °C	Time hrs	X%	1/LHSV	Product Yield %							
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
III-34-1	420	1.333	47.01	2.5	1.2	3.6	2.0	20.9	32.3	13.5	9.9	16.6
	420	1.33	46.62	2.5	1.3	3.7	2.1	21.6	33.5	14.0	10.3	13.6
III-34-2	420	5.33	43.08	2.5	1.6	2.7	1.6	16.7	3.2	9.7	7.3	57.2
	420	5.33	42.84	2.5	1.7	2.8	1.7	17.4	3.3	10.1	7.6	55.5
III-34-3	419	10.33	33.99	2.5	2.7	4.6	2.5	28.7	5.3	19.9	17.8	18.5
	419	10.33	33.24	2.5	2.7	4.6	2.5	28.7	5.3	19.9	21.3	22.2
III-34-4	419	13.25	24.85	2.5	3.3	4.6	2.8	25.2	5.9	20.6	15.8	21.2
	419	13.25	24.85	2.5	3.3	4.6	2.8	25.2	5.9	20.6	15.8	21.7
III-34-5	419	15.23	27.55	2.5	4.2	5.1	2.9	23.5	6.4	18.2	16.5	27.4

Table II - Lack of Fit for Equation 8**

N	β	r^2 (correlation of determination)
1	1	0.53
-1	2	0.21
-1	1	0.46
1	2	0.40
1	0	0.07
-1	0	0.12
1/2	1	0.43
0.634*	0.71*	0.58
1.25*	0.87*	0.57

*Obtained by starting with different values of a, b, N, and β and doing a non-linear regression on conversion.

$r^2 = 1$ is a perfect fit.

**These calculations show that the rate equation for methanol should include the effects of the partial pressures of the products as indicated by Equation 6.

Table III- Equilibrium Calculations

Feed Gas: 0.895 : 0.105 ; H ₂ : CO				
500 psia			1000 psia	
Temp °C K _{eq}	Mole Fraction	Conversion	Mole Fraction	Conversion
250 2.11x10 ⁻³	0.0795	0.6533	0.1135	0.8812
300 2.88x10 ⁻⁴	0.0230	0.2091	0.0599	0.5096
350 5.32x10 ⁻⁵	0.0050	0.0467	0.0178	0.1635
400 1.24x10 ⁻⁵	0.0012	0.0114	0.0047	0.0439
450 3.51x10 ⁻⁶	0.0003	0.0032	0.0014	0.0128
Feed Gas: 0.50 : 0.50 ; H ₂ : CO				
250	0.1500	0.2305	0.9384	0.6523
300	0.0359	0.0670	0.1044	0.1727
350	0.0075	0.0147	0.0275	0.0521
400	0.0018	0.0036	0.0070	0.0138
450	0.0005	0.0010	0.0020	0.0040

Figure 1. Product distribution from a tubular reactor

Figure 2. Product distribution from a tubular reactor

Figure 3. Product distribution when feeding DME into the tubular reactor system. (Lin, Chao, Anthony, 1977)

Figure 4. Bertv® Reactor System

FIGURE 5. CATALYST ACTIVITY IN THE ABSENCE OF CS_2

Figure 6. Effect of CS_2 on Activity and Yields

Date: 6/19/78 Run II-7
 Catalyst: AW500 ReCl_3 Amm Regenerated
 Feed: 64% water, 36% MeOH by mole and 2000 ppm CS_2
 Reactor Pressure: 25 psig
 Temp: Top 425°C Bottom 401°C
 Conversion: 82%
 Space Time: 1.41 minutes

Figure 7. Effect of Water on Yields in Presence of CS_2

Figure 8. Effect of Pressure on Feeding Pure MeOH in the Presence of CS_2

Figure 9. Conversions uncorrected for catalyst decay

Figure 10. Variation of Yields with Time on Stream

Figure 11. Effect of temperature on Carbon Yields

Figure 12. Variation of methanol conversion with time on stream and reciprocal liquid hourly space velocity (1/LHSV)

Figure 13. Product distribution obtained for a decaying catalyst at time on stream of 1 to 2.5 hrs.

Figure 14. Product distribution for time on stream of 5 to 8 hrs on a decaying catalyst

Figure 15. Product Distribution obtained at Time-on-Stream of Ten Hours or Greater on a Decaying Catalyst