Errata:
Data that show
reaction pressure of
25 psig were actually
taken at approximately
1 atm.

R. J. Anthony
1/8/80

CATALYTIC CONVERSION OF METHANOL TO LOW
MOLECULAR WEIGHT HYDROCARBONS

A Dissertation

by

BALAJI BONDILI SINGH

Submitted to the Graduate College of
Texas A&M University
in partial fulfillment of the requirement for the degree of
DOCTOR OF PHILOSOPHY

December 1979

Major Subject: Chemical Engineering

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ABSTRACT

Catalytic Conversion of Methanol to Low
Molecular Weight Hydrocarbons. (December 1979)

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The recent demands on the available energy have stimulated the search for alternatives to oil. Methanol, because of its abundance and the availability of technology to produce it from coal, is projected as an alternative source for producing low molecular weight olefins. Utilizing 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 633 to 723°K 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 two hours to twenty hours. At carbon disulfide concentrations of 3000 ppm or greater, the catalyst goes through three stages. The first stage 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.

Experiments with 64% water and 36% methanol by mole, indicated that water enhances the catalytic activity in producing olefins. Increase in pressure increases the production of propylene and propane at the expense of ethylene.

X-ray diffraction studies, using Cu-K radiation, show no permanent structural changes after a long use. No permanent deactivation was observed even though the catalyst was overheated once, and had been deactivated and regenerated as many as 21 times. The ammonium exchange coupled with the water at high temperature suggest the formation of an ultra-stable zeolite.

Ethylene yields increase as the temperature increases from 633°K to 723°K.

The product distributions and the selectivities obtained at the above mentioned temperature range suggest that the decomposition of methanol is occurring on two different sites, which differ slightly in acidity. The first type of sites are responsible for complete dehydration to dimethyl ether and the second type of sites are active in formation of olefins. The increase in the dimethyl ether yields with time on stream at all temperatures and the corresponding decrease in the olefin yields suggest that as the time increases, either the sites of first type are converted to sites of

type two or are lost due to coke buildup. The catalyst can be regenerated using air at an average temperature of 773°K .

A possible rate expression that fits the data reasonably well is presented.

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BALAJI BONDILI SINGH

October 10, 1979

To
My Family

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CHAPTER I

INTRODUCTION

Currently the world is faced with a major energy crisis due to the excessive demands and the dwindling supplies of oil, the major source of energy. At the present rate of consumption, the availability of oil will not be enough to meet the world needs by the end of 20th century. Most of the organic chemicals produced in the United States are presently manufactured from crude oil and natural gas. The United States now imports 8.6 million bbl. of oil per day and an equivalent of 0.5 million bbl. of natural gas per day. Shell Oil Co. recently predicted that by 1990 the oil imports will rise to 11.3 million bbl. and gas imports to 1.8 million bbl. (C&EN, Feb. 20, 1978). Total energy demand of the United States, as predicted by the Shell Oil Co., is as shown in Table 1.

The search for alternative sources of energy should be given top priority. One quarter of the world's original oil, according to the latest estimates, has already been exhausted including much of it from the North American Continent. As is the case with any research and development, conversion of energy dependence from oil to an alternative

The citations on the following pages follow AICHE Journal for style and format.

TABLE 1. TOTAL ENERGY DEMAND OF THE UNITED STATES

	Total energy demand in millions of bbl/day of crude oil equivalent
1965	26.0
1970	32.9
1975	34.4
1980	40.3
1985	45.2
1990	50.6

TABLE 2. THE RECOVERABLE FUEL ESTIMATES OF THE WORLD

<u>Recoverable Fuels</u>	<u>Peta grams</u> *
Coal (Lower Estimates)	2000
Petroleum 20 ⁺ API	220
Natural gas	160
Heavy oils, pitch	85
Natural gas liquids	30

* Peta gram = 10^{18} Kilograms

source of energy requires 15 to 20 years. This long lead time is necessary for development of new technologies, optimization of the processes and building new plants or converting the existing plants for alternative raw material utilization.

There is sufficient coal and technology available to use the coal. Processes can be optimized in time for widespread commercial acceptance in the near future. There are enough known reserves of coal to supply the world's required energy through the 21st century. The available recoverable fuel estimates, according to a latest survey, are as shown in Table 2. At the present time the economics are not favorable for coal-based chemicals. The commercial processes to reduce dependence on oil are to be motivated by non-economic incentives. The long lead time required for the total conversion and the dwindling supplies of oil are strong incentives for reasearch in this field.

Chemical Feedstocks

The organic chemical industry manufactures products from materials that are commonly called feedstocks. Most of the feedstocks are presently manufactured in turn from oil and natural gas. The most common feedstocks of the chemical industry are synthesis gas, ethylene, propylene, butadiene, benzene and p-xylene. These six feedstocks satisfy all the

requirements of being the building blocks of the required industrial chemicals. These key chemicals are chemically reactive, sufficiently stable for storage and transportation. These feedstocks may not be replaced by other chemicals. Hence, effort should be oriented towards manufacture of these key chemicals from alternative sources.

Ethylene is one of the major key chemicals of the industry. The remarkable growth in the production of synthetic fibres, plastics and petrochemicals is a direct consequence of an expanding supply of ethylene, propylene and other low molecular weight olefins. Ethylene is also called the backbone of the chemical industry because the plants that manufacture ethylene also manufacture other key chemicals required for the chemical industry. The chief source of production of ethylene and propylene at the present time is the steam cracking of naphtha. The major consumer of ethylene is the polymer industry in making various polymers. Ethylene is also used in manufacture of ethylene oxide and ethylene glycol. Most of the propylene produced is used as fuel either directly or combined with gasoline. Major derivatives from propylene are polymers, acrylonitrile, isopropyl alcohol and propylene oxide.

Economic Considerations

Coal based methanol is an attractive alternative, because

of the tremendous technical progress in this field. Present spot price of methanol ranges from 42 to 46 cents per gallon (C&EN April 2, 1979). Westinghouse Corporation estimated that, to be competitive as a feedstock, the price of methanol should range anywhere between 25 to 29 cents per gallon. According to the Department of Energy technical advisor, Neal P. Cochran, the technology now in existence for coal gasification and methanol synthesis can meet these maximum cost requirements. Relying on a study conducted for the Department of Energy in 1978, Mr. Cochran quoted a price of 24 to 34 cents per gallon of coal-based methanol assuming a coal price of \$25 per ton. Based on \$12.50 per ton of lignite, Dr. Othmer of Polytechnic Institute of New York predicted a price of 15 cents per gallon for methanol. The estimates given above are based on the present and the projected developments in this field.

Prices of ethylene and propylene are approximately 10 to 13 cents per pound (C&EN November 20, 1978). The price fluctuations for these two key chemicals presently are minimal due to the large expansions in capacities, under utilization and slow gains in demand. Assuming no change in raw material prices, the prices for ethylene and propylene should hold steady for another few years. But the raw material prices are sure to increase in the near future forcing the ethylene and propylene prices up, or increasing the rate of conversion to alternatives. Based on the stoichiometry as

shown below, 2.29 pounds of methanol are required to produce either one pound of ethylene or one pound of propylene.

Using the estimate of 40 cents per gallon (roughly 6.06 cents per pound) for methanol, it costs 13.9 cents to produce a pound of ethylene or propylene. Assuming a processing cost of about 1 cent per pound, based on the latest estimates for the processing cost of gasoline from methanol by Mobil, ethylene could be manufactured at a price of 14 to 15 cents per pound. As predicted, when the oil prices go up, conversion of coal-based methanol to ethylene and propylene will be competitive.

Process for Conversion of Coal to Methanol

The process for a plant making sequentially methanol from CO and H₂ derived from vintage coal of the 1920's, as presented by Stiles (1977) is given in Figure 1. Synthesis gas required for methanol is most conveniently and economically produced in the gas sets in which coal or coke is first heated to incandescence in a converter. Then steam plus air is passed over the incandescent coke to produce the above mentioned gases. The purification process consists

Fig. 1. Process for production of methanol from coal.

of ash by scrubbing with water and removal of sulfur by scrubbing with alkaline solutions. Some or all of the CO_2 is simultaneously removed with sulfur compounds. The cleaned gas containing CO , H_2 and N_2 is first compressed to operating conditions and then passed over a methanol synthesis catalyst. The methanol is condensed from the gas stream before it is passed over to the ammonia converter.

The technology for this process was not given much importance due to the world's dependence on oil as a prime source of energy. Between 1950 and 1974, the process has been commercially demonstrated and 25 of these plants were built in various parts of the world (McKelvy, 1979). The largest plant for production of methanol from coal, operated by African Explosives and Chemicals in South Africa, is based on Koppers-Totzek gasifiers with a design capacity of 60 tons/day of methanol. In addition to this, more advanced technology is nearing the commercial stage.

CHAPTER II

HISTORICAL

The first reported observation of hydrocarbon formation from methanol may be credited to Mattox (1962) for his patent. Mattox reported minor amounts of C_2-C_5 olefins during methanol dehydration to dimethyl ether over NaX zeolite catalyst. Venuto and Landis (1968) suggested an alpha elimination process for the production of hydrocarbons from methanol.

Swabb and Gates (1972) in their investigation of diffusion, reaction and fouling in H-Mordenite crystallites with dehydration of methanol, identified in one of their runs at 240 degrees centigrade at roughly 40% conversion, trace amounts of ethylene and propylene by their retention times on the chromatographic column.

Topchieva, Kubasov and Dao (1972) reported a study of dehydration of methanol on alkaline forms of zeolite X and Y. In their investigation, they reported that the decationated zeolites usually have strong Brønsted and Lewis acidity. The creation of strong protonic acidity by ion exchange obviously promotes formation of 1-butene. They also obtained similar results for the dehydration of methanol on zeolites containing polyvalent cations. Various hydrocarbons including butene were obtained together with ether on ZnX and ReX zeolites. They concluded that the dehydration of

methanol on zeolites can proceed independently by two pathways, formation of dimethyl ether and formation of olefins. Electron accepting centers are active in the first pathway. The activity in the second pathway is associated with the presence of proton donating activity in the catalyst. Apart from the above mentioned investigators, Heiba and Landis (1964) also reported formation of trace amounts of olefins in their work on dehydration of methanol on a zeolite catalyst.

All of the above processes reported trace amounts of olefins and none characterized or proposed a process for direct synthesis of olefins from methanol. The problem was given renewed interest in 1974 as a consequence of the energy crisis. Because of the reasons discussed in the first chapter, methanol was projected as a viable alternative. Professor R.G. Anthony of Texas A&M University and some individuals at Mobil Oil Corporation are the first known workers to independently pursue the objective of obtaining a selective and efficient process for the conversion of methanol to olefins. Chang, Lang and Silvestri (1977) obtained a patent assigned to Mobil Oil Corporation for converting methanol to gasoline boiling range aromatics and aliphatics. Mobil Oil Corporation also obtained a number of patents over a period of the last four years on conversion of oxygen containing compounds, dimethyl ether and methanol to gasoline boiling range hydrocarbons and ethylene. Chang, Lang and

Silvestri (1977) summarized the Mobil process for conversion of methanol and other oxygenated compounds to C_2-C_{10} hydrocarbons using a new class of shape selective zeolites, chabazite, erionite, zeolite T, zeolite ZK-5 and zeolite ZSM-5. Verdine et al., (1977), using chromatography and C^{13} -NMR studies showed that the methanol to hydrocarbons conversion on HZSM-5 zeolite proceeds via dehydration to dimethyl ether and ethylene. They suggested that the reaction occurs by two competitive mechanisms, successive dehydration-methanolation to give branched aliphatics and polycondensation reactions leading to linear and aromatic compounds. Because of the renewed interest in the catalytic applications of the above mentioned zeolites, acidic properties of the ZSM-5 type catalysts have been studied for their acidity and application in hydrocarbon reactions by Verdine et al., (1979). Catalytic reactions and the sorption measurements of different compounds on ZSM-5 type catalysts were conducted by Anderson et al., (1979).

Summary of the Research at Texas A&M University

In 1974, Professor Anthony in the Chemical Engineering Department at Texas A&M University, initiated a program to study the catalytic decomposition of methanol. The initial study examined the decomposition reactions over zinc chromite catalyst by Y.P. Gupta (1975). 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 gamma alumina catalyzed the conversion of methanol to dimethyl ether and water. This program was funded for two years beginning October 1, 1975, by National Science Foundation-Research Applied to National Needs (NSF-RANN) with the stated objective of converting methanol to gaseous fuel and ethylene.

Approximately fifty catalysts 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, it was 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, it was concluded that the ethylene was probably being formed by adsorbed methanol dehydrogenating to an adsorbed formaldehyde specie which in turn polymerized to a dimer. Even though the yields over this catalyst were encouraging, a tungsten carbonyl precipitate was observed in the reactor effluent. An attempt to sulfide the catalyst resulted in loss of activity for conversion of methanol to hydrocarbons.

In 1977, based on results of Venuto and Landis (1968), it was reasoned that a small pore zeolite such as Linde 4A, 5A and AW500 might convert methanol to ethylene and propylene with significant yields. These catalysts were tested and in particular 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 the methanol was converted to ethylene, 30% to propylene and 18% to propane. Results of this work conducted in a tubular reactor were summarized by Lin, Chao and Anthony (1977). The present work was started as a continuation of the work conducted by Lin, Chao and Anthony (1977).

Based on the results reported by Lin, Chao and Anthony (1977), Cobb, Coon and Tipnis (1978) and Tipnis (1978) studied catalytic characteristics of Chabazite for methanol conversion to light hydrocarbons. They explored the independent variables extent of lanthanum exchange, temperature, space velocity and short term aging. They reported that the selectivity was greatly affected by aging with paraffins being the major products in the first few minutes, olefins being present at intermediate times and dimethyl ether being the major product toward the end as the catalyst deactivates. They reported that the aged samples contained

approximately 10% carbon and seem to have lost about 80% of the crystal structure.

Conversion of CO and H₂ Mixture to Hydrocarbons

A reliable route for producing hydrocarbons from coal is to first convert the coal to synthesis gas and then to methanol and then convert this methanol to hydrocarbons using the processes available. If a process to convert synthesis gas directly to hydrocarbons is developed, it would eliminate the intermediate step of methanol synthesis.

Processes to convert carbon monoxide and hydrogen mixture were first discovered in 1925. Franz Fischer and Hans Tropsch of Kaiser Wilhelm Institut für Kohlenforschung at Mülheim Ruhr made the discovery that carbon monoxide and hydrogen react in the presence of active iron and cobalt catalysts at atmospheric pressure, producing higher gaseous liquid, and solid aliphatic hydrocarbons (July, 1925). Since 1925, an amazing amount of diligence and money were devoted toward the chemical and technical development of the Fischer-Tropsch process. Helmut Pichler (1957) presents an excellent summary of the twenty-five years of synthesis of gasoline by conversion of carbon monoxide and hydrogen.

Fischer-Tropsch synthesis yields a very broad spectrum of products ranging from methane to heavy oils and waxes. The product requirements can be approximately selected by

controlling the parameters, temperature, pressure and the metal content in the catalyst. Significant amounts of oxygenated compounds are also formed. In most of the product distributions of the Fischer-Tropsch synthesis, paraffins dominate the product distributions. The major disadvantage of this process is the low selectivity to low molecular weight olefins. The catalyst also deactivates in the presence of steam and sulfur compounds.

Zeolite catalysts, which are being developed for the synthesis of hydrocarbons from methanol, are being studied for synthesis of hydrocarbons from CO and H₂ mixtures. Research in this area is being conducted independently by Prof. R.G. Anthony, J.C. Hill (1979) and the Mobil Oil Corporation. Chang, Lang and Silvestri (1979) have reported on the conversion of synthesis to aromatic hydrocarbons over a new class of zeolites comprising a CO reduction function combined with a ZSM-5 class zeolite. Using 3% Fe on a ZSM-5 class zeolite, they obtained 25.2% aromatics and 5.1% olefins in the product stream.

CHAPTER III

ZEOLITES

Zeolites, as synthesized or formed in nature, are crystalline hydrated aluminosilicates of groups I and II elements. Structurally, they comprise a framework based on an infinitely extending three-dimensional network of SiO_4 and AlO_4 tetrahedra linked together through common oxygen atoms. The isomorphic substitution of Si by Al gives rise to a net negative charge compensated by cations. Zeolites can be represented by the formula

Where M is the compensating cation with valency n.

Structurally, the formula of zeolite can be represented by its unit cell composition

Until now, in both fundamental and practical catalysis, only a limited number of zeolites have been studied. Excellent reviews of the structural and chemical data of the most common zeolites were given by Breck (1974) and Jacobs (1977).

The framework structures of zeolites are composed of arrangements of tetrahedra in building units going from ring structures to polyhedra. Silicon and aluminium atoms are tetrahedrally coordinated with four oxygen atoms. The oxygen atoms are mutually shared between tetrahedral units

contributing one of the two valence charges of each oxygen to each tetrahedron. Since silicon has valence of +4, the overall charge on SiO_4 is zero. The AlO_4 with a +3 aluminium atom, on the other hand, is negatively charged. The charge on these units is balanced by cations, generally sodium or potassium in the synthesized molecular-sieve zeolites. The cations are exchangeable with other cations, which account for the base exchange properties of molecular sieves.

Early interpretations of the physical and chemical properties of zeolites were based upon fragmentary structural information. As a result of investigations during the last ten years, there is extensive information on the crystal structure of over 35 different zeolites. Zeolites are classified into groups according to common features of the aluminosilicate framework structures. The important properties that are structure related are:

1. High degree of hydration and the behavior of zeolitic water.
2. Low density and large void volume when dehydrated.
3. Stability of the crystal structure of many zeolites when dehydrated and when as much as 50% of the dehydrated crystals are void.
4. Cation exchange properties.
5. Uniform molecular-sized channels in the dehydrated crystals.

6. Various physical properties such as electrical conductivity.

7. Adsorption of gases and vapors.

The structural classifications and relative properties are discussed in detail by Breck (1974).

Zeolites as Catalysts

The unique catalytic properties of synthetic molecular sieve zeolites and their applicability in processing feed streams were recognized in the 1960's. Molecular sieve cracking catalysts were first introduced in 1962 by Mobil Oil Company. Pickert, Bolton and Lanewala (1968) report that the zeolites have replaced conventional amorphous catalysts in nearly 90% of all the catalysis functions. Savings from reduced crude oil needs and increased product values are now probably one million dollars per day.

The discovery that the crystalline molecular sieve zeolites possess catalytic activity has added a new dimension in the fields of heterogeneous catalysis and catalytic process engineering. Because they are readily tailored to specific reactants by accurate control of the type and degree of activity and selectivity they provide, these new catalysts will play an increasingly important role as their unusual properties become better understood. Table 3 summarizes the potential molecular sieve catalyst applications.

TABLE 3. POTENTIAL MOLECULAR-SIEVE CATALYST APPLICATIONS

<u>Process</u>	<u>Feed/products</u>	<u>Competitive Features</u>
Catalytic Reforming	Naphtha/gasoline	Activators unnecessary; gasoline with reduced sensitivity; feed pretreatment minimized.
Polymerization	Low molecular weight olefins/gasoline	Noncorrosive
Hydrogenation	Benzene/cyclohexane	Improved resistance to S poisoning
Dehydrogenation	Ethylbenzene/Styrene	Improved selectivity
Dehydration	Alcohols+acids/esters	Improved rates and yields
Methanation	Synthesis gas/methane	High yields; resistance to poisons
Dehydrohalogenation	Alkylhalides/olefins	Molecular size selectivity
Selective Hydrogenation	Straight and branched olefins/n-alkanes and branched olefins	Separation problems minimized
Hydrodealkylation	Toluene/benzene	High activity; improved selectivity

Source: Pickert, Bolton and Lanewala (1968)

The resistance of zeolite catalysts to sulfur and nitrogenous impurities that poison conventional catalysts, and the high ionic activity they are able to provide, will give chemical engineers more latitude in designing and in improving the economics of the existing processes. Since the molecular sieve crystal structure and composition may be precisely varied, changes in the active surfaces can be studied by X-ray diffraction and other techniques that have hitherto had limited applicability with other catalysts. Thus, with these catalysts, new insights will be obtained into the mechanism of heterogeneous catalysts.

Although many factors influence the catalytic activity of molecular sieves, the three most important are framework structure with its attendant pore size, the silica/alumina ratio and the type of cation in the structure. Pore size is important in that it must be larger than the reactant and product molecule to allow diffusion of these species to and from the internal catalyst surfaces.

Many of the conventional catalysts for petroleum and petrochemical industries consist of single or multicomponent inorganic oxide compositions. Silica-alumina or silica-magnesia composites, for example, are used where acidic properties are necessary, i.e., where they either donate protons (H^+) or abstract hydride ions (H^-) to bring about the formation of carbonium ion intermediates from hydrocarbons.

Oxide forms are prepared using different methods. The most common problem with the conventional catalysts is the non uniform surface and minimal control over the end product. The problems encountered with the amorphous catalysts are circumvented in molecular sieve catalysts. These can be reproducibly synthesized with a uniform pore system. More than 90% of the surface area is inside the zeolite crystal. Whereas conventional silica alumina catalysts are deactivated by alkaline earth cations such as Mg^{+2} and Ca^{+2} , these multivalent cations are a source of the ionic activity of molecular sieve catalysts, particularly those with a framework silica to alumina mole ratio greater than 3. By simple ion exchange techniques that change or remove cations, Ca^{+2} , the properties of molecular sieves can be profoundly altered and manipulated to suit many different applications. The molecular sieves differ from the conventional catalysts in many different ways. Their ionic surfaces provide unusually strong ionic activity. Their ion exchangeable cations facilitate the introduction of catalytic metals in the highest degree of dispersion. They are completely crystalline with uniform internal pores of molecular dimensions.

Properties of Zeolites Related to Their Use as Catalysts

Ion-exchange Capability Owing to the isomorphic substitution of silicon by aluminium, the three-dimensional oxygen framework carries an excess negative charge, compensated

by cations. These cations can be exchanged by other cations of different valence and nature, which permits the introduction of catalytically important elements. By changing the nature of the cation and the degree of exchange, a whole family of catalysts can be prepared with gradually changing properties. Complex cations such as $\text{Cu}(\text{NH}_3)_4^{2+}$ and $\text{Pt}(\text{NH}_3)_4^{2+}$ can be used. The only limitation to the nature of the cations that can be introduced by ion exchange is the acid stability of the zeolite. Generally, the zeolite is more stable in acidic solution when the Si/Al ratio is high.

Thermal Stability When zeolites are slowly heated in a vacuum or in a dynamic inert atmosphere, water molecules are gradually desorbed, resulting in an endothermic weight loss. Upon dehydration, polyvalent cations generally show a tendency to move into the small cages or pores, where they can be coordinated to a greater number of oxygen atoms. The structural stability of the less stable zeolites is increased after exchange with polyvalent ions such as Ca, Mg and La. For high-temperature reactions catalyzed by acidic forms of zeolite, it is necessary to stabilize the zeolite structure by prior exchange with polyvalent cations. In this way, rare earth-exchanged NH_4Y zeolites after dehydration are suitable cracking catalysts in terms of thermal stability and acidity of the solid. The thermal stability of zeolites is also increased after gradual leaching out of aluminium

atoms from the lattice.

The practical use of zeolites as cracking and hydrocracking catalysts also requires a high hydrothermal stability. The structural resistance against steam treatment is also higher for the zeolites with higher thermal stability and lower aluminium content.

Acidity Both Brønsted and Lewis acid sites are found in zeolites. The former are protons attached to lattice oxygen atoms, while the latter can be the charge-compensating cations or trigonal aluminium atoms at oxygen-deficient sites or at cation positions.

Protons can be introduced into the structure through ion exchange, thermal decomposition of the NH_4 -exchanged form, hydrolysis of water of hydration of cations or reduction of cations to a lower valency state. A good example of this reaction is:

The lack of reactivity of the hydroxyl groups with an excess amount of base reactants may be due to their low acidic strength or to their inaccessibility in small zeolitic cages. Further dehydration of these structures results in dehydroxylation and the formation of Lewis sites.

Molecular Sieve Effect Sieving of one type of molecule out of a feed containing a mixture of molecules with different shapes and/or sizes is possible as the free apertures of the zeolites have molecular dimensions. From the catalytic point of view, such a system constitutes a very selective catalyst if the sites responsible for the catalytic action are located inside the cavities or pores. Therefore, the accessibility of reactant molecule is the first limitation to the use of a zeolite as a catalyst.

Accommodation of Cations in the Structure The location of cations depends on their degree of hydration. Dehydration results in the migration of cations to the smaller cages. Therefore, if one tries to relate zeolitic properties to the location of cations, the degree of hydration under working conditions should be considered. Protons also show increasing mobility with increasing temperature. The localization of the cations depends strongly on the pretreatment conditions of the zeolites: final calcination temperature and heating rate, nature of the calcination atmosphere, residual water in the atmosphere during calcination, thickness of the zeolite bed and the possibility of reduction of cations with hydrocarbons from the vacuum grease used.

CHAPTER IV

CATALYST

The development of an effective catalyst to convert methanol to low molecular weight olefins poses a challenge to the fundamental understanding of catalytic chemistry. From our experiments and a survey of the literature, the major catalytic reactions for decomposition of methanol are dehydration to form dimethyl ether, dehydrogenation to carbon monoxide and hydrogen, or partial dehydrogenation to formaldehyde. The overall reactions of decomposition of methanol are

			Kcal/mole at 427°C	
			ΔG°	ΔH°
Decomposition				
$2\text{CH}_3\text{OH}$	$\rightleftharpoons$	$(\text{CH}_3)_2\text{O} + \text{H}_2\text{O}$	-2.18	-4.74
Dehydrogenation				
CH_3OH	$\rightleftharpoons$	$\text{CO} + 2\text{H}_2$	-16.69	24.47
Partial Dehydrogenation				
CH_3OH	$\rightleftharpoons$	$\text{CH}_2\text{O} + \text{H}_2$	1.25	21.71
Target Reaction				
$n(\text{CH}_3\text{OH})$	$\rightarrow$	$(\text{CH}_2)_n + n\text{H}_2\text{O}$		
$2(\text{CH}_3\text{OH})$	$\rightarrow$	$(\text{CH}_2)_2 + 2\text{H}_2\text{O}$	-27.88	-5.51

Side Reactions				Kcal/mole at 427°C	
				ΔG°	ΔH°
2CO	$\rightleftharpoons$	CO ₂	+ C	-11.44	-41.35
CO	+ H ₂ O	$\rightleftharpoons$	CO ₂ + H ₂	- 3.05	- 9.05
(CH ₂) _n	$\rightarrow$	"Coke"	+ H ₂		
(3n+1)CH ₃ OH	$\rightarrow$	3C _n H _{2n+2}	+ CO ₂ + (3n-1)H ₂ O		
(2n+1)CH ₃ OH	$\rightarrow$	2C _n H _{2n+2}	+ CO + 2nH ₂ O		
n(CH ₃ OH)	+ H ₂	$\rightarrow$	C _n H _{2n+2} + nH ₂ O		

The basic reasons for selecting a catalyst with the capabilities of dehydration and dehydrogenation are very well summarized by Lin, Chao and Anthony (1977). Lin, Chao and Anthony suggested that the formation of a H₂C⁺-O- site, a formaldehyde type intermediate, is the rate controlling factor in the formation of olefins. These species then migrate to sites where external bonding between the sites and oxygen is stronger than the internal bonding between C⁺ and O⁻. The divalent specie CH₂ is then formed and subsequently polymerized to produce the olefins.

Based on the approach taken above, a zeolite catalyst would be an excellent choice because of three reasons. The chief materials in a zeolite are alumina and silica which are well known dehydration and dehydrogenation agents. These supply the required background for the above reactions. The ion exchange capability of zeolites is handy in

designing a catalyst with varying acidity. As suggested in the mechanism, the reactions are occurring on two sites with differing acidities. The third and most important aspect of the zeolite used for this reaction scheme is the special property of the shape selectivity.

Based on the above mentioned reasons and with the purpose of obtaining low molecular weight olefins, a small pore Chabazite has been selected as the potential candidate. Ion exchange with a mixture of rare earth chlorides and ammonium chloride is conducted to improve the acidic nature of the Chabazite.

Chabazite

Chabazite belongs to zeolites of group IV characterized by the double 6-ring structure. The Chabazite crystal structure was first reported in 1933. The crystal structure of Chabazite contains large ellipsoidal cavities each of which is entered by 6 apertures that are formed by 8 rings. When dehydrated, the zeolite contains a three-dimensional channel system consisting of the cavities joined through the 8-rings. A schematic structural arrangement of the zeolite Chabazite is shown in Figure 4. The physical and structural properties are summarized in Table 4. Breck (1974) and Jacobs (1977) present good reviews of the properties of Chabazite.

The Chabazite used in this reasearch was purchased

Fig.2. Chabazite crystal structure

Source: Pickert, Bolton and Lanewala (1968)

TABLE 4. PHYSICAL AND STRUCTURAL PROPERTIES OF CHABAZITE

<u>Structure group</u>	4																												
<u>Other designation</u>	Acadialite, Haydenite																												
<u>Unit cell contents</u>	$\text{Ca}_2((\text{AlO}_2)_4(\text{SiO}_2)_8) \cdot 13 \text{H}_2\text{O}$																												
<u>Variations</u>	Na and K; Ca Na,K; Si/Al=1.6-3;																												
<u>Occurrence</u>	Ireland, Nova Scotia, Colorado, Italy, Africa, Nevada																												
<u>System</u>	Triagonal, $a=9.42$ $\alpha=94^\circ 28'$ Hexagonal, $a=13.78$, $c=15.06$																												
<u>Habit</u>	Rhombohedral																												
<u>Hardness</u>	4.5																												
<u>Nominal pore size, $\text{\AA}$</u>	4																												
<u>Bulk density, lb/cu ft</u>	45.4																												
<u>Pellet density, lb/cu ft</u>	72.7																												
<u>Heat of adsorption for H_2O Btu/lb</u>	1450																												
<u>Specific heat of pellets</u>	0.24 at 460 deg. F																												
<u>X-Ray Powder Data</u>	<table><tr><td>hkl</td><td>d(A)</td><td>I</td><td>2θ</td></tr><tr><td>101</td><td>9.351</td><td>50</td><td>9.42</td></tr><tr><td>003</td><td>5.021</td><td>30</td><td>17.67</td></tr><tr><td>211</td><td>4.320</td><td>76</td><td>20.55</td></tr><tr><td>212</td><td>3.870</td><td>28</td><td>22.97</td></tr><tr><td>401</td><td>2.925</td><td>100</td><td>30.55</td></tr><tr><td>214</td><td>2.890</td><td>30</td><td>30.95</td></tr></table>	hkl	d(A)	I	2 θ	101	9.351	50	9.42	003	5.021	30	17.67	211	4.320	76	20.55	212	3.870	28	22.97	401	2.925	100	30.55	214	2.890	30	30.95
hkl	d(A)	I	2 θ																										
101	9.351	50	9.42																										
003	5.021	30	17.67																										
211	4.320	76	20.55																										
212	3.870	28	22.97																										
401	2.925	100	30.55																										
214	2.890	30	30.95																										
<u>Commercial Name</u>	Acid-resistant Molecular Sieve Type AW-500 of Union Carbide, Linde Div.																												

from the Linde division of Union Carbide Corporation under the trade name of AW500. This zeolite was developed by the Union Carbide Corporation to dry and purify process streams containing strong acid contaminants such as hydrogen chloride, sulfur dioxide and the oxides of nitrogen. AW500 is produced in the 1/8 and 1/16-inch pellets having the general properties shown in Table 4.

Procedures Used for the Catalyst Preparation

Commercial Chabazite, Linde AW500 Molecular Sieve, lot# 579038 was obtained from Union Carbide corporation in 1/8 inch cylindrical pellets. The catalyst has average bulk density of 1.15 gm/cc and 49.2% void volume. General procedure for the ion exchange of the catalyst is as shown below. The specific conditions for the particular catalyst are given in Table 5.

1. Rinse the fresh catalyst in twice its volume of methanol and keep in ultrasonic cleaner for 20 minutes. This process is used to clean any foreign particles and dust from the catalyst surface.

2. The methanol used for rinsing the catalyst is decanted and the catalyst allowed to stay at the room temperature for an additional half hour.

3. Mix the required quantities of the AW500, rare earth chloride mixture (obtained from Molly Corp. Inc., New York)

TABLE 5. DETAILS OF THE CATALYST PREPARATION

<u>Designation</u>	AW500 ReCl Amm
<u>Procedure</u>	Refluxing
<u>Temperature °C</u>	50
<u>Time of ion exchange</u>	96 hours
<u>Solution used</u>	1000 ml. AW500 1/8" pellets, 1000 ml. 0.3M Rare earth chlo- ride* solution in water, 1000 ml. 0.5M NH ₄ Cl solution in water.
<u>Heat treatment</u>	Heated at 200 °F for 2 hours Calcined at 500 °F for 10 hours.

* Rare earth chloride mixture was obtained from Molly Corp. Inc., 6 Corporate Park Drive, White Plains, New York, 10604, Lot #LH-31, Lanthanum Re Hydrate.

The composition was reported in weight percent as LaCl₃ 25.0%, CeCl 47.2%, PrCl₃ 5.9%, NdCl 19.3%, SmCl 1.9% and GdCl₃ 0.7%.

and ammonium chloride solution in a triple neck flask and stir manually for 10 minutes.

4. The triple neck flask is fitted with a reflux condenser and a thermometer and kept under the hood.

5. Ion exchange is carried out for specified period of time with occasional stirring for 5 minutes.

6. At the end of the exchange period, the solution is filtered through a filter paper and glass wool in a Buchner funnel and washed with de-ionized distilled water at about 100°C.

7. The pellets are drained and kept in porcelain dishes and subjected to thermal treatment as specified.

8. In the preparation of the ultra stable zeolite, the ion exchange is carried out for the second time as indicated.

CHAPTER V

EXPERIMENTAL APPARATUS

The experimental apparatus used in this investigation consists of feed system, preheater, Berty reactor, auxiliary equipment for maintaining reactor conditions and analytical equipment. A schematic drawing of the apparatus is shown in Figure 3.

High purity methanol, reagent grade supplied by Fisher Chemical Company is pumped from a buret with the metering pump, Lapp model MLS-10. Methanol is vaporized in a stainless steel tube preheater packed with steel turnings. The vaporized methanol is passed over the catalyst bed contained in the Berty reactor. The temperatures at the top and bottom of the catalyst bed are measured using strategically placed thermocouples. The temperatures were initially controlled using a Therimoline temperature controller and subsequently using a Thermoline controller and a variac. The reactor effluent is passed through a condenser and trap to remove methanol, water and some dissolved DME, so they would not affect the gas chromatographic analysis further down the line. The uncondensed gases are then passed through the gas chromatograph for analysis and the bubble meter for flow measurement. The liquid sample is collected periodically, weighed and analyzed. All the lines

Fig. 3. Schematic diagram of the Berty reactor set-up.

starting from the preheater to the bubble meter are heated and insulated using heating tapes and asbestos cloth tapes to prevent any condensation of liquid. The detailed description of the individual units is as follows.

Feed System

The feed system consists of Lapp model MLS-10 pump, buret, damper and a pressure gauge connected together using 1/8" stainless steel tubing. Methanol is pumped using the pump, the pressure gauge indicates the pressure on the line and the flow is damped to be free of fluctuations.

The pulsa feeder Lapp pump model MLS-10, Sr. # R-2676, was obtained from Power Speciality Company, Houston, Texas. It has a maximum capacity of 265 ml/hr and is designed to withstand pressures up to 1000 psig. It has a piston diameter of 0.125" and a maximum stroke of 0.5". It is fitted with a 1/20 Hp size expulsion proof motor. Pulsa feeder Lapp pump is a combination plunger-diaphragm pump. It has positive displacement; that is, a plunger reciprocates within an accurately sized cylinder at an established stroke length, displacing an exact volume of liquid. The liquid is pumped using a special property petroleum oil named "Pulsa Lube". Using this oil, the plunger hydraulically moves a diaphragm alternately backward and forward. The displacement from the diaphragm movement in turn takes the liquid being

pumped through a suction check valve on the suction stroke of the plunger and discharges a like amount of liquid through a discharge check valve on the forward or discharge stroke. The plunger operating in a sized cylinder and at exact stroke length gives exact displacement and accurate pumping rate.

Because the Lapp pump is a positive displacement pump and the flowrates involved are slow, pulsations in the flow could be observed. A damper made of a gas bomb and coiled 1/8" stainless steel tubing is used to dampen the pulsations. The gas bomb partially filled with air acts essentially as a capacitor. A Nupro check valve, rated 25 psig. is used on the exit line of the pump to maintain the back-pressure required for the Lapp pump operation. A pressure gauge supplied by Tech Controls Co., Houston, Texas, rated to 1000 psig. is used to indicate the actual pumping pressure of the Lapp pump.

Preheater

Preheater has been designed using a stainless steel tubing 1/2" in diameter. The tube, 12" in length, is fitted with 1/2" Swagelok caps at both the ends. Two 1/4" Swagelok fittings at the top serve as inlets for the reactants and the regenerating air. The 1/4" Swagelok fitting at the bottom is used as outlet for the vaporized methanol. The tube is packed with steel turnings for better heat

transfer. The design and the details of the preheater are shown in Figure 4. The preheater is heated using heating tapes and insulated with asbestos tape to facilitate the evaporation of methanol prior to its feeding into the catalytic reactor.

Berty Catalytic Reactor

Berty catalytic reactor is a relatively new concept in the laboratory reactors for heterogeneous kinetic studies. The main advantages of the Berty catalytic reactor over the conventional tubular reactors are the ease of data analysis and excellent isothermality. It has been designed by Jozsef Berty and developed by the Union Carbide Corporation. The design and the details of the reactor are reported by Berty (1974).

One of the unique features of the Berty reactor is the bearing design which permits the reactor to be heated to 1200 F without damaging the bearings. The details of the Magne drive assembly which operates the impeller and the cooling jacket are shown in Figure 5. A second unique feature of the reactor is the flow system design. Design of the flow system of the reactor is as shown in Figure 6. The reactant mixture enters the vessel through the inlet and is driven up the draft tube by the motion of the impeller. The reactant

Fig. 4. Design of the preheater and prereactor

Fig. 5. Design of the magne drive assembly for the Bertly catalytic reactor.

Fig. 6. Internal design of the Berty reactor.

passes through the catalyst bed. After 20 to 100 passes, the mixture is expelled through the outlet connection by the pressure difference. The high recycle rate insures that the vapor phase mixture inside the reactor is completely back-mixed, i.e., at a uniform temperature and composition and the reactor essentially operates as a continuous stirred type reactor.

The degree of mixing is a function of the impeller speed, the temperature and the gas phase density. The best indicator of the perfect mixing is the uniformity of the temperature across the catalyst bed. Perfect mixing is achieved under most operating conditions. However, at high temperatures and low pressures some difficulty was encountered. Controlling the temperature carefully is important in this situation. By controlling the temperature using a variac and a controller independently, the desired temperature conditions can be achieved.

Control Equipment

All the lines from the preheater to the gas chromatograph are heated using heating tapes and insulated with the asbestos cloth tape. Temperature on these heaters is controlled by means of variacs. The backpressure on the reactor is maintained using a Mity Mite, external loading type backpressure regulator model 90, supplied by the Grove Valve and Regulator

Company, New Orleans. The digital temperature indicators, calibrated to indicate temperatures to $\pm 1^{\circ}\text{F}$, were obtained from the Omega Thermocouple Company. The temperature in the reactor is controlled by means of a Thermoline temperature controller and a variac. The heater of the Berty reactor is constructed in three separate parts. Controlling the two top heaters together and the bottom heater separately, minimal temperature drops can be obtained. The Thermoline Furnatrol temperature controller, model CP-18210, rated to 240 volts was supplied by Thermoline Corporation, Iowa.

Analytical Equipment

The quantitative analysis of the product was conducted using a GowMac thermal conductivity gas chromatograph and a CRS-104 digital integrator. Series 150, thermal conductivity gas chromatograph was obtained from GowMac Instrument Company. The sampling system was modified using a GowMac gas sampling valve, as shown in Figure 7, so that the gas sampling valve can be operated at any desired temperature and the oven can be operated at any desired temperature. For the dual column gas chromatograph, one side has been by-passed and the other side fitted with a 6 ft. stainless steel column $1/8$ " in O.D and packed with porapak Q 100/120 mesh. Typical chromatograms for the analysis of the gas and the liquid condensate analysis are as shown in Figures 8 and 9.

Fig.7 . Gas sampling valve positions during purge and sample modes.

Fig. 8. Gas chromatogram of the product gas: Conditions: stainless steel column, 6 ft. X 1/8" O.D. packed with 100/120 mesh Porapak Q; Helium flow-rate 15 ml/min; column temp. 50 C up to C₂H₆ then to 150°C; Detector temp. 250°C;

Fig. 9. Gas chromatogram of the liquid condensate. Conditions: stainless steel column, 6 ft. X 1/8" O.D. packed with 100/120 mesh Porapak Q; Helium flowrate: 15 ml/min; Column temp. 65°C; Detector temp. 250°C; Injector temp. 150°C.

Prereactor

A prereactor has been designed to be used in the experiments involving mixtures of methanol, dimethyl ether and water. The design details of the prereactor are exactly the same as those of the preheater. The prereactor is arranged after the preheater and before the Berty reactor in a parallel loop. When required, the flow of the reactants were passed through the prereactor before passing them through the Berty reactor. The prereactor is heated using heating tapes and insulated with asbestos tapes.

Condenser and Trap

Due to the limitations on the gas chromatographic system and the quantities of the products involved, all the product could not be passed through the gas chromatograph at one time. The liquid product containing water, methanol and traces of dimethyl ether was separated using the condenser system, so that it would not affect the gas chromatograph further down the line. Different methods for the condensation were tried. Most precise and convenient to use was a conical flask fitted with a rubber septum stopper. The inlet and the outlet lines for the condenser were fitted with needles for efficient arrangement. For a predetermined amount of time, the liquid condensate was collected, weighed

and analyzed independently. When material balances are not being determined or when the reactor is not at steady state, a trap made from a Coke bottle fitted with cork stopper is used in place of the condenser. Both the condenser and the trap can withstand pressures up to 50 psig. and are cooled using crushed ice and salt mixture in a flask.

CHAPTER VI

EXPERIMENTAL PROCEDURE

The Berty reactor used in this study can be used for different sizes and different quantities of catalyst. To obtain more recirculation and also to reduce the resistance to the flow of the reactants, the largest possible basket was used without any inserts. For 100 ml. of catalyst, the bed height is approximately $1\frac{1}{2}$ ". The stirrer is operated at the maximum possible rpm of 1800 for efficient recycle. The temperatures at the bottom and top of the bed are measured, from which a linear interpolation is possible to determine the exact temperature at the top of the catalyst bed.

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 a run, nitrogen 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 required, the system is flushed with nitrogen and kept under nitrogen blanket. Regeneration of the catalyst is conducted for 10 to 12 hours at 750°K to 800°K using air at 40 ml/min. A fresh catalyst charged once was found to be active for 3 months without

permanent loss of activity.

A GowMac gas chromatograph with a thermal conductivity detector, a porapak Q column 100/120 mesh, helium flowrate of 15 ml/min, and an oven temperature of 50 to 150 C were used to analyze the reactor effluent. Preliminary analysis using a Carle gas chromatograph with multiple columns indicated presence of hydrogen in the product stream. However, this instrument was not generally available to us. Therefore hydrogen was determined using two methods, forced hydrogen balances over the reactor and forced oxygen balances over the reactor. A CRS-104 digital integrator and a recorder are used with the gas chromatograph to obtain quantitative information. A detailed computer program to tabulate the quantitative information and represent the data is used for the material balances.

The experimental procedure described above may be classified into the following sections. The details of each

Start Up Procedure

Progress of the Run

Regeneration Procedure

Shut Down Procedure

Maintenance of the Equipment

Precautions

of the sections are given in the next sections.

Start Up Procedure

1. Assemble the Berty reactor, with the required amount of the catalyst, as described in the equipment maintenance procedure.

2. Set the back-pressure regulator at the required pressure setting.

3. Close the methanol input valve to the preheater and the exit valve from the Berty reactor. Bring the system to a high pressure using nitrogen and check the leaks and fix them. Vent the nitrogen gas via vent valve.

4. Turn on the power to the heating tapes of the preheater, connecting lines and Berty reactor using the individual variacs. It is easier to approach the required temperature in the Berty reactor system from a lower value. It takes a long time to cool the system due to its mass, even by few degrees. First turn on the power to the top heaters and control it by means of the Thermoline temperature controller to approximately achieve the required temperature. Turn on and adjust the bottom heaters using the manually controlled variac to achieve the required temperature drop between the thermocouple indications.

5. Turn on the Magne-drive stirrer and set it to 1800 rpm. This is the maximum safe operating speed for the Magne-drive stirrer. Upon stirring, the temperature drop between the top and the bottom decreases and stabilizes.

6. After reaching the required temperatures, pass nitrogen at 40 to 60 ml/min. for 1 hour and shut off the nitrogen valve at the preheater.

7. Check the Lapp pump for trapped air, by setting the stroke to the maximum value and bleeding the relief valve. Once the air is completely removed, tighten the relief valve and close the methanol input valve to the preheater. Pump methanol at a high setting till the gauge indicates at least 250 psig. This ensures that the system is filled with methanol. Open the methanol input valve and reduce the Lapp pump setting to the required value.

8. Record the values of the room temperature and barometric pressure. Keep track of the burette reading of methanol and the top and bottom temperatures of the catalyst bed.

9. When using the reactor for high pressure runs, bring the system to the required pressure using methanol or the reactants being used. The use of nitrogen to pressure the system and the purge would take a long time to exit.

Progress of the Run

1. At least every 15 minutes, record the burette reading of methanol and the top and bottom temperatures of the catalyst bed. This monitors the operation of the pump to protect against loss of flow.

2. To take a gas sample, cool the gas chromatograph

to 50°C with the column heater off, fan on and the top of the gas chromatograph open. Upon reaching 50°C, shut the top of the gas chromatograph, set the integrator on auto mode and shoot the sample using the sampling valve. After C₂H₆ (5th peak in sequence), turn on the column heater, setting the maximum at 150°C. After the sampling is completed, cool the gas chromatograph to 50°C to prepare for the next sample.

3. Measure the flowrate of the gas using the bubble meter under the hood.

4. Prepare the liquid condensate sampling bottle by fixing a rubber septum stopper to a 150 ml. conical flask and fastening securely with a copper wire. Weigh and mark the empty sample bottle. The sample bottle is put in place by replacing the Coke bottle which is being used as the trap. Collect the liquid condensate for the predetermined amount of time by immersing the sample bottle in the flask containing crushed ice and salt mixture. At the end of the collection time, the sample bottle is replaced with the Coke trap, weighed and the liquid condensate analyzed. The liquid analysis is conducted on the gas chromatograph at a constant temperature of 65°C, using 2 µl of liquid sample.

5. The liquid samples are collected usually in the intervals of 1 hour. The progress of the reaction is monitored by using ethylene yields. The catalyst is considered deactivated when the ethylene yields become low and the yields of dimethyl ether increase. The runs are conducted

at the predetermined conditions.

Regeneration Procedure

1. Turn off the Lapp pump and close the methanol input valve to the preheater. Open the gas inlet valve to the preheater. Usually the regeneration is conducted with the stirrer off, but for some of the runs the stirrer was kept on.

2. Open the nitrogen cylinder valve and flush the system with nitrogen for 15 minutes, collecting the unreacted methanol in the trap. This is very important because, if the equipment valves are shut off without flushing the methanol out, coke would build up and excessive heat may cause the catalyst bed to melt.

3. Stop the nitrogen flow and with the exit valve open, increase settings on the Thermoline controller for the top heaters and the variac for the bottom heater to the regeneration temperatures. Simultaneously switch the flow from nitrogen to air at 40 ml/min.

4. Once the regeneration is complete, the Berty reactor is cooled to the reaction temperature under nitrogen blanket and kept under nitrogen blanket until the next run.

Shut Down Procedure

1. The shut down procedures described herein are used for a complete shut down of the equipment either for a

catalyst change or for maintenance purposes.

1. Turn off the power to the Berty reactor top heaters and the variac of the bottom heater.

2. Turn off the power to the heating tapes on the connecting lines, preheater and the gas chromatograph sampling valve.

3. Cool the Berty reactor to room temperature before further operations.

4. Turn off the power to the gas chromatograph and cool the detector with the helium flow.

Maintenance of the Equipment

The proper maintenance of the equipment is essential to the progress of the experiments. Each piece of equipment in the apparatus has different maintenance requirements. The individual maintenance procedures for the equipment are as given below.

Disassembly of the Berty reactor

1. Relieve all the pressure in the system.
2. Cool the system to the room temperature.
3. Disconnect the heater power input and lift off the furnace. Keep the furnace in a safe place to avoid damage.
4. Remove the hex socket cap screws from the cover.
5. Remove the cover by hooking it on to the block and tackle arrangement provided.

6. Remove the thermocouple in the catalyst bed by removing the nut.
7. Remove the catalyst assembly draft tube.
8. Remove the catalyst by removing the screens at the top and bottom of the draft tube.
9. Remove and clean the closure gasket.
10. Clean the body and cover surfaces.

Assembly of the Berty reactor

1. Clean and spray WD-40 on the Magnedrive bearings.
2. Adjust gland at the bottom end of Magnedrive housing until the correct clearance between the underside of the impeller and body bottom is reached. Lack of fit for this adjustment is clearly indicated by the rubbing noise in the impeller assembly even at slow rpm. After the above adjustment is made, the lock nut at the bottom has to be securely tightened.
3. Replace the required size of the draft tube with some glass wool covering the top of the bottom screen. This would prevent any catalyst dust escaping from the catalyst bed.
4. Replace the thermocouple in the body and tighten securely.
5. Fill the draft tube chosen with the catalyst particles to the required depth. Replace the top screen along with some glass wool to contain the catalyst dust.

6. Replace the closure gasket. The gasket should be replaced the same way it came off. The word "UP" is etched on the outer edge of the gasket.

7. Replace the cover in the original position by slowly lowering it with the block and tackle. Be sure cover is located correctly in reference to the thermocouple connections.

8. Clean and lubricate the hex socket screws using a high temperature lubricant and screw hand-tight into the body. Snug down all the screws one at a time diametrically in the beginning and in a counter clockwise sequence at the end. Continue this procedure, gradually tightening one screw at a time in even increments until proper torque is applied.

9. Check for leaks in the system before replacing the heater. Replace the furnace heater and connect the power input to the heaters.

10. The Berty reactor is now ready for operation.

Maintenance of the gas chromatograph

1. Check the carrier gas flowrate regularly.
2. Porapak Q column has to be conditioned every night at 200°C with helium flow.
3. Turn off the detector power when not in use.
4. When changing the carrier gas or during any maintenance, cool the detector to room temperature before stopping helium flow to prevent oxidation of the detector.

Maintenance of the Lapp pump

Priming of oil side of diaphragm

1. Start the motor.
2. Increase the stroke adjustment to maximum setting.
3. With the cover removed, depress the vacuum compensator valve with finger until any trapped air at the base of vacuum compensator valve has been discharged. Such air would come out at the juncture of the piston return spring and rear face of the pump head.
4. Open the air vent at the top of the pump head. This will relieve air from the top of hydraulic system. To expedite air release, depress compensator valve on the suction stroke only. Release the compensator valve on the discharge or forward stroke. This will overfill pump head and force the excess oil out at air vent. Retighten the air vent.

Priming of the reagent head

1. With flooded suction and low discharge pressures, Lapp pumps are normally selfpriming. If the reagent does not prime, turn off the motor and proceed as follows.
2. Be sure that valves on suction and discharge lines are open.
3. Increase stroke adjustment to maximum capacity.
4. Relieve pressure from discharge line. Arrange by-pass for discharge to drain.

5. Start the motor and allow to run until the liquid flows from discharge pipe.

6. After a few hours of operation, bleed air vent at top of pump head for the last traces of air.

Precautions

1. Check the water flow to the Magedrive bearing cooling system regularly.

2. Do not overheat the porapak Q column beyond 250 °C.

3. Do not set the vacuum compensator valve in the Lapp pump loose.

4. Always relieve the pressure into the hood.

5. In case of a persistent leak, set the hood suction on and leave the lab till the gases are completely removed.

6. Before operating the apparatus set up, make sure all the operating and maintenance procedures are followed carefully.

CHAPTER VII

DISCUSSION OF RESULTS

Experimental Results

The experimental results calculated based on the original data obtained, using the material balance procedure described in the Appendix, are presented here. The preliminary experiments indicated presence of hydrogen in the product stream. Hydrogen could not be analyzed due to the limitations on the analytical equipment. Hence amounts of hydrogen were determined from the material balances by forcing hydrogen and oxygen. The procedures used in the forcing and the model calculations are presented in the Appendix.

Total 44 runs were conducted in this study. The initial set of experiments in runs 1 through 20, was designed to investigate the catalyst life, temporary decay, the effects of water, pressure and carbon disulfide on the yields, selectivities and the activity of the catalyst. In runs 1 through 20, material balances are not available. The reported yields are based on the gas chromatographic outputs obtained by passing all the exit products through the gas chromatograph. The yield percents calculated as follows are presented in Table 6.

$$\text{Yield\%} = \frac{(\text{Moles of component } i) \times (\# \text{ of C atoms in } i)}{\text{Moles of methanol reacted}}$$

TABLE 6. EXPERIMENTAL DATA OBTAINED FOR RUNS 1 THROUGH 20

Date: 5/19/78

Catalyst: AW500 Amm ReCl-I

Feed: Methanol with 3000 ppm Carbon disulfide

Reactor Pressure: 100 psig

Room Temperature: 76°F Barometric Pressure

Previous History: On stream for 10 hours. Regenerated for 13 hours.

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	Product Yield%					
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
I-1-1	1.50	418	13.12	74.20	90.44	1.33	0.24	0.00	0.00	0.00	0.00	7.98
I-1-2	1.58	427	13.12	93.10	76.99	8.73	3.48	6.29	3.24	0.00	0.00	1.40
I-1-3	1.83	427	13.12	91.40	70.18	7.00	6.23	10.03	6.56	0.00	0.00	0.00
I-1-4	2.25	428	13.12	83.00	25.86	14.62	10.34	31.51	12.61	2.60	0.00	2.37
I-1-5	3.00	430	13.12	39.00	0.21	19.30	4.51	54.87	18.67	0.00	0.00	2.44
I-1-6	4.00	431	13.12	13.80	1.57	31.63	0.76	5.32	2.03	2.65	0.00	40.63
I-1-7	4.50	432	13.12	34.63	0.76	8.24	0.54	0.40	1.48	0.00	0.00	88.59
I-1-8	5.00	432	13.12	38.86	0.01	0.62	0.18	0.00	0.08	0.00	0.00	99.10
I-1-9	6.00	432	13.12	61.44	3.34	24.22	2.70	0.94	3.59	0.00	0.00	65.21
I-1-10	7.00	442	13.12	80.15	5.91	34.20	1.43	8.21	2.03	0.00	0.00	48.32

Table 6. Continued..

Date: 5/26/78

Catalyst: A fresh charge of catalyst is loaded into reactor. AW500 Amm ReCl-II

Feed: Methanol with 6000 ppm CS₂ for 4.5 hrs., then CS₂ reduced to 1000 ppm.

Reactor Pressure: 100 psig.

Room Temperature: 76°F Barometric Pressure: 29.80 in. Hg

Previous History: Fresh Charge.

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	Product Yield%					
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
II-2-1	1.25	400	16.39	98.43	97.03	2.07	0.00	0.00	0.00	0.00	0.00	0.00
II-2-2	1.50	398	16.39	94.67	98.12	1.88	0.00	0.00	0.00	0.00	0.00	0.00
II-2-3	2.25	392	16.39	91.79	98.42	1.58	0.00	0.00	0.00	0.00	0.00	0.00
II-2-4	6.25	398	13.12	100.00	96.00	2.92	0.58	0.50	0.00	0.00	0.00	0.00
II-2-5	6.75	391	13.12	82.20	48.80	5.37	0.37	3.49	0.00	14.32	27.66	0.00
II-2-6	7.25	389	13.12	78.00	32.90	9.19	0.95	9.23	0.00	22.50	25.48	0.00
II-2-7	7.75	388	13.12	74.56	29.53	12.47	1.70	14.50	0.00	36.24	5.58	0.00
II-2-8	8.25	389	13.12	83.70	12.87	9.01	1.34	11.93	0.42	33.49	5.93	0.00
II-2-9	9.00	386	13.12	77.83	25.86	29.12	2.40	35.30	0.97	0.00	0.00	6.34
II-2-10	9.75	385	13.12	56.00	19.67	17.41	0.67	17.63	0.00	34.63	21.25	0.00

Table 6 Continued..

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	Product Yield%					
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
II-2-11	10.75	383	13.12	29.00	14.06	17.59	1.99	20.12	0.40	45.42	0.42	0.00
II-2-12	11.75	384	13.12	80.00	15.24	14.54	1.93	18.58	0.32	37.77	1.83	0.00
II-2-13	12.25	384	13.12	82.15	11.64	11.89	1.61	15.12	0.50	15.32	43.92	0.00
II-2-14	12.75	385	13.12	82.88	8.93	12.84	1.78	14.94	0.75	18.77	41.99	0.00
II-2-15	13.75	386	13.12	74.88	9.92	14.25	1.92	16.03	1.46	24.50	31.92	0.00
II-2-16	14.75	385	13.12	78.63	16.08	32.53	2.17	22.03	4.65	20.61	1.93	0.00
II-2-17	15.75	386	13.12	79.78	14.17	20.45	2.40	25.22	1.20	29.88	6.68	0.00
II-2-18	17.00	387	13.12	39.25	18.81	17.60	2.81	28.12	0.81	24.75	7.09	0.00
II-2-19	18.25	389	13.12	81.17	16.80	20.70	1.68	22.94	1.39	30.20	6.29	0.00
II-2-20	19.00	388	13.12	78.29	10.71	12.83	2.00	16.06	1.52	24.71	32.18	0.00

Table 6 Continued.,

Date: 5/31/78

Catalyst: AW500 Amm ReCl-II

Feed: Methanol with 6000 ppm CS₂

Reactor Pressure: 100 psig

Room Temperature: 75°F Barometric Pressure: 29.82 in. Hg

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

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	Product Yield%					
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
II-3-1	1.25	382	13.12	92.28	99.04	0.96	0.00	0.00	0.00	0.00	0.00	0.00
II-3-2	1.50	383	13.12	73.20	91.81	4.00	3.10	1.09	0.00	0.00	0.00	0.00
II-3-3	1.75	383	13.12	82.17	44.85	13.75	7.05	9.36	4.71	19.15	1.15	0.00
II-3-4	2.75	383	13.12	81.17	29.43	14.92	9.92	16.78	7.01	20.65	1.29	0.00
II-3-5	3.42	388	13.12	75.06	25.77	19.91	9.93	28.18	5.78	9.96	1.47	0.00
II-3-6	4.42	402	13.12	94.12	24.51	17.44	10.19	25.31	5.27	15.41	2.88	0.00
II-3-7	5.42	395	13.12	92.11	62.17	4.18	3.46	5.01	2.97	9.52	1.48	11.19

Table 6 Continued.,

Date: 6/2/78

Catalyst: AW500 Amm ReCl-II

Feed: Methanol

Reactor Pressure: 100 psig.

Room Temperature: 73°F Barometric Pressure: 29.88 in. Hg

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

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	Product Yield%							DME
					CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	
II-4-1	1.32	399	4.72	99.23	33.96	3.48	0.07	0.09	0.00	0.00	0.00	62.40
II-4-2	3.58	401	4.72	94.59	43.92	10.82	0.14	0.15	0.32	0.00	0.00	45.20
II-4-3	4.58	399	4.72	95.19	37.24	18.25	0.80	1.52	2.79	0.00	0.00	38.69

Table 6 Continued.,

Date: 6/8/78

Catalyst: AW500 Amm ReCl-II

Feed: Methanol

Reactor Pressure: 100 psig

Room Temperature: 74°F Barometric Pressure: 29.85 in. Hg

Previous History: Regenerated at 828°F with air for 27 hours and kept under N₂ blanket

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	Product Yield%								
				X%	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	404	13.46	87.41	40.60	17.42	17.82	3.84	1.03	0.00	0.00	19.28
II-5-2	3.83	403	13.46	62.50	17.21	9.16	6.54	8.18	4.04	0.00	0.00	54.87
II-5-3	4.33	403	13.46	89.75	18.51	13.36	7.52	10.84	0.00	0.00	0.00	49.80
II-5-4	6.03	402	13.46	89.92	58.66	6.85	4.73	6.30	4.72	0.00	0.00	18.75
II-5-5	8.53	402	13.46	39.27	0.00	0.10	0.18	0.00	20.00	0.00	0.00	79.73
II-5-6	9.53	402	13.46	80.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100.00

Table 6 Continued.,

Date: 6/9/78

Catalyst: AW500 Amm ReCl-II

Feed: 64% water, 36% methanol by mole.

Reactor Pressure: 25 psig

Room Temperature: 75°F Barometric Pressure: 29.78 in. Hg

Previous History: Regenerated overnight

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	Product Yield%					
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
II-6-1	3.25	401	13.46	46.20	1.38	1.06	1.42	44.93	4.19	46.23	0.00	0.79
II-6-2	4.25	402	13.46	97.90	0.52	0.01	2.13	0.21	0.00	0.00	0.00	97.04
II-6-3	6.25	404	13.46	98.52	1.77	0.01	3.19	6.93	1.13	0.00	0.00	89.96

Catalyst is completely deactivated. Therefore stopped the run.

Table 6 Continued.,

Date: 6/19/78

Catalyst: AW500 Amm ReCl-II

Feed: 64% water, 36% methanol by mole. 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 73°F Barometric Pressure: 29.9 in Hg

Previous History: The catalyst has been regenerated and kept under nitrogen

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	Product Yield%					
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
II-7-1	1.15	413	12.55	48.54	0.02	8.03	0.43	32.43	0.62	49.09	9.34	0.00
II-7-2	1.72	413	2.17	13.23	0.00	5.07	0.07	37.73	0.00	29.83	27.31	0.00
II-7-3	3.06	413	4.33	84.92	0.00	4.95	0.17	49.91	0.69	44.29	0.00	0.00
II-7-4	4.31	413	2.80	86.58	0.23	4.50	0.51	36.27	1.84	51.22	0.00	5.43
II-7-5	6.06	413	16.26	97.09	0.02	1.04	0.08	86.78	0.52	10.71	0.00	0.85
II-7-6	10.12	411	16.26	54.78	0.00	7.66	0.00	59.87	1.42	24.38	0.00	20.96

Table 6 Continued.,

Date: 6/20/78

Catalyst: AW500 Amm ReCl-II

Feed: 64% water, 36% methanol by mole. 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 74° F Barometric Pressure: 29.92 in Hg

Previous History: Regenerated overnight

Run#	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	Product Yield%					DME
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	
II-8-1	0.50	407	1.62	51.08	0.27	5.58	0.38	29.29	0.55	44.34	19.21	0.38
II-8-2	2.06	406	6.50	90.08	0.09	3.01	2.06	24.35	0.62	36.40	33.00	0.46
II-8-3	3.06	407	2.37	90.61	0.23	0.66	1.08	52.07	0.57	19.72	20.31	5.37

Stopped the run because of leak in the system

Table 6 Continued.,

Date: 6/23/78

Catalyst: AW500 Amm ReCl-II

Feed: 64% water, 36% methanol by mole. 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 74 °F Barometric Pressure: 29.92 in Hg

Previous History: Kept under nitrogen, no regeneration

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	Product Yield%					
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
II-9-1	0.25	391	1.39	65.48	0.12	1.57	0.33	6.82	1.48	3.59	3.81	82.28
II-9-2	0.50	395	1.45	21.24	0.09	1.18	0.25	5.06	1.09	2.66	38.09	51.58
II-9-3	1.25	390	2.17	87.80	0.21	11.42	1.11	58.79	5.48	13.00	1.25	8.74
II-9-4	1.75	390	1.77	45.39	0.04	1.97	0.19	16.11	0.36	4.68	0.00	76.65
II-9-5	2.25	390	2.70	90.70	0.21	9.54	0.85	67.90	5.62	7.99	0.94	6.95

Table 6 Continued.,

Date: 6/26/78

Catalyst: AW500 Amm ReCl-II

Feed: Methanol with 2000 ppm CS₂

Reactor pressure: 100 psig

Room Temperature: 74 F Barometric Pressure: 29.80 in Hg

Previous History: Regenerated from 23rd June 5.30 PM to 24th 11.45 PM

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	Product Yield%					
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
II-10-1	0.50	399	11.70	75.00	2.15	6.01	0.62	60.30	0.00	14.67	16.32	0.00
II-10-2	1.75	400	9.47	60.19	14.07	17.60	1.99	20.14	0.40	45.38	0.42	0.00
II-10-3	3.47	400	13.00	75.74	7.54	10.52	15.43	14.62	0.62	15.78	35.48	0.00
II-10-4	5.25	399	10.83	100.00	5.80	7.78	12.82	11.62	10.82	20.19	13.29	17.69
II-10-5	6.50	398	6.19	34.80	3.83	6.88	7.89	21.63	2.41	17.81	39.55	14.32
II-10-6	7.25	398	9.89	38.7	1.03	2.22	3.10	7.57	8.29	67.15	9.44	1.20
II-10-7	8.40	405	7.50	78.31	25.94	6.90	6.79	24.24	3.64	28.18	3.76	0.53

Table 6 Continued..

Date: 6/27/78

Catalyst: AW500 Amm ReCl-II

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 100 psig

Room Temperature: 74 °F Barometric Pressure: 29.86 in Hg

Previous History: Regenerated overnight

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	Product Yield%					
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
II-11-1	2.50	401	3.58	56.76	68.20	2.35	3.49	9.28	0.87	10.21	4.55	1.14
II-11-2	2.90	398	3.10	74.83	28.05	6.04	11.18	19.72	4.77	13.64	15.72	0.88
II-11-3	3.90	397	5.11	74.49	13.83	6.74	9.32	36.22	9.61	21.72	10.01	2.56
II-11-4	4.90	402	6.11	96.43	9.20	65.40	3.82	9.50	1.98	5.78	0.72	3.52
II-11-5	6.40	402	11.00	84.32	6.41	10.95	0.00	40.73	5.30	24.31	16.25	0.00
II-11-6	9.50	405	12.18	81.50	0.80	13.96	0.54	44.09	7.09	28.56	1.39	3.16

Table 6 Continued.,

Date: 6/28/78

Catalyst: AW500 Amm ReCl-II

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 100 psig

Room Temperature: 73 F Barometric Pressure: 29.72 in Hg

Previous History: Regenerated for 10 hours at 825 F with 60 ml/min of air

Run #	Time hr	Temp °C	$\frac{1}{LHSV}$	X%	CO	CH ₄	Product Yield%					
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	DME
II-12-1	1.75	373	14.32	92.39	0.00	56.84	0.00	23.29	10.54	7.59	1.69	0.00
II-12-2	2.50	373	2.32	94.07	0.18	17.14	0.56	42.06	5.90	16.58	9.86	6.72
II-12-3	4.50	375	6.07	94.57	0.81	12.94	0.50	39.87	5.31	23.49	11.75	5.33
II-12-4	5.50	377	14.45	96.62	0.74	13.13	0.48	40.35	6.16	25.77	8.86	4.51
II-12-5	6.65	378	14.12	96.02	1.16	11.79	0.30	36.06	5.06	28.79	12.26	4.58
II-12-6	7.15	380	20.79	97.80	1.32	13.40	0.51	37.08	9.47	26.11	7.48	4.03
II-12-7	9.25	386	15.17	96.00	1.29	14.69	0.91	37.99	5.77	24.05	7.53	7.77
II-12-8	10.25	386	13.55	93.10	0.87	15.68	0.86	36.10	6.71	19.12	0.00	12.34

There is no run #13. The next run is #14

Table 6 Continued.,

Date: 8/8/78

Catalyst: AW500 Amm ReCl-II

Feed: 64% water, 36% methanol by mole with 2000 ppm CS₂

Reactor Pressure: 100 psig

Room Temperature: 73 °F Barometric Pressure: 29.90 in Hg

Previous History: Regenerated for 11 hours and kept under nitrogen

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	Product Yield%					DME
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈ *	
II-14-1	0.75	386	7.07	-----	0.02	0.02	0.01	0.03	0.03	0.00	0.00	0.00
II-14-2	1.50	386	6.25	85.80	0.25	4.02	0.46	35.06	1.57	53.86	0.00	4.78
II-14-3	2.42	386	6.25	85.40	0.23	3.28	0.32	30.43	1.30	60.05	0.00	4.39
II-14-4	3.75	386	5.80	84.50	0.13	6.05	0.47	49.74	1.42	37.02	0.00	5.27
II-14-5	4.08	385	5.32	85.40	0.12	6.50	3.76	34.89	1.11	47.21	0.00	6.41
II-14-6	4.91	384	2.16	77.20	0.72	5.84	12.96	40.60	0.66	27.37	0.00	11.84
II-14-7	5.43	383	2.20	73.80	0.54	4.07	16.21	39.18	0.90	26.76	0.00	12.33
II-14-8	6.16	383	2.32	83.22	0.76	2.79	9.23	17.04	0.65	21.46	0.00	48.07
II-14-9	6.58	383	2.34	83.80	0.53	3.57	7.66	14.93	0.65	21.92	0.00	50.74
II-14-10	8.83	385	2.32	75.48	0.85	9.97	5.16	26.14	1.01	45.25	0.00	11.63

* Reported yields include the propane

Table 6 Continued.,

Date: 8/14/78

Catalyst: AW500 Amm ReCl-II

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 72 °F Barometric Pressure: 28.98 in Hg

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

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	Product Yield%					DME
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈ *	
II-15-1	2.15	383	4.59	88.52	4.21	3.72	1.03	21.85	0.00	68.76	0.00	0.43
II-15-2	2.85	380	4.59	88.00	2.31	3.34	1.06	21.13	0.08	71.70	0.00	0.38
II-15-3	3.93	381	4.59	87.90	3.02	3.21	1.09	21.73	0.74	69.60	0.00	0.00
II-15-4	5.68	382	4.59	76.80	0.95	3.11	0.48	31.79	0.23	62.26	0.00	1.18
II-15-5	6.25	383	1.92	28.96	1.82	11.70	0.02	9.33	0.05	25.12	0.00	51.96

* Reported yields include the propane

Table 6 Continued.,

Date: 8/16/78

Catalyst: AW500 Amm ReCl-II

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 200 psig

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

Previous History: Regenerated with air at 100 ml/min for 13 hours at 792 °F

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	Product Yield%					DME
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈ *	
II-16-1	1.58	406	2.70	77.30	6.14	4.74	1.28	26.18	1.44	59.80	0.00	0.42
II-16-2	1.99	403	2.69	43.00	4.07	6.08	2.49	18.93	5.01	61.35	0.00	2.07
II-16-3	2.99	408	2.67	48.00	9.29	2.53	2.71	22.57	1.51	57.31	0.00	4.07
II-16-4	9.21	387	3.24	67.30	6.70	4.90	1.43	17.64	2.52	60.60	0.00	6.22
II-16-5	12.62	386	3.24	67.4	5.99	4.67	1.92	10.97	1.87	68.72	0.00	5.86

* Reported yields include the propane

Table 6 Continued.

Date: 8/20/78

Catalyst: AW500 Amm ReCl-II

Feed: Methanol with 2000 ppm CS₂

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

Reactor Pressure: 250 psig

Previous History: Regenerated overnight.

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	Product Yield%					DME
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	
II-17-1	0.50	398	2.71	59.00	6.92	5.48	3.83	11.24	2.34	32.16	12.98	0.00
II-17-2	0.75	394	2.70	87.00	7.42	3.89	2.94	10.94	4.86	28.48	10.46	0.00
II-17-3	1.05	395	12.10	86.00	6.94	5.46	4.23	9.89	5.32	33.62	9.29	0.00
II-17-4	1.30	393	12.10	96.00	5.91	4.05	2.74	8.38	1.14	42.53	34.24	0.02
II-17-5	2.05	393	12.20	96.00	7.49	5.35	3.52	12.42	1.65	59.86	9.71	0.00
II-17-6	3.63	393	12.10	96.00	4.06	3.16	1.29	7.42	1.26	46.56	36.26	0.00
II-17-7	4.88	393	12.20	97.00	8.89	7.19	5.36	15.27	1.81	53.71	7.76	0.00
II-17-8	6.38	393	12.30	97.00	3.90	5.66	3.46	20.70	2.77	53.69	9.82	0.00
II-17-9	7.13	392	12.10	96.00	7.69	6.75	4.37	21.19	2.95	48.35	8.68	0.00
II-17-10	7.63	392	12.10	96.00	7.28	5.13	3.58	20.68	2.20	50.45	10.79	0.00
II-17-11	8.13	393	12.10	96.00	6.31	4.18	3.53	19.84	2.42	51.15	12.58	0.00

Table 6 Continued.

Date: 8/22/78

Catalyst: AW500 Amm ReCl-II

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 250 psig

Room Temperature: 69°F Barometric Pressure: 29.94 in Hg

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

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	Product Yield%					DME
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	
II-18-1	0.50	398	2.03	96.80	6.99	7.02	2.82	22.83	1.37	55.90	0.53	2.53
II-18-2	0.76	398	2.03	90.30	2.45	4.98	1.03	16.31	1.40	39.60	31.44	2.78
II-18-3	1.56	398	6.25	93.20	5.21	4.93	1.40	20.25	0.85	44.00	20.86	2.52
II-18-4	2.39	399	6.28	93.00	4.80	4.31	1.07	16.34	8.14	41.73	21.58	2.03
II-18-5	3.39	399	6.28	93.00	4.71	2.49	1.32	19.06	1.00	46.59	22.29	2.54
II-18-6	4.72	401	12.74	93.80	4.13	3.51	1.96	12.07	0.97	50.14	22.60	5.63
II-18-7	5.78	401	12.72	86.50	0.19	0.38	0.02	0.18	0.01	0.14	0.00	99.09

Table 6 Continued.,

Date: 8/24/78

Catalyst: AW500 Amm ReCl-II

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 72 °F Barometric Pressure: 29.88 in Hg

Previous History: Regenerated for 22 hours at 880 °F using air at 52 ml/min. 45 grams of γ-Alumina is charged into the prereactor. Feed is passed through prereactor before passing into the Berty reactor.

Run #	Time hr	Temp °C	$\frac{1}{LHSV}$	X%	CO	CH ₄	Product Yield%					DME
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	
II-19-1	0.51	397	1.71	89.01	0.00	0.29	0.00	1.67	0.00	1.93	0.00	96.11
II-19-2	0.76	398	1.71	85.03	0.00	0.30	0.00	2.50	0.00	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	0.00	100.00

Table 6 Continued.,

Date: 8/28/78

Catalyst: AW500 Amm ReCl-II

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 72 F Barometric Pressure: 29.85 in Hg

Previous History: No regeneration after run 19. The reactor was kept under nitrogen
Feed is passed through the prereactor before passing into the Berty reactor.

Run #	Time hr	Temp °C	$\frac{1}{LHSV}$	X%	CO	CH ₄	Product Yield%*					DME
							CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	
II-20-1	1.30	397	16.26	49.60	0.00	0.14	0.00	1.06	0.00	1.85	0.00	96.94
II-20-2	1.76	397	16.28	62.40	0.00	0.77	0.00	5.37	0.11	11.73	0.00	82.02
II-20-3	2.52	396	16.20	71.41	0.01	0.74	0.02	5.61	0.30	10.02	0.00	83.30
II-20-4	3.02	395	16.20	67.58	0.00	0.34	0.00	2.91	0.06	16.61	0.00	80.08
II-20-5	4.52	395	13.00	59.68	0.00	0.51	0.00	3.96	0.21	3.52	0.00	91.80
II-20-6	5.18	395	13.04	58.20	0.04	0.88	0.05	4.34	0.55	3.20	0.00	87.20

*Yield% = $\frac{(\text{Moles of component } i) \times (\# \text{ of C atoms in } i)}{\text{Moles of methanol reacted}}$

The average temperature of the catalyst bed, based on the measured values at the top and the bottom of the bed, is reported. Runs 15, 16, 17 and 18 were conducted at high pressure. In runs 14, 15 and 16 there was some difficulty in separating propylene and propane. The values tabulated are the sums of propylene and propane yields together. Runs 19 and 20 were conducted with the prereactor on line with 45 grams of γ -Alumina catalyst to study the effect of dimethyl ether on the product distributions.

Table 7 represents the data of the set of experiments conducted to study the kinetics and the deactivation characteristics. In all of these runs, material balances were calculated by forcing hydrogen and by forcing oxygen. The results reported in Table 7 are obtained by forcing hydrogen. The selectivities are reported as the moles of each component formed per mole of methanol reacted. The bed temperature during these experiments was accurately controlled within $\pm 4^{\circ}\text{C}$, using an additional variac in combination with the thermoline temperature controller. In most of the cases the material balances were within 10%. The data reported in runs 2 through 21 were obtained on the catalyst charged on May 26, 1978, designated as AW500 Amm ReCl-II. After run number 21, the catalyst was accidentally heated to 1380°F . Hence, a fresh charge of catalyst

TABLE 7. EXPERIMENTAL DATA OBTAINED FOR RUNS 21 TO 44

Date: 9/18/78

Catalyst: AW500 Amm ReCl-II • 100 cc, 1/8" pellets, bed depth 1/2"

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 73 °F Barometric Pressure: 29.5 in Hg

Previous History: Regenerated at 875 °F with 40 ml/min of air for 10.15 hours

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity*		C ₃ H ₆	C ₃ H ₈	DME	H ₂
II-21-1	1.75	396	11.68	92.50	0.0099	0.0519	0.0074	0.1556	0.0049	0.8667	0.0988	0.0741	0.0173	0.0592
II-21-2	4.50	396	6.94	69.80	0.0123	0.0443	0.0049	0.1009	0.0025	0.2241	0.0738	0.0566	0.0172	0.0887
II-21-3	8.60	392	5.00	80.04	0.0099	0.0796	0.0049	0.0647	0.0124	0.2139	0.0199	0.0323	0.0447	0.0000
II-21-4	11.08	396	3.84	62.28	0.0075	0.0423	0.0024	0.0349	0.0049	0.5012	0.0099	0.0049	0.0872	0.0000
II-21-5	12.33	395	2.50	29.76	0.0000	0.0050	0.0000	0.0000	0.0000	0.5819	0.0000	0.0000	0.2497	0.0000

* Selectivity = $\frac{\text{Moles of component i}}{\text{Moles of methanol reacted}}$

All selectivity calculations are based on
material balances

Table 7 Continued.,

Date: 10/25/78

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 74° F Barometric Pressure: 29.5 in Hg

Previous History: Fresh sample of catalyst charged on 10/20/78

Run #	Time hr	Temp °C	$\frac{1}{LHSV}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-22-1	1.92	363	12.19	88.37	0.0199	0.1362	0.0103	0.1628	0.0066	0.9539	0.0997	0.0864	0.0365	0.0365
III-22-2	6.72	362	5.45	66.83	0.0065	0.0548	0.0032	0.0510	0.0064	0.2480	0.0097	0.0161	0.0677	0.0000

Table 7 Continued.,

Date: 11/13/78

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 76°F Barometric Pressure: 29.56 in Hg

Previous History: Regenerated at 892°F for 14.5 hours with 46 ml/min of air

Run #	Time hr	Temp °C	$\frac{1}{LHSV}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-23-1	1.25	423	13.33	94.50	0.0143	0.0686	0.0171	0.1600	0.0086	0.8457	0.0742	0.0857	0.0200	0.0371
III-23-2	4.67	423	8.66	83.00	0.0085	0.0253	0.0056	0.1183	0.0056	0.9267	0.0470	0.0366	0.0253	0.0000
III-23-3	6.42	422	5.00	65.10	0.0151	0.0271	0.0091	0.0967	0.0121	1.1390	0.0420	0.0483	0.0604	0.0000
III-23-4	8.58	423	2.81	38.34	0.0059	0.0328	0.0059	0.0388	0.0089	1.1582	0.0179	0.0179	0.0179	0.0000

Table 7 Continued.,

Date: 11/15/78

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 73°F Barometric Pressure: 29.56 in Hg

Previous History: Regenerated at 960°F for 10 hours with air at 54 ml/min

Run #	Time hr	Temp °C	$\frac{1}{LHSV}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-24-1	2.00	421	12.82	94.50	0.0147	0.0702	0.0175	0.1637	0.0082	0.8655	0.0760	0.0877	0.0205	0.0409
III-24-2	5.00	421	12.82	90.88	0.0131	0.0654	0.0131	0.1503	0.0091	0.9935	0.0718	0.0784	0.0261	0.1470
III-24-3	7.00	420	12.82	83.80	0.0132	0.0132	0.0751	0.1369	0.0089	0.9040	0.0655	0.0822	0.0724	0.0361
III-24-4	10.20	421	12.82	82.30	0.0231	0.0728	0.0194	0.1509	0.0066	1.0066	0.0728	0.0794	0.0364	0.0000
III-24-5	11.60	421	12.82	83.00	0.0353	0.0288	0.0192	0.0540	0.0096	1.0128	0.0352	0.0600	0.0481	0.0000

Table 7 Continued.,

Date: 11/28/78

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 73° F Barometric Pressure: 29.5 in Hg

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

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-25-1	2.33	416	6.67	87.24	0.0173	0.0491	0.0173	0.2081	0.0347	0.7572	0.0751	0.0693	0.0289	0.0375
III-25-2	5.08	416	6.67	83.56	0.1087	0.0602	0.0181	0.1747	0.0361	0.7649	0.0964	0.0663	0.0331	0.0120
III-25-3	8.67	416	6.67	76.45	0.0230	0.0724	0.0230	0.1645	0.0460	0.6974	0.0738	0.0757	0.0461	0.0230
III-25-4	10.92	416	6.67	71.65	0.0211	0.0352	0.0211	0.1400	0.0422	0.7922	0.0770	0.0739	0.0599	0.0000
III-25-5	12.42	416	6.67	52.16	0.0096	0.0240	0.0096	0.0385	0.0144	0.6490	0.0049	0.0048	0.3173	0.2087

Table 7 Continued..

Date: 12/11/78

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 73°F Barometric Pressure: 29.50 in Hg

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

Run #	Time hr	Temp °C	$\frac{1}{LHSV}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity C ₂ H ₆	H ₂ O	C ₃ H ₆	C ₃ H ₈	DME	H ₂
III-26-1	0.67	438	13.16	94.28	0.0169	0.0424	0.0113	0.1695	0.0169	0.7881	0.1045	0.0791	0.0310	0.0000
III-26-2	1.58	438	8.20	88.08	0.0113	0.0491	0.0075	0.1509	0.0113	0.7924	0.1089	0.0755	0.0339	0.0604
III-26-3	2.00	438	5.49	81.49	0.0136	0.0335	0.0218	0.1448	0.0218	0.7950	0.1092	0.0409	0.0409	0.0000
III-26-4	3.50	438	2.58	55.57	0.1205	0.0626	0.0475	0.0194	0.0216	0.7754	0.1189	0.0920	0.0864	0.0000
III-26-5	6.25	437	1.72	32.30	0.0129	0.0453	0.0237	0.0065	0.0065	0.5645	0.0062	0.4090	0.9730	0.0000

Table 7 Continued..

Date: 11/31/78

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 73°F Barometric Pressure: 29.85 in Hg

Previous History: Regenerated at 875°F for 12 hours with air at 50 ml/min

Run #	Time hr	Temp °C	$\frac{1}{LHSV}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-27-1	2.33	415	11.63	91.77	0.0103	0.0513	0.0051	0.1539	0.0102	0.8000	0.0974	0.0718	0.0308	0.0666
III-27-2	2.65	415	6.09	85.14	0.0116	0.0435	0.0232	0.1536	0.0203	0.7942	0.0985	0.0841	0.0377	0.0173
III-27-3	4.18	415	3.29	65.07	0.0122	0.0592	0.0510	0.1122	0.0440	0.7510	0.0837	0.0735	0.0612	0.0408
III-27-4	8.50	415	2.34	51.66	0.0092	0.0642	0.0311	0.1098	0.0311	0.8663	0.0623	0.0439	0.1025	0.0000
III-27-5	10.10	415	1.87	35.72	0.0106	0.0659	0.0319	0.1149	0.0319	0.5723	0.0659	0.0468	0.1106	0.0829

Table 7 Continued.,

Date: 12/6/78

Catalyst: AW500 Amm ReCl-III

Feed: Methnaol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 72 F Barometric Pressure: 29.82 in Hg

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

Run #	Time hr	Temp °C	$\frac{1}{LHSV}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
III-28-1	1.92	384	16.13	91.39	0.0143	0.0500	0.0143	0.1358	0.0286	0.7857	0.1071	0.0643	0.0429	0.0357
III-28-2	3.17	384	7.94	75.25	0.0229	0.0686	0.0171	0.1429	0.0171	0.7600	0.1028	0.0629	0.0514	0.0571
III-28-3	4.27	384	5.68	70.82	0.0099	0.0493	0.0098	0.0887	0.0148	0.8079	0.0689	0.0591	0.0492	0.2955
III-28-4	5.19	385	3.94	69.61	0.0153	0.0612	0.0122	0.1039	0.0183	0.7798	0.0795	0.0612	0.0581	0.1834
III-28-5	5.86	385	3.01	59.32	0.0288	0.0699	0.0123	0.1194	0.0288	0.7325	0.1069	0.0535	0.0494	0.1358
III-28-6	6.94	385	2.23	28.54	0.0275	0.0826	0.0110	0.1101	0.0229	0.6238	0.0688	0.0413	0.1238	0.0000

Table 7 Continued.,

Date: 12/8/78

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 70 F Barometric Pressure: 29.70 in Hg

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

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-29-1	1.17	361	12.05	86.59	0.0192	0.0288	0.0192	0.1298	0.0288	0.7938	0.0962	0.0481	0.0481	0.0000
III-29-2	2.67	361	6.58	80.29	0.0199	0.0331	0.0199	0.1391	0.0265	0.7881	0.0993	0.0795	0.0529	0.0000
III-29-3	3.92	362	3.52	54.91	0.0234	0.0391	0.0195	0.1562	0.0312	0.7500	0.0937	0.0625	0.0742	0.0195
III-29-4	4.84	362	2.76	46.11	0.0182	0.0365	0.0401	0.124	0.0438	0.7372	0.0949	0.0583	0.0876	0.0474
III-29-5	5.92	359	2.46	28.33	0.0093	0.0374	0.0421	0.0888	0.0421	0.6355	0.0654	0.0421	0.1636	0.1308

Table 7 Continued ..

Date: 12/18/78

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 70°F Barometric Pressure: 30.80 in Hg

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

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-30-1	0.58	450	19.23	91.50	0.0128	0.0596	0.0085	0.1617	0.0170	0.7872	0.1148	0.0468	0.0211	0.1063
III-30-2	2.25	451	10.75	93.79	0.0187	0.0558	0.0093	0.1628	0.0279	0.7488	0.1163	0.0559	0.0232	0.0976
III-30-3	3.08	451	6.13	83.84	0.0179	0.0655	0.0119	0.1488	0.0298	0.7024	0.1071	0.0655	0.0297	0.1071
III-30-4	3.66	449	4.39	90.82	0.0118	0.0431	0.0078	0.1488	0.0235	0.4235	0.0745	0.0628	0.0392	0.0000
III-30-5	4.74	450	3.50	73.59	0.0191	0.0565	0.0710	0.0980	0.0298	0.7232	0.0952	0.0774	0.0298	0.1101
III-30-6	6.07	449	2.69	56.62	0.0233	0.0612	0.0087	0.1428	0.0348	0.6414	0.0962	0.0787	0.0525	0.1224
III-30-7	6.74	449	2.37	46.36	0.0217	0.0652	0.0124	0.1254	0.0378	0.6149	0.0994	0.0714	0.0652	0.0962

Table 7 Continued.,

Date: 12/21/78

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 72°F Barometric Pressure: 29.87 in Hg

Previous History: Regenerated at 906°F for 10.4 hours with air at 42 ml/min

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-31-1	1.25	415	12.19	94.04	0.0162	0.0540	0.0270	0.1892	0.0216	0.7621	0.0811	0.0594	0.0432	0.0810
III-31-2	4.67	416	12.19	90.66	0.0112	0.0670	0.0335	0.1451	0.0279	0.7150	0.0782	0.0614	0.0447	0.1564
III-31-3	7.08	417	12.19	84.95	0.0059	0.0119	0.0059	0.0419	0.0119	0.6946	0.0239	0.0119	0.1857	0.0478
III-31-4	10.04	416	12.19	76.87	0.0243	0.0596	0.0243	0.1530	0.0397	0.6820	0.0662	0.0530	0.0618	0.1192

Table 7 Continued.,

Date: 12/25/78

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

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

Previous History: Regenerated at 910° F for 10.85 hours with air at 40 ml/min

Run #	Time hr	Temp °C	$\frac{1}{LHSV}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-32-1	1.83	419	3.98	75.28	0.0355	0.0419	0.0355	0.1250	0.0367	0.7770	0.0662	0.0441	0.0710	0.2494
III-32-2	4.10	419	3.98	76.62	0.0238	0.0434	0.0477	0.1170	0.0456	0.7790	0.0773	0.0477	0.0706	0.1247
III-32-3	6.33	421	3.98	72.39	0.0367	0.0550	0.0367	0.1100	0.0554	0.7087	0.0665	0.0642	0.0779	0.1055
III-32-4	9.75	421	3.98	63.70	0.0313	0.0677	0.0547	0.0936	0.0468	0.6901	0.0651	0.0599	0.0937	0.1119
III-32-5	11.66	422	3.98	57.88	0.0401	0.0830	0.0630	0.0974	0.0401	0.5988	0.0659	0.0630	0.1031	0.1604

Table 7 Continued.,

Date: 12/26/78

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 73°F Barometric Pressure: 30.50 in Hg

Previous History: Regenerated at 908°F for 11.50 hours with air at 40, ml/min

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-33-1	1.67	418	3.13	59.56	0.0488	0.0425	0.0297	0.1253	0.0531	0.6709	0.0637	0.0573	0.0722	0.1932
III-33-2	3.50	417	3.13	55.05	0.0529	0.0381	0.0345	0.1126	0.0460	0.6736	0.0690	0.0391	0.0782	0.2851
III-33-3	6.50	417	3.13	52.97	0.0646	0.0383	0.0287	0.1196	0.0550	0.6531	0.0694	0.0598	0.0837	0.1699
III-33-4	7.33	417	3.13	55.48	0.0731	0.0411	0.0388	0.1027	0.0411	0.6438	0.0753	0.0502	0.1187	0.1552
III-33-5	9.66	418	3.13	50.90	0.0747	0.0522	0.0473	0.1070	0.0248	0.6119	0.0871	0.0597	0.1219	0.1318

Table 7 Continued.,

Date: 12/28/78

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 72°F Barometric Pressure: 30.66 in Hg

Previous History: Regenerated at 906°F for 12.8 hours with air at 40 ml/min

Run #	Time hr	Temp °C	$\frac{1}{LHSV}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-34-1	1.33	420	2.50	47.01	0.0107	0.0323	0.0172	0.0946	0.1484	0.6344	0.0409	0.0301	0.0753	0.1935
III-34-2	5.33	420	2.50	43.08	0.0141	0.0235	0.0141	0.0751	0.0141	0.5869	0.0282	0.0211	0.2559	0.2253
III-34-3	10.33	419	2.50	33.99	0.0327	0.0565	0.0298	0.1726	0.0327	0.5625	0.0803	0.0714	0.1101	0.0000
III-34-4	13.25	419	2.50	24.85	0.0407	0.0569	0.0366	0.1545	0.0366	0.4431	0.0854	0.0650	0.1382	0.0000
III-34-5	15.23	419	2.50	27.55	0.0183	0.0586	0.0293	0.1611	0.2527	0.0806	0.0696	0.0513	0.1282	0.3297

Table 7 Continued..

Date: 2/15/79

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 71°F Barometric Pressure: 29.88 in Hg

Previous History: Regenerated at 980°F for 8.75 hours with air at 40 ml/min

Run #	Time hr	Temp °C	$\frac{1}{LHSV}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-35-1	3.25	271	2.58	68.10	0.0460	0.0445	0.0046	0.0046	0.0040	0.5391	0.0000	0.0000	0.4430	0.0000
III-35-2	4.75	259	6.75	72.66	0.0075	0.0150	0.0075	0.0075	0.0000	0.7471	0.0000	0.0000	0.3509	0.0000
III-35-3	10.08	271	17.24	78.30	0.0088	0.0176	0.0265	0.0353	0.0000	0.9557	0.0000	0.0000	0.3008	0.0000

Table 7 Continued.,

Date: 6/5/79

Catalyst: AW500 AmmReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 72°F Barometric Pressure: 29.84 in Hg

Previous History: Regenerated at 982°F for 4 hours with and 7 hours without stirring using air at 40 ml/min

Run #	Time hr	Temp °C	$\frac{1}{LHSV}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-36-1	1.20	348	5.35	83.95	0.0309	0.0721	0.0360	0.1623	0.0618	0.8891	0.0309	0.0541	0.0438	0.0000
III-36-2	4.25	349	5.35	82.04	0.0765	0.1030	0.0263	0.1163	0.0422	0.6094	0.0290	0.0448	0.0448	0.0000
III-36-3	6.33	349	5.35	63.83	0.0711	0.0949	0.0237	0.1288	0.0644	0.7728	0.0338	0.0508	0.0779	0.0000
III-36-4	10.25	348	5.35	69.83	0.0062	0.0200	0.0062	0.0062	0.0000	0.7422	0.0000	0.0000	0.3602	0.0000

Table 7 Continued.,

Date: 6/9/79

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 74 °F Barometric Pressure: 29.88 in Hg

Previous History: Regenerated at 976 °F for 3 hours with and 9 hours without agitation using air at 40 ml/min.

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-37-1	3.00	351	3.21	70.75	0.0496	0.0441	0.0459	0.1158	0.0376	0.7500	0.0312	0.0441	0.0919	0.0000
III-37-2	5.85	353	3.21	64.02	0.0386	0.0975	0.0325	0.1260	0.0284	0.8272	0.0325	0.0243	0.1280	0.0000
III-37-3	7.27	352	3.21	69.99	0.0620	0.0390	0.0566	0.1206	0.0440	0.5167	0.0250	0.0350	0.0560	0.0446
III-37-4	9.67	349	3.21	56.23	0.0671	0.0740	0.0740	0.0509	0.0486	0.7175	0.0208	0.0486	0.2060	0.0000

Table 7 Continued..

Date: 6/11/79

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 74°F Barometric Pressure: 28.97 in Hg

Previous History: Regenerated at 968°F for 11.7 hours with air at 40 ml/min

Run #	Time hr	Temp °C	$\frac{1}{LHSV}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity C ₂ H ₆	H ₂ O	C ₃ H ₆	C ₃ H ₈	DME	H ₂
III-38-1	2.00	351	2.20	71.00	0.0286	0.0410	0.0223	0.0833	0.0286	0.6816	0.0223	0.0223	0.0771	0.0000
III-38-2	3.75	353	2.20	62.69	0.0412	0.0483	0.0298	0.0867	0.0455	0.6756	0.0256	0.0241	0.1152	0.0000
III-38-3	4.89	353	2.20	55.23	0.0741	0.0548	0.0451	0.0790	0.0387	0.7661	0.0080	0.0274	0.1661	0.0000
III-38-4	7.33	355	2.20	56.68	0.0396	0.0380	0.0570	0.0871	0.0285	0.7416	0.0364	0.0507	0.1759	0.0792
III-38-5	9.08	353	2.20	66.00	0.0688	0.0700	0.0480	0.0570	0.0430	0.6531	0.0229	0.0420	0.2105	0.0000
III-38-6	10.41	353	2.20	57.11	0.0590	0.0450	0.0372	0.0621	0.0388	0.6723	0.0263	0.0248	0.1847	0.0000

Table 7 Continued.,

Date: 6/13/79

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 76°F Barometric Pressure: 29.70 in Hg

Previous History: Regenerated at 978°F for 8.9 hours with air at 40 ml/min

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-39-1	1.15	349	1.72	65.81	0.0668	0.0583	0.0233	0.1234	0.0430	0.6974	0.0154	0.0297	0.1560	0.0000
III-39-2	2.38	350	1.72	60.88	0.0745	0.0481	0.0387	0.1146	0.0286	0.7431	0.0275	0.0355	0.1508	0.0000
III-39-3	3.88	349	1.72	59.90	0.0593	0.0640	0.0535	0.0590	0.0314	0.6367	0.0291	0.0349	0.1711	0.0000
III-39-4	5.13	351	1.72	53.34	0.0776	0.0665	0.0485	0.0776	0.0263	0.7267	0.0194	0.0402	0.2163	0.0000
III-39-5	6.21	351	1.72	50.39	0.0595	0.0554	0.0595	0.0512	0.0000	0.8476	0.0263	0.0387	0.1935	0.0000
III-39-6	9.21	350	1.72	44.80	0.0903	0.0576	0.0451	0.0249	0.0000	0.6713	0.0249	0.0467	0.2570	0.0000

Table 7 Continued.,

Date: 6/14/79

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 72°F Barometric Pressure: 29.76 in Hg

Previous History: Regenerated at 968°F for 8 hours with air at 40 ml/min

Run #	Time hr	Temp °C	$\frac{1}{LHSV}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-40-1	2.00	304	11.74	69.55	0.0406	0.0338	0.0610	0.0745	0.0372	0.8754	0.0271	0.0406	0.0881	0.0000
III-40-2	2.93	304	11.74	71.23	0.0220	0.0560	0.0329	0.0617	0.0411	0.8024	0.0184	0.0329	0.1350	0.0000
III-40-3	6.92	305	11.74	64.90	0.0400	0.0943	0.0212	0.0636	0.0000	0.7264	0.0117	0.0259	0.2216	0.0000
III-40-4	9.40	306	11.74	57.12	0.0230	0.0520	0.0180	0.0460	0.0000	0.8220	0.0074	0.0284	0.2880	0.0000

Table 7 Continued..

Date: 6/16/79

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 76° F Barometric Pressure: 29.83 in Hg

Previous History: Regenerated with air at 40 ml/min at 958° F for 8.5 hours

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-41-1	1.25	301	6.12	60.46	0.0362	0.1187	0.0321	0.0663	0.0201	0.7487	0.0221	0.0221	0.1549	0.0000
III-41-2	4.25	301	6.12	55.38	0.1153	0.1124	0.0414	0.0680	0.0473	0.6360	0.0135	0.0000	0.1923	0.0000
III-41-3	6.25	302	6.12	54.78	0.0880	0.1128	0.0677	0.0428	0.0000	0.5936	0.0158	0.0000	0.2090	0.0000
III-41-4	8.75	302	6.12	51.73	0.0813	0.1459	0.0502	0.0239	0.0000	0.6483	0.0000	0.0000	0.2464	0.0000

Table 7 Continued.,

Date: 6/21/79

Catalyst: AW500 Amm ReCl-III

Feed: Methnanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 74°F Barometric Pressure: 29.99 in Hg

Previous History: Regenerated at 976°F for 6 hours with and 4 hours without stirring using air at 40 ml/min

Run #	Time hr	Temp °C	$\frac{1}{\text{LSHV}}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-42-1	3.00	303	2.77	43.08	0.0883	0.1454	0.0649	0.0311	0.0000	0.7402	0.0311	0.0000	0.2500	0.0000
III-42-2	6.25	303	2.77	45.46	0.0444	0.8890	0.0359	0.0493	0.0197	0.5334	0.0172	0.0000	0.2519	0.0000
III-42-3	7.25	302	2.77	40.52	0.0360	0.0700	0.0360	0.1905	0.0167	0.6011	0.0110	0.0000	0.2766	0.0000
III-42-4	8.50	304	2.77	46.13	0.0265	0.1229	0.0520	0.0000	0.0000	0.7518	0.0000	0.0000	0.2868	0.0000

Table 7 Continued.,

Date: 6/28/79

Catalyst: AW500 AmmReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 74° F Barometric Pressure: 29.99 in Hg

Previous History: Regenerated at 965° F for 7.5 hrs. using air at 40 ml/min. 45 grams of AW500 ReCl is charged into the prereactor. The feed was switched through the prereactor at the end of 1.25 hours

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-43-1	1.08	427	14.62	93.30	0.0127	0.0253	0.0190	0.1392	0.0506	0.8861	0.0506	0.0443	0.0443	0.0000
III-43-2	3.00	428	14.62	74.15	0.0160	0.0240	0.0320	0.1120	0.0160	1.0320	0.0240	0.0400	0.0800	0.0000
III-43-3	6.67	427	14.62	71.70	0.0230	0.0390	0.0135	0.0856	0.0248	0.9504	0.0185	0.0185	0.1507	0.0000
III-43-4	7.82	428	14.62	69.84	0.0120	0.0424	0.0168	0.0424	0.0000	0.8475	0.0085	0.0254	0.2458	0.0000

Table 7 Continued.,

Date: 6/29/79

Catalyst: AW500 Amm ReCl-III

Feed: Methanol with 2000 ppm CS₂

Reactor Pressure: 25 psig

Room Temperature: 74° F Barometric Pressure: 29.80 in Hg

Previous History: Regenerated at 978° F for 8.5 hours using air at 40 ml/min. The feed was switched through the prereactor at the end of 2.00 hours.

Run #	Time hr	Temp °C	$\frac{1}{\text{LHSV}}$	X%	CO	CH ₄	CO ₂	C ₂ H ₄	Selectivity		C ₃ H ₆	C ₃ H ₈	DME	H ₂
									C ₂ H ₆	H ₂ O				
III-44-1	1.67	424	5.62	64.95	0.0069	0.0174	0.0065	0.0868	0.0382	0.9306	0.0417	0.0417	0.0625	0.0000
III-44-2	3.00	429	5.62	73.35	0.0481	0.0644	0.0429	0.1288	0.0613	0.8387	0.0399	0.0307	0.0920	0.0000
III-44-3	4.25	430	5.62	66.12	0.0680	0.0580	0.0408	0.0680	0.0238	0.7313	0.0170	0.0340	0.1531	0.0000
III-44-4	7.25	430	5.62	64.30	0.0635	0.0535	0.0401	0.0635	0.0201	0.7257	0.0167	0.0334	0.1438	0.0000

designated as AW500 Amm ReCl-III was placed in the reactor. The catalyst bed height was changed from 3.5 inches to 0.5 inches after the run # 21. Run 35 was conducted to study the possibility of replacing the Alumina in the prereactor with AW500 AmmReCl. Runs 43 and 44 were conducted with the prereactor packed with 45 grams of AW500 Amm ReCl maintained at 270°C.

Initial Experiments

The initial experiments were designed to investigate the catalyst life, temporary decay, the effects of water, pressure and carbon disulfide on the yields, selectivities and the activity of the catalyst.

A difficulty with the catalyst prepared and tested by Lin et al., (1977) was the short time of activity between regenerations. This short term deactivation was due to coke accumulation on the catalyst surface, because the catalyst could be regenerated by burning off carbon using air and high temperature.

In the experiments conducted by Lin, it was observed that 100 ppm of carbon disulfide appeared to restore the catalyst activity and sustain it for a longer time. Therefore, in this investigation, carbon disulfide 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 were utilized. Figure 10 illustrates the rapid decay of the catalyst when methanol was used without carbon disulfide. Figure 11 illustrates the effect of feeding methanol with 6000 ppm of carbon disulfide. Initially, only dehydrogenation of methanol to carbon monoxide and hydrogen is observed. After the carbon disulfide concentration was reduced to 1000 ppm, ethylene, propylene and propane were produced.

The effect of carbon disulfide appears to be similar to the results obtained in the following studies. In a study of methanol decomposition over a copper catalyst, Bakshi and Gosh (1929) report that the carbon disulfide in methanol feed stabilizes the formaldehyde intermediate steps. The reaction of methanol is proposed to occur in two steps as shown below.

At moderate concentrations of carbon disulfide, the velocity constant for the first reaction decreases slightly while that of the second reaction is almost halved. Above a level of 4112 ppm carbon disulfide, the copper catalyst used in the above study was completely deactivated. The rate of decrease in the velocity constant for the first reaction was observed to be a function of the carbon disulfide concentration.

Fig. 10. Catalyst activity in the absence of CS_2

Fig. 11. Effect of CS₂ on activity and yields.

Frommet et al., (1976) report the use of carbon disulfide on cracking catalysts to maintain catalyst activity and to prevent coking. Catalytic activity of sulfur impregnated zeolites has been studied by Dudzik and Preston (1968). They report that upon sulfur impregnation, due to the presence of long sulfur chains in the zeolite lattice, the sulfur saturated Linde molecular sieve 3A is stable and active in the heterogeneous decomposition of hydrocarbons. They also suggest that sulfur free-radicals participate directly or indirectly in the cracking reactions. Using Electron Paramagnetic Radiation Studies (EPR), paramagnetic sulfur free-radical species were identified on the surface of the different catalysts, MoO_3/MgO , WO_3/MgO , CrO_3/MgO , $\text{MoO}_3/\text{SiO}_2$ and $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ by Kosdov et al., (1977 and 1978) They attribute the catalyst activity to the presence of paramagnetic species. During personal communications with Somorjai (1979), he suggested that the coke formation on the surface of the catalyst is due to the weakening of the carbon carbon bond in the hydrocarbons formed, resulting in carbon atoms forming a stronger bond with the surface active sites. The carbon disulfide or any sulfur compounds form inert intermediate species on the surface of the catalyst increasing carbon carbon bond strength and preventing coke formation.

The effect of sulfur compounds on the catalysts used in cracking and similar reactions has been a focus of various studies in the recent years. Of special interest is the

special emphasis on the reactions of Claus type involving the sulfur compounds hydrogen sulfide, carbon disulfide and sulfur dioxide on cracking catalysts at high temperatures in the presence of water.

To determine the effect of water on the catalyst activity and selectivity, a molar mixture of 64% water and 36% methanol was passed over the catalyst. As illustrated in Figure 12, ethylene yields were as high as 60%. Hence water substantially increases the catalyst selectivity towards ethylene. Topchieva et al., (1968), in a study of cumene cracking on zeolites, observed a two fold reversible increase in the catalytic activity due to the presence of water. Givens et al., (1978), have also found that the water enhances the selectivity in converting methanol to ethylene. Ceaser and Morrison (1978) obtained a patent for producing ethylene by conversion of methanol in the presence of water diluent on a HZSM-5 type of catalyst.

The effect of pressure on the selectivity of producing olefins is illustrated in Figure 13. These data illustrate that increasing the pressure increases the yields of propylene at the expense of ethylene. This is partially due to the fact that the formation of olefins is made possible as a consequence of the polymerization of the methylene specie formed during the decomposition of the surface formaldehyde specie. Increase in pressure gives the

Fig. 12. Effect of water on yields in presence of CS₂

Fig. 13. Effect of pressure on feeding pure methanol in the presence of CS₂

methylene species opportunity for polymerization.

The effect of feeding an equilibrium mixture of methanol, dimethyl ether and water was investigated. Methanol was passed over a γ -Alumina catalyst and the reaction products were passed over the chabazite catalyst, AW500 Amm ReCl-II, in the Berty reactor system. As illustrated in runs 19 and 20, ethylene yields were low to begin with and the selectivity toward olefins disappeared in due time, suggesting the reaction is completely progressing toward dehydration of methanol to dimethyl ether.

In the majority of the experiments conducted in this set, methanol conversions were high. For most of the experiments, the material balances were not obtained because of difficulty involved with faulty pump operation and the pulsating gas flows. The positive displacement pump used in this work imparts a certain amount of pulsations to the flow of methanol. These pulsations become significant at the low flowrates involved. The method of condensation of the liquid products also affects the flowrate measurement greatly. It appeared from examination of the data that the catalytic activity was essentially constant for eight to ten hours. Therefore the next set of experiments was obtained to study the kinetics of the reaction of conversion of methanol.

Kinetic Experiments

Since the catalyst activity appeared to be constant, a set of runs was conducted with changing liquid hourly space velocity. 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 and the X-ray diffraction studies, a fresh batch of catalyst was charged to the reactor. Runs 22 through 31 constitute this set. Runs 24 and 25 were conducted at 420°C and 416°C and at $1/\text{LHSV}$ of 12.82 and 6.67, respectively. Examination of the data in these experiments indicated the catalyst activity and selectivity were changing substantially over the run time of 10 to 12 hours. Corrections for runs 22, 23, 24, 26, 27, 28, 29 and 30 to zero time would be significant. These data uncorrected for catalyst decay are shown in Figure 14.

The time on stream for each run at high reciprocal LHSV and the high conversions was less than 2 hours. In each run the maximum conversion is 90 to 94%. This seems to suggest some type of limit on conversion at least for this type of reactor. Figure 14 also illustrates that space velocities of 0.1 to 10 should be used to collect the kinetic data. Figure 15 illustrates the changes in selectivity of different products at fixed liquid hourly space velocity and temperature. The major change occurs in the yields of

Fig. 14. Methanol conversions uncorrected for catalyst decay

Fig. 15. Variation of yields with time on stream

ethylene which decrease from 40 to 30% over a 10 hour period and dimethyl ether yields which increase with time.

Runs 31 through 42 constitute the set of experiments studied to understand the kinetic aspects of the conversion. In this set of experiments, the liquid hourly space velocity and the temperature were held constant. The catalyst was regenerated for approximately 10 to 12 hours between each run. The conversion as a function of liquid hourly space velocity and time on stream for temperatures 400, 350 and 300 °C are shown in Figures 16, 17 and 18. Runs 22 and 24 illustrate that no permanent loss in the catalytic activity has occurred. The fact that these curves are nearly parallel suggests that the decay is independent of space velocity. Similar results were obtained by Weekman (1968) for the decay of cracking catalysts. These curves are substantially different than those reported by Cobb et al., (1978). This difference may be due to the fact that Cobb et al., operated their reactor for 15 to 20 hours before regeneration. They also did not feed any carbon disulfide. During this long reaction period, the decomposition reaction changes from producing olefins to producing dimethyl ether. Therefore, a substantial portion of their reaction time would be the study of the decline of catalyst activity for conversion of methanol to dimethyl ether rather than the decline of activity for hydrocarbon production. The same explanation

Fig. 16 Variation of methanol conversion with time on stream and 1/LHSV at 690 K

Fig. 17 Variation of methanol conversion with time on stream and 1/LHSV at 623 K

Fig. 18 Variation of methanol conversion with time on stream and $1/\text{LHSV}$ at 576°K

could account for permanent loss of catalyst activity due to regeneration reported by Cobb et al., (1978). Since significant quantities of carbon (coke) accumulated on the catalyst surface, excessive temperatures, which would destroy the catalyst, probably occurred during the regeneration.

Figures 19, 20 and 21 illustrate the effect of space velocity on the selectivity of each of the products. 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 may be formed due to a secondary reaction. Similar curves can also be obtained in a parallel network involving methanol to dimethyl ether and olefins. This concept is discussed in greater detail in the chapter on mechanism and rate expression. The trends indicated by the data in Figures 19, 20 and 21 are similar to those reported by Chang, Lang and Silvestri (1977) for the conversion of methanol to gasoline on a ZSM-5 zeolite.

Lower reciprocal liquid hourly space velocities yielded in general lower conversions and higher selectivities toward formation of dimethyl ether. The increase in temperature increased the yields of hydrocarbons and decreased the yields of dimethyl ether, thus increasing the efficiency of the catalyst.

Fig. 19. Product distribution obtained at time on stream of 1 to 2.5 hours on decaying catalyst

Fig. 20. Product distribution for time on stream of 5 to 8 hours on a decaying catalyst

Fig. 21. Product distribution obtained at time on stream of ten hours or greater on a decaying catalyst

CHAPTER VIII

X-RAY DIFFRACTION STUDIES

The crystal structure of AW500 zeolite has been studied using Cu-K_α 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 actual x-rays for different samples were obtained by Ms. Sufain with the courtesy of Drs. Deepak Thakur and Abraham Clearfield. 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, however, 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 has been deactivated indicate presence of some external substance, possibly carbon on the surface. From the comparison of the experiments conducted, it can be concluded that after about 21 regenerations and 3 months of use the catalyst could be regenerated and returned to the initial activity. These observations coupled with the x-ray analysis suggest that no permanent deactivation 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 crystals have been reported by Grude and Sheppard, as presented by Breck (1974). Grude and Sheppard used powder photography to identify and characterize the significant peaks with their intensities. From the experimental results of the x-ray analysis, the most significant peaks with reasonable intensities have been selected to identify and compare with those reported by Grude and Sheppard. The peaks with significant intensities from X-ray analysis reported by Grude and Sheppard are presented in Table 8.

The actual x-ray spectra obtained are presented in a reduced form in Figures 22, 23, 24 and 25. Samples subjected to the analysis have been selected to represent conditions involved in the experimental study.

Sample 1 is an x-ray pattern for AW500 without any ion exchange or heat treatment. The structure complies with the significant peaks as suggested by Grude and Sheppard.

Samples 2, 3 and 4 represent the samples of AW500 exchanged with ammonia and rare earth chloride mixture, rare earth chloride mixture 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 have not been

TABLE 8. X-RAY DIFFRACTION DATA FOR CHABAZITE

h k l	d(A)	I*	2 θ
1 0 1	9.351	50	9.42
1 1 0	6.894	10	13.22
0 0 3	5.021	30	17.67
2 1 1	4.324	76	20.55
2 1 2	3.870	28	22.97
1 0 4	3.590	23	24.80
2 2 0	3.448	13	25.85
4 0 1	2.925	100	30.55
2 1 4	2.890	30	30.95
4 1 0	2.605	10	34.45
2 1 5	2.507	11	35.87

* Relative intensities

Fig. 22 . X-ray diffraction patterns for samples 4 and 1.

Fig.23. X-ray diffraction patterns for samples 2 and 3.

Fig.24 . X-ray diffraction patterns for samples 7 and 6

Fig.25. X-ray diffraction patterns for samples 5 and 8..

exposed to the reactants or the reaction temperatures.

Sample 5 is an x-ray pattern for the catalyst used in this study, AW500 ion exchanged with ammonia and rare earth chloride mixture. This pattern was obtained after subjecting the catalyst to the reaction temperature of 400°C for 35 hours with a nitrogen blanket. Compared to the sample 2, the structure shows noticeable modifications in the peak intensities, indicating that exposure to heat does modify the structure slightly.

Sample 6 is an x-ray pattern for the catalyst used in this study, AW500 ion exchanged with ammonia and rare earth chloride mixture, after 21 regenerations. The pattern was obtained on a deactivated sample. Clearly the deactivation does have an effect in reducing the intensities of the peaks.

Sample 7 is an x-ray pattern for the above catalyst after regenerating it with air. The regenerated catalyst has properties similar to the catalyst that has been subjected to temperature of 400°C for 35 hours as represented by sample 5. By comparison with samples 5 and 6, which were obtained when the catalyst was active, we inferred that the deactivation modifies the crystal structure in certain planes due to coking and returns to normal active condition after regeneration with air.

Sample 8 is an x-ray pattern for the AW500 ion

exchanged with ammonia and rare earth chloride mixture, which was accidentally overheated to 1300 F. 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 the 10th D-R cycle, the conversion to olefins nearly disappeared.

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

The conclusions drawn by Cobb et al., from these results were that the carbon laydown is the cause of short time deactivation and that the 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 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 on the surface of the catalyst. 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 need further study. The basic difference between the two studies is the type of ion exchange used for the preparation of the catalyst. In the studies conducted at the University of Pittsburgh, they used the catalyst reported by us in the early stages of our investigation, chabazite ion exchanged with Lanthanum. The chabazite used by them was obtained from Norton Chemical Company, and it had a substantial difference in the composition. They also conducted the runs until the catalyst had no activity for dimethyl ether or ethylene production. We discontinued the run and regenerated when the ethylene yields decreased and the dimethyl ether yields increased. Since our early report, the catalyst has been significantly improved with respect to its life, activity and selectivity using different procedures for ion exchange, which was not taken into consideration by the investigators at the University of Pittsburgh. The catalyst used in this present study is a result of much improvement and development in the catalyst preparation procedures

As indicated in the previous chapters, the presence of water increases the selectivity of the catalyst toward forming olefins. The effect of ammonia and water vapor in combination on a zeolite is very complex. The reaction temperatures involved and the water formed during the olefin formation have a distinct effect on forming an ultrastable zeolite. The concept of ultrastable zeolites was first conceived by Barrer and Bratt as presented in Breck (1974). This has been defined as "Ultrastable" zeolite. The crystal structure of ultrastable zeolite Y is retained after heating it 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 zeolite, it was reported that the thermal stability is a function of the degree of ammonia 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 the zeolite Y dehydroxylates rapidly when heated to 650°C in an inert gas atmosphere. If water is removed by heating in vacuum, the resulting zeolite has relatively poor thermal stability. If the zeolite is calcined in the 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 deactivation regeneration cycles and 3 months of use.

CHAPTER IX

MECHANISM AND STOICHIOMETRY

Methanol Decomposition on Zeolites

Alcohols when dehydrated form ethers at low to moderate temperatures. The reactivity of alcohols with oxide surfaces and in particular with SiO_2 , MgO and Al_2O_3 has been investigated extensively. The dehydration catalysts yield, upon dehydration at high temperatures, substantial amounts of olefins. Classic example of this is the dehydration of ethanol to form diethyl ether at low to moderate temperatures and to ethylene at high temperatures. There is considerable controversy as to whether the dehydration step to ether formation is an intermediate step in the formation of olefins or if the olefin formation is by a primary reaction.

Topchieva, Kubasov and Dao (1972) reported a study of dehydration of methanol on the alkaline forms of zeolite X and Y. In their investigation, they reported that the de-cationated zeolites usually have strong Bronsted and Lewis acidity. The creation of strong protonic acidity by ion exchange promotes formation of 1-butene. They also obtained similar results for the dehydration of methanol on zeolites containing polyvalent cations. Various hydrocarbons, including butene were obtained together with ether. They

concluded that the dehydration of methanol on zeolites can proceed independently by two pathways, formation of dimethyl ether and formation of olefins. Electron accepting centers are active in the first pathway. The activity in the second pathway is associated with the presence of proton donating activity in the catalyst. Chang, Lang and Silvestri (1977) reported on conversion of methanol to hydrocarbons as a two step reaction. The first step is the dehydration to dimethyl ether and subsequently to hydrocarbons on a ZSM-5 type of catalyst. The major portion of the product distribution is in the gasoline boiling range with small amounts of ethylene and propylene.

Anderson et al., (1979) studied different catalytic reactions including dehydration of methanol on ZSM-5 type catalyst. They suggested that the fact that ZSM-5 yields less ethylene, indicates that a different active site is responsible for formation of ethylene than that for formation of other olefins. They suggest that the following types of reactions occur in the decomposition of methanol.

They clearly indicate that they avoided writing a C_2 adsorbed specie because it uses a different type of acidic site and has different characteristics.

Swabb and Gates (1972) elaborated on the Venuto and Landis elimination scheme in an effort to explain the role of H-mordenite in catalyzing olefin formation from methanol. They proposed a separation mechanism involving a concerted α -elimination by the co-action of Bronsted acidic sites and basic lattice sites. The mechanism proposed is shown below

Chang, Lang and Silvestri (1977); based on their data, suggested a pathway involving formation of carbonoid species as a primary step. They suggest that the methylene diradical once formed can dimerize:

or interact with methanol and dimethyl ether via sp^3 C-H insertion:

The primary mechanism in methanol/DME conversion to olefins according to them is a concerted bimolecular reaction.

Verdine et al., (1979) studied the acidic properties of HZSM-5 type zeolites by IR, ESR and microcalorimetry. Using pyridine adsorption, they showed the presence of Bronsted and Lewis types of acid sites on the surface of the catalyst. They report that depending upon temperature, the active sites interchange, or transform to different sites. Aurox et al., (1979) studied the acidity of ZSM-5 zeolite by microcalorimetry and infra-red spectroscopy. They observed a progressive transformation of Bronsted sites to Lewis sites using IR spectroscopy to study the adsorption of pyridine at different exposures to temperatures and reactants.

Mechanism of Methanol Decomposition

There are various mechanisms suggested by different authors for the decomposition of methanol over acidic and basic catalysts. The important ones are summarized as follows.

Venuto and Landis (1968) suggested an α -elimination for the production of hydrocarbons from methanol as shown below

The $:\text{CH}_2$ radical polymerizes to different hydrocarbons. They suggested that the dehydration of methanol is probably the rate controlling step in the complete scheme. The

reaction between methylene donor and acceptor (methanol or methyl ether) with subsequent protolysis yields olefins.

R, R' = H or alkyl. Carbene addition to the double bond of the initially formed olefins may also occur.

Salvador 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

At moderate temperatures, these $-\text{OCH}_3$ groups would react

with methanol molecules that are filling the cavities as,

with the greatest formation of dimethyl ether occurring at 210 C. At high temperatures, they propose the formation of olefins by decomposition of methoxylated specie, as proposed by Topchieva et al., (1972), with subsequent polymerization to olefins, i. e.,

In all of the possible mechanisms suggested above, there is always controversy as to whether the dehydration of methanol to dimethyl ether is an intermediate step or not. The results reported in this investigation are in continuation of the work reported by Lin, Chao and Anthony (1977 and 1978). In most of the work, the progress of the reaction is monitored by using the ethylene yields. Always, during the progress of the reaction, when the ethylene

yields decrease the dimethyl ether yields increase suggesting deactivation. Typical product distributions are illustrated in Figure 15. In the experiments conducted with feeding a mixture of dimethyl ether, water and methanol, methanol was initially passed directly on to the catalyst, establishing the active product distributions. At a predetermined time, the flow of methanol is diverted through the prereactor on to the catalyst. The yields of ethylene decrease and the yields of dimethyl ether increase indicating deactivation. Tipnis (1978) and Cobb et al., (1978) obtained similar results. Based on the above experiments and the data collected on the tubular reactor by Lin, Chao and Anthony (1977 and 1978), the mechanism basically consists of the premise that the methanol molecule adsorbs on the surface, forming two types of intermediates on two different active sites. Acidic sites are the sites for formation of methoxy species, which subsequently decompose to dimethyl ether and water. Slightly basic or less acidic sites are responsible for formation of the formaldehyde type of intermediate species that can decompose to form a methylene radical for subsequent polymerization to form olefins. The concept of formaldehyde type specie is also supported by the effects of the carbon disulfide discussed in Chapter VII.

The mechanism postulated is as follows:

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 showed more paraffins are produced than indicated by these two reactions. The additional paraffins may come from consideration of reactions 8 and 9. The observed product distributions have characteristics similar to a set of sequential or parallel reactions, i.e.,

or

The fact that the olefins yields dropped substantially when feeding an equilibrium mixture of dimethyl ether, water and methanol and that higher temperatures are required to obtain a reasonable yield of olefins, suggests that the 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 it is converted to the first site for producing dimethyl ether.

CHAPTER X
DEVELOPMENT OF RATE EXPRESSION AND SELECTIVITY
DATA CORRELATION

As discussed previously, the catalyst is in the development stage. The product distributions and the overall conversion of methanol varied with time on stream. The maximum time of activity observed once was 20 hours. The average time of activity based on reasonably good yields of the desired product, ethylene, is about 13 hours. In considering the kinetics of the reaction, the deactivation of the catalyst plays a major role.

To obtain the kinetic data along with the deactivation characteristics, the experiments were conducted at average temperatures of 420°C , 351°C and 303°C . These experiments were conducted at different liquid hourly space velocities as functions of the time on stream.

The set of data at 420°C was initially treated based on the time on stream theory of catalyst decay. In the time on stream theory of catalyst decay, Wojciechowski (1968) assumes that catalyst ages as a result of being used. In the case of cracking, some catalyst may be lost during the reaction as a result of impurities in the feed or due to the deposition of coke. The major cause of deactivation in conversion of methanol appears to be coke accumulation.

Hence, similar analysis was used in our reaction.

In the absence of significant resistance to pore and film diffusions, the rate, a function of temperature, composition and catalytic activity, 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 catalytic activity

t = Time on stream

r_A = Rate of disappearance of reactant A

The treatment of the decay function is simplified if the intrinsic kinetics and the activity are treated separately as suggested by Wojciechowski (1968).

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

For a perfectly mixed flow reactor, the rate of disappearance of reactant A may be expressed as

$$r_A = \rho_A S_1 X \text{ moles/(cc)(hr)} \quad (3)$$

where ρ_A = Molar density of methanol moles/cc

S_1 = Liquid hourly space velocity, 1/hr

X = Conversion of methanol

Elimination of r_A from equations 2 and 3 and rearrangement

yields,

$$X = \frac{1}{\rho_A S_1} a(T, P_i, t) f(T, P_i) \quad (4)$$

Pachovsky et al., (1973) have shown for coking on cracking catalysts that the activity may be represented as a generalized function of the time on stream, as follows

$$-\frac{da}{dt} = k_d a^m \quad (5)$$

where m = Order of the decay

k_d = Deactivation constant

The generalized solution for the above equation may be represented as follows,

$$a = (1 + Gt)^{-M} \quad (6)$$

for $m \neq 1$

$$M = 1/(m-1)$$

$$G = (m-1)k_d$$

for $m = 1$

$$a = a_0 e^{-k_d t}$$

a_0 = Initial activity

For a power law function representing the intrinsic kinetics,

$$f(P_i, T) = k_p \prod_{i=1}^C P_i^{\beta_i} \quad (7)$$

where k_p = Velocity constant, a function of temperature

c = Number of components in the system

β_i = Order of the reaction with respect to component i

Rearranging equation 4 and using 6 and 7,

$$X = (1 + Gt)^{-M} \frac{k_p}{\rho S_1} \prod_{i=1}^c P_i^{\beta_i} \quad (8)$$

The above equation may be rearranged to

$$t = \frac{k_p^{1/M}}{G} \left(\frac{1}{\rho S_1 X} \right)^{1/M} \prod_{i=1}^c P_i^{\beta_i/M} - 1/G \quad (9)$$

To obtain an initial set of guesses for the constants involved, assume initially $1/G$ approximately equal to zero and fit the equation using linear regression as

$$\ln t = \ln K_0 + K_1 \ln S + \sum K_i \ln P_i \quad (10)$$

where $K_0 = k_p^{1/M} / G$

$$S = (1 / \rho S_1 X)$$

$$K_i = \beta_i / M$$

The results obtained were used as initial guesses for the non linear solution of equation 8. From the results of the non linear regression

$$1/(m-1) = M = 62895678.9$$

or m is approximately equal to 1.

Hence, for further modeling, the deactivation of order 1 is

utilized with the activity function being,

$$a = e^{-k_d t} \quad (11)$$

Based on the above preliminary analysis and the literature search, three approaches were taken to model the system

- (1) Assume a power law model with all the components present in the rate expression
- (2) Hougen Watson type models derived based on mechanistic considerations for the particular system.
- (3) Empirical Hougen Watson models proposed for the methanol dehydration.

Almost all the models used based on the above premise indicated a large deviation in the experimental versus observed values for the overall conversion of methanol. The models attempted above are presented by Anthony (1979). Because of a regular trend in the residual plots, it was felt that some of the variables were not being treated properly. Further analysis using the cross plots at different times on stream suggested that the overall kinetics cannot be separated as suggested by the time on stream theory.

Therefore, efforts were concentrated on treating the deactivation as an integral part of the overall kinetics. It is essential that the rate equation must include the effects of deactivation. Hougen and Watson (1947) suggested

there is not usually sufficient information available on any one system to establish with certainty the best procedure for introducing a factor of deactivation into the fundamental rate equation. A "fouling factor" might be introduced as a multiplier in the numerator of the rate equation or an alternative method is to introduce the deactivation factor as an added term in the group in the denominator of the rate expression with the view that the deactivation has the same effect as the equilibrium adsorption of a constituent on the active sites.

Using the above principles, models of the following type were tested using the data collected at 420°C.

$$f_j = a + \sum \alpha_i P_i + \alpha_f \quad (12)$$

where

$$f_j = (P_A^n / r_A)^{1/m}$$

$$f_j = (P_A^2 - P_B P_C / K)^{1/m}$$

$$f_j = (P_A - P_B P_C / K P_A)^{1/m}$$

$$f_j = (P_A^{0.5} - P_B P_C / P_A^{1.5} K)^{1/m}$$

$$m = 1, 2 \text{ or } 3$$

$$n = 1, 2 \text{ or } 3$$

$$\alpha_f = c S_1 t + d t + e S_1^2 t + f S_1 t^2 + g t^2$$

- A = Methanol
 B = Dimethyl ether
 C = Water

The best of this set that yielded positive coefficients for the partial pressures was the following equation

$$X = \frac{P_{\text{MeOH}}^2}{(A + B P_{\text{MeOH}} + C S_1 t + D t)^3 \cdot S_1} \quad (13)$$

The above model was fitted to the data at 420°C and 303°C. The smoothed data at 351 were also fitted to the above expression. The randomness of conversions calculated using the above equation and the constants presented in Table 9 is presented in Figure 26. The average deviation between the experimental and the predicted conversion is 0.035 and the maximum deviation is 0.09. The constants evaluated using the nonlinear regression for the three temperatures are presented in Table 9 along with the asymptotic standard error limits. The dependency of the constants on temperature did not conform to the exact Arrhenius type. The reason for this could be the regeneration temperature and the conditions under which the catalyst was maintained during the time when no experiments were conducted. The experiments conducted at 420°C were regenerated at an average temperature of 900°F and the runs at 351 and 303°C were regenerated at an

TABLE 9. PARAMETER ESTIMATES FOR THE RATE EQUATION

Temp °C	A	B	C	D
420	7.8147 ± 0.4449	1.9130 ± 0.0707	-2.6026 ± 0.6283	0.9416 ± 0.1136
351	8.9556 ± 0.6047	1.5160 ± 0.0681	-4.4237 ± 0.4158	2.0677 ± 0.1590
303	38.3893 ± 3.7289	0.4272 ± 0.2697	-3.1256 ± 1.2736	1.5762 ± 0.2021

Units

$$A : \left(\frac{\text{cc hr } \text{psia}^2}{\text{moles}} \right)^{1/3}$$

$$B : \left(\frac{\text{cc hr } \text{psia}}{\text{moles}} \right)^{1/3}$$

$$C : \left(\frac{\text{cc hr } \text{psia}^2}{\text{moles}} \right)^{1/3}$$

$$D : \left(\frac{\text{cc } \text{psia}^2}{\text{moles}} \right)^{1/3}$$

$$\rho : 0.025 \text{ gm. moles/cc}$$

$$A' = A / (4V)^{2/3}$$

$$B' = \cancel{B / (4V)} B (4V)^{1/3}$$

$$C' = \cancel{C / (4V)} C / (4V)^{2/3}$$

$$D' = D / (4V)^{2/3}$$

Change psia to atm.
RMA 1/7/80

Fig. 26 Randomness of conversions calculated using equation 9 and the constants in table 9

average temperature of 980°F . The equation at the individual temperatures describes the system reasonably well.

Selectivity Data Correlation

The selectivity data obtained as a function of time on stream for a fixed liquid hourly space velocity at a fixed temperature is presented in Figure 15. The selectivity varies from olefin production to total dehydration as the time on stream increases suggesting deactivation. The plots of selectivity as the moles of component i produced per mole of methanol reacted were drawn as function of conversion of methanol. The plots of the data at 420°C along with the correlated expressions are presented in Figures 27 and 28.

All components except ethylene, water and dimethyl ether could be correlated as linear functions of the overall conversion. The curves obtained for ethylene and dimethyl ether seem to be complementary to each other. In general olefins' formation increases with the temperature, and the dimethyl ether formation increases with a decrease in temperature. Throughout the experiments, the yields of CO , CO_2 and CH_4 were very small. The major portion of the product distribution is water.

The results of the correlations of the selectivity data are presented in Tables 10 through 18. These data, with the accompanying asymptotic error limits represent

TABLE 10. SELECTIVITY CORRELATION OF CO

$$S_{CO} = K_{CO} \cdot X$$

Temp °C	K_{CO}
420	$(33.08 \pm 1.38) \times 10^{-3}$
351	$(45.40 \pm 5.07) \times 10^{-3}$
303	$(41.39 \pm 4.53) \times 10^{-3}$

$$\text{Selectivity} = \frac{\text{moles of } i \text{ produced}}{\text{mole of methanol reacted}}$$

TABLE 11. SELECTIVITY CORRELATION OF CH₄

$$S_{CH_4} = K_{CH_4} \cdot X$$

Temp °C	K_{CH_4}
420	$(77.25 \pm 2.94) \times 10^{-3}$
351	$(60.80 \pm 3.28) \times 10^{-3}$
303	$(44.57 \pm 1.33) \times 10^{-3}$

TABLE 12. SELECTIVITY CORRELATION OF CO₂

$$S_{\text{CO}_2} = K_{\text{CO}_2} X$$

Temp °C	K_{CO_2}
420	$(36.02 \pm 4.04) \times 10^{-3}$
351	$(41.30 \pm 4.01) \times 10^{-3}$
303	$(94.50 \pm 19.21) \times 10^{-3}$

TABLE 13. SELECTIVITY CORRELATION OF C₂H₄

$$S_{\text{C}_2\text{H}_4} = K'_{\text{C}_2\text{H}_4} X + K''_{\text{C}_2\text{H}_4} X^2$$

Temp °C	$K'_{\text{C}_2\text{H}_4} \times 10^3$	$K''_{\text{C}_2\text{H}_4} \times 10^3$
420	136.18 ± 40.60	50.27 ± 5.07
351	88.70 ± 3.70	22.97 ± 5.72
303	49.60 ± 3.43	131.65 ± 5.74

TABLE 14. SELECTIVITY CORRELATION OF C_2H_6

$$S_{C_2H_6} = K_{C_2H_6} X$$

Temp °C	$K_{C_2H_6}$
420	$(55.099 \pm 2.049) \times 10^{-3}$
351	$(64.634 \pm 18.94) \times 10^{-3}$
303	$(26.790 \pm 8.944) \times 10^{-3}$

TABLE 15. SELECTIVITY CORRELATION OF H_2O

$$S_{H_2O} = K'_{H_2O} X + K''_{H_2O} X^2$$

Temp °C	K'_{H_2O}	K''_{H_2O}
420	1.472 ± 0.169	-0.3243 ± 0.214
351	1.830 ± 0.121	-1.0062 ± 0.183
303	1.468 ± 0.237	-0.5514 ± 0.3978

TABLE 16. SELECTIVITY CORRELATION OF C_3H_6

$$S_{C_3H_6} = K_{C_3H_6} \times$$

Temp °C	$K_{C_3H_6}$
420	$(81.17 \pm 2.096) \times 10^{-3}$
351	$(54.45 \pm 3.125) \times 10^{-3}$
303	$(22.75 \pm 2.172) \times 10^{-3}$

TABLE 17. SELECTIVITY CORRELATION OF C_3H_8

$$S_{C_3H_8} = K_{C_3H_8} \times$$

Temp °C	$K_{C_3H_8}$
420	$(72.96 \pm 2.179) \times 10^{-3}$
351	$(47.39 \pm 4.023) \times 10^{-3}$
303	$(28.74 \pm 3.289) \times 10^{-3}$

TABLE 18. SELECTIVITY CORRELATION OF DME

$$S_{\text{DME}} = K_1 + K_2 X + K_3 X^2$$

Temp °C	K_1	K_2	K_3
420	0.1618 ± 0.025	-0.1038 ± 0.087	-0.0504 ± 0.087
351	0.3742 ± 0.083	-0.6451 ± 0.260	-0.0336 ± 0.020
303	0.2657 ± 0.067	-0.4789 ± 0.078	-0.0186 ± 0.008

Fig. 27 Experimental and calculated selectivity data at 420 °C for C₃H₈, C₃H₆, DME and H₂O

Fig. 28 Experimental and calculated selectivity data at 420°C for CO, CH₄, CO₂, C₂H₄, and C₂H₆

the variability in the data and are reasonably good correlations. When using these data, extra caution should be used so that the overall material balances would be satisfied.

Because of the inherent error in the system, the correlations presented may result in infraction of the mass balances.

One procedure for utilizing the correlations would be to force a carbon balance and calculate the moles of water produced by an oxygen balance.

CHAPTER XI

CONCLUSIONS AND RECOMMENDATIONS

The objective of the project, which this study is part of, was to develop or invent a catalyst and study the catalyst and reactions for conversion of methanol to low molecular weight olefins. The efforts towards achieving the above objective were initiated by Professor R. G. Anthony in 1975. F. N. Lin and R. G. Anthony in 1977 discovered a catalyst to convert methanol to olefins by utilizing a chabazite catalyst ion exchanged with ammonium chloride and rare earth chloride mixture. In continuation of the above objective, the catalyst characterization, improvement of the life of the catalyst and product distribution were obtained in this work.

This study therefore included the effects of pressure, temperature, liquid hourly 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. Because of the complexity of the reaction pattern involved, a clearly defined mechanism could not be proposed. However, the data collected seem to indicate that the decomposition of methanol on the surfaces of zeolites is a combination of dehydration, partial dehydrogenation and complete dehydrogenation. These three modes of

decomposition occur on the catalyst at different conditions, especially the dehydration to dimethyl ether is the predominant reaction at low temperatures and at high temperatures when the catalyst is deactivated. A brief review of different possibilities of the mechanism of conversion of methanol to low molecular weight olefins is also presented.

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 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 the catalytic 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 after 21 regenerations followed by deactivation cycles.

Time on stream data at fixed temperatures and the liquid

hourly space velocities were collected. The product distributions were correlated using empirical functions. A possible rate expression which correlates the data reasonably well is presented.

Based on the results of this investigation and the literature survey, the following recommendations are suggested for future studies on the topics related to production of coal-based low molecular weight olefins.

1. The catalyst regeneration procedures have a profound effect on the reaction of conversion of methanol to low molecular weight olefins. Hence, the catalyst deactivation should be studied as a special topic by itself. This information is vital to the optimization of the process at the production level.

2. As observed during this study, carbon disulfide at 2000 ppm is advantageous in stabilizing and improving the active life of the catalyst. Sulfur compounds in general may be advantageous in a similar manner. Carbon disulfide at different concentrations and different sulfur containing compounds should be investigated with respect to the above reaction.

3. Each of the products should be passed over the catalyst at the reaction conditions with and without methanol.

These studies would increase our understanding of how the products affect the catalyst and the reaction scheme.

4. The observed effects of water vapor and the high pressure should be further investigated.

5. The catalyst developed, because of its superior quality, warrants further study at a fundamental level by surface chemists.

6. Evaluate the use of erionite as a potential catalyst. This zeolite should be ion exchanged with ammonium chloride and rare earth chloride, and evaluated for catalyst activity and stability. Chang, Lang and Silvestri (1977) obtained higher yields of olefins with an erionite catalyst as compared to a Chabazite catalyst. However, the yields obtained in this investigation are comparable to the yields obtained by them on erionite catalyst. Therefore, erionite catalyst with ion exchange with ammonium and rare earth chlorides requires further study.

7. Due to the short life of the catalyst, a fluid bed catalytic reactor system with continuous regeneration and recycle should be investigated. This helps to maintain a constant level of activity of the catalyst and can easily be optimized for the production scale.

8. As suggested in the introduction, a route for manufacture of hydrocarbons from coal is to convert the coal to synthesis gas and then convert the synthesis gas directly to

the required hydrocarbons. This process would avoid the methanol synthesis step for manufacture of olefins. The catalyst studied herein, when combined with a hydrogenation catalyst, should be investigated for direct synthesis of low molecular weight olefins from synthesis gas. This process would eliminate the methanol synthesis step.

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APPENDIX

The Computer Algorithm for the Material Balances

The data collected after each run are entered into the material balance computer program. The material balance computer program processes the raw data to perform a variety of calculations as detailed below and prints out the results. The model calculations for the run 36 are presented in this section.

Input data are room temperature, barometric pressure, reactor pressure, time, reactor top and bottom temperatures and the feed rate of the reactants. For each of the samples, the areas of the gas chromatographic analysis from the gas and liquid analyses, gas flowrate and the amount of liquid condensate collected and the time of collection of the sample are entered.

The gas chromatographic analysis for the gas stream is computed to give the mole percents, weight percents, yield percent composition and the percentage composition among the hydrocarbons in the exit gas stream. This analysis would give a basic inference regarding the progress of the reaction. As explained earlier, for the purposes of this investigation the catalyst is considered deactivated when the ethylene yields are low and the dimethyl ether yields are high. If the gas flowrate and the amount of liquid collected

are not available, the calculations are terminated for this sample.

When the liquid sample is collected and the gas flowrates are available, the gas flowrate, amount of liquid collected and the time of collection are printed. The material balance calculations are initiated using these values. The amount of hydrogen formed is calculated by forcing oxygen and hydrogen balances over the reactor.

Whenever the moles of hydrogen calculated turn out to be negative, the forcing is aborted and the actual measurements used in further calculations. If during the forcing procedures, the moles of any component calculates to be negative, it is set to zero for further calculation.

The quantities of each of the components are used in calculating moles in and moles out for sampling period. The moles in the exit are used to calculate the partial pressures of each of the components. Total mass balances in the form of grams of gas, grams of liquid and the grams of feed are reported.

Moles of each of the components calculated in the exit are used in estimating the yield percentage by weight, the normalized grams of component i formed per gram of methanol

reacted. The carbon yields are estimated as moles of each component formed per mole of methanol reacted multiplied by the carbon number of each of the components. Normalized carbon yields are also reported based on the carbon yields. The discrepancy between the normalized carbon yields and the unnormalized carbon yields represents the lack of closure on carbon balance as a consequence of the forcing of hydrogen.

The percentage of hydrocarbons in the exit including the unreacted reactants by weight and the product distributions among the hydrocarbons by weight are calculated to give an idea of hydrocarbon production and the distribution.

The individual material balances calculated on the moles in the feed and the moles in the exit are presented in terms of carbon balance, hydrogen balance and the oxygen balance. These balances are used in calculating the C/H ratio IN versus C/H ratio OUT, H/O ratio IN versus H/O ratio OUT. Carbon/hydrogen ratio would give an idea regarding the coke characteristics on the catalyst surface. The hydrogen/oxygen ratio would infer the efficiency of the water balances.

The overall conversion of methanol is calculated using the moles of methanol in the feed and the exit. The individual rates based upon the moles of product formed per hour per gram of catalyst are reported.

Determination of Hydrogen Using Material Balances in Absence of Hydrogen Analysis

Preliminary analysis of the gas samples indicated the presence of hydrogen in the product stream. 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 individual balances.

The arrangement of analytical equipment is as shown in the Figure 3. The products leaving the reactor are passed through an ice bath to condense water, methanol and some of the dimethyl ether. The uncondensed gases are then passed through the gas chromatograph to get a complete analysis of the components, excluding the hydrogen concentration. The flowrate of the gas leaving is measured using a bubble meter. The liquid condensate collected is weighed and analyzed with the gas chromatograph.

Let

- n_T : Total number of moles exiting from the reactor.
- n_L : Moles of liquid product collected.
- n_G : Moles of gas measured using the bubble meter.
- n_{HFG} : Moles of hydrogen free gas in the exit.
- n_{H_2} : Moles of hydrogen in the product.
- n_i : Moles of component i .

Total mole balance over the reactor

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

Using the oxygen balance to determine the hydrogen

$$\text{Oxygen IN} = \sum_{i=1}^{14} n_i \text{ON}_i \text{ IN} \quad (2)$$

where ON_i = moles of oxygen per mole of the component

$$\text{Oxygen OUT} = n_{HFG} \sum_{i=1}^{13} Y_i \text{ON}_i + n_L \sum_{i=\text{H}_2\text{O}}^{\text{MeOH, DME}} X_i \text{ON}_i \quad (3)$$

where Y_i = mole fractions obtained from the GC analysis
on hydrogen-free basis

X_i = mole fraction of the components in the liquid
condensate

Forcing an oxygen balance, we obtain

$$\sum_{i=1}^{14} n_i \text{ON}_i \text{ IN} = n_{HFG} \left(\sum_{i=1}^{13} Y_i \text{ON}_i \right) + n_L \left(\sum_{i=\text{H}_2\text{O}}^{\text{MeOH, DME}} X_i \text{ON}_i \right) \quad (4)$$

$$n_{HFG} = \frac{\sum_{i=1}^{14} n_i \text{ON}_i \text{ IN} - n_L \left(\sum_{i=\text{H}_2\text{O}}^{\text{MeOH, DME}} X_i \text{ON}_i \right)}{\sum_{i=1}^{13} Y_i \text{ON}_i} \quad (5)$$

From equation 1, we obtain

$$n_{H_2} = n_T - n_{HFG} - n_L$$

The moles of hydrogen obtained can be used in the overall balances.

Forced Hydrogen Balance

$$\text{Hydrogen IN} = \sum_{i=1}^{14} n_i \text{ HN}_i \text{ IN} \quad (6)$$

$$\begin{aligned} \text{Hydrogen OUT} = & n_{H_2} + n_{HFG} \sum_{i=1}^{13} Y_i \text{ HN}_i + \\ & n_L \sum_{i=H_2O}^{\text{MeOH, DME}} X_i \text{ HN}_i \end{aligned} \quad (7)$$

From equation 1

$$n_{H_2} = n_T - n_{HFG} - n_L$$

substituting for n_{H_2} in equation 7, we obtain

$$\begin{aligned} \text{Hydrogen OUT} = & n_T + n_{HFG} \left(\sum_{i=1}^{13} Y_i \text{ HN}_i - 1 \right) + \\ & n_L \left(\sum_{i=H_2O}^{\text{MeOH, DME}} X_i \text{ HN}_i - 1 \right) \end{aligned} \quad (8)$$

Forcing a hydrogen balance we obtain,

$$n_{\text{HFG}} = \frac{\sum_{i=1}^{14} n_i H N_i / I N - n_T - n_L \left(\sum_{i=\text{H}_2\text{O}}^{X_i} H N_i - 1 \right)}{\sum_{i=1}^{13} Y_i H N_i - 1} \quad (9)$$

MeOH, DME

and

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

The moles of hydrogen obtained can be used in the overall material balances. Whenever the moles of hydrogen calculates to be negative, the actual measured moles of gas are assumed to be equal to the moles of hydrogen-free gas and the moles of hydrogen equal to zero.

The assumptions involved in conducting the material balances using the above procedure are as follows.

- (i) Liquid product obtained in the condenser contains water, dimethyl ether and methanol.
- (ii) There are no losses of oxygen in the reactor or no accumulation of hydrogen in the reactor. The oxygen balance is expected to yield the best estimate of hydrogen. Hydrogen is more likely to accumulate in the coke than oxygen.

Model calculations

The material balance calculations for the sample 2 in run 36 are presented below. The data input to the sample 2 are as follows.

Run number: 36

Sample number: 2

Time: 9.20 AM

Top temperature: 654 °F

Bottom temperature: 661 °F

Reactor pressure: 25 psig.

Barometric pressure: 29.84" of Hg.

Feed rate of methanol: 18.70 ml/hr

Measured gas flowrate: 7950 ml/hr

Amount of liquid condensate: 5.63 grams

Time of collection: 1 hour

Total amount of feed: 14.8 grams

Calculation of space velocity

$$\begin{aligned}
 \text{Liquid hourly space velocity} &= \frac{\text{ml/hr. of methanol flow}}{\text{ml of the catalyst}} \\
 &= 18.70/100. \\
 &= 0.1870 \text{ 1/hr.}
 \end{aligned}$$

Gas hourly space velocity =

$$\frac{\text{ml/hr of gas flow at reactor conditions}}{\text{ml. of the catalyst}}$$

$$\begin{aligned}
 &= \frac{(\text{gm./hr. of methanol}) \times R \times T/P}{(\text{Molecular weight of methanol}) \times (\text{ml. of the catalyst})} \\
 &= \frac{18.70 \times 0.79 \times 1206.15 \times 622.4}{100. \times 32 \times (25. + 14.67)} = 88.430 \text{ 1/hr.}
 \end{aligned}$$

$$\text{Residence time} = 1/\text{GHSV} = 0.6784 \text{ min.}$$

Gas chromatographic analysis of the gas stream

Let

$A(i)$ = Area of component i

$K(i)$ = Gas chromatographic response factor for i

$\text{MPCT}(i)$ = Mole fraction of component i

$$\begin{aligned}
 &= \frac{A(i)/K(i)}{\sum A(i)/K(i)} \times 100.
 \end{aligned}$$

$W(i)$ = Molecular weight of component i

$\text{WPCT}(i)$ = Weight percent of component i

$$\begin{aligned}
 &= \frac{\text{MPCT}(i) \times W(i) \times 100.}{\sum \text{MPCT}(i) \times W(i)}
 \end{aligned}$$

$\text{CN}(i)$ = # of carbon atoms per mole of component i

$\text{YPCT}(i)$ = Yield percent of component i

$$\begin{aligned}
 &= \frac{(A(i)/K(i)) \times \text{CN}(i) \times 100.}{\sum_{i \neq 13} (A(i)/K(i)) \times \text{CN}(i)}
 \end{aligned}$$

$\text{HPCT}(i)$ = Percent composition of hydrocarbon component i

$$\begin{aligned}
 &= \frac{\text{WPCT}(i) \times 100.}{\sum_{i \neq 1,3,6,9,12,13,14} \text{WPCT}(i)}
 \end{aligned}$$

The above calculations for the sample 2 of run 36 are presented in Table 1. The liquid analyses are calculated in a similar manner and are presented in Table 2.

Calculation of n_{HFG} by forcing hydrogen balance

Total moles of gas product formed

$$= \frac{\text{Gas flowrate (ml/hr)} \times \text{Time (hr)} \times \text{Br.Pr (Psia)}}{R \times (\text{Room Temperature K})}$$

$$= \frac{7950.00 \times 14.62}{1206.15 \times 295.4} = 0.3262$$

$$\text{Moles of methanol IN} = 14.8/32 = 0.463$$

Using the results obtained in the Table 3. for the calculation of n_{HFG} and the equation 9 for the hydrogen forcing we obtain,

$$n_{\text{HFG}} = \frac{0.926 - 0.61084 - 0.28464 (1.1609 - 1.)}{1.80 - 1.}$$

$$= 0.33670$$

Using equation 1

$$n_{\text{H}_2} = 0.61084 - 0.28464 - 0.33670$$

$$= -0.01050$$

The moles of hydrogen turn out to be negative. Therefore the moles of hydrogen in the product is set to zero. The moles of hydrogen-free gas is set equal to the actual measured moles of gas product

$$n_{\text{HFG}} = 0.3262$$

Table 1. THE GAS CHROMATOGRAPHIC ANALYSIS OF SAMPLE 2 OF RUN 36

i	Compound	A(i)	K(i)	A(i)/K(i)	MPCT(i)	W(i)	MPCT(i)x W(i)
1	CO	129.0	1.00	129.00	3.79	28	106.12
2	CH ₄	291.9	1.00	291.90	8.58	16	137.28
3	CO ₂	170.0	1.14	149.12	4.38	44	192.72
4	C ₂ H ₄	714.0	1.09	655.05	19.24	28	538.72
5	C ₂ H ₆	291.0	1.17	248.72	7.31	30	219.30
6	H ₂ O	1058.0	1.00	1058.00	31.08	18	559.44
7	C ₃ H ₆	187.0	1.47	127.21	3.74	42	157.08
8	C ₃ H ₈	290.0	1.31	221.37	6.50	44	286.00
9	DME	149.1	1.30	114.69	3.37	46	155.02
10	C ₄	000.0	1.65	000.00	0.00	58	000.00
11	C ₅	000.0	1.00	000.00	0.00	72	000.00
12	Other	000.0	1.00	000.00	0.00	--	000.00
13	MeOH	409.0	1.00	409.00	12.02	32	384.64
14	H ₂	000.0	1.00	000.00	0.00	2	000.00

$\Sigma = 3404.06$

$\Sigma = 2736.40$

Table 1. Continued.,

i	Compound	WPCT(i)	CN(i)	(A(i)/K(i)) xCN(i)	YPCT(i)	HPCT(i)
1	CO	3.88	1	129.00	3.53	00.00
2	CH ₄	5.01	1	291.90	7.99	10.25
3	CO ₂	7.04	1	149.12	4.08	00.00
4	C ₂ H ₄	19.69	2	13100.92	35.87	40.26
5	C ₂ H ₆	8.01	2	497.44	13.62	16.38
6	H ₂ O	20.45	0	000.00	00.00	00.00
7	C ₃ H ₆	5.74	3	381.63	10.45	11.73
8	C ₃ H ₈	10.46	3	664.12	18.18	21.38
9	DME	5.66	2	229.38	6.28	00.00
10	C ₄	00.00	4	000.00	00.00	00.00
11	C ₅	00.00	5	000.00	00.00	00.00
12	Other	00.00	0	000.00	00.00	00.00
13	MeOH	14.05	1	000.00	00.00	00.00
14	H ₂	00.00	0	000.00	00.00	00.00

Σ = 15443.52

Table 2. THE GAS CHROMATOGRAPHIC ANALYSIS OF THE LIQUID CONDENSATE

i	Compound	A(i)	K(i)	A(i)/K(i)	MPCT(i)	W(i)	MPCT(i)x W(i)	WPCT(i)
1	CO	000.00	1.00	000.00	00.00	28	0000.00	00.00
2	CH ₄	000.00	1.00	000.00	00.00	16	0000.00	00.00
3	CO ₂	000.00	1.00	000.00	00.00	44	0000.00	00.00
4	C ₂ H ₄	000.00	1.00	000.00	00.00	28	0000.00	00.00
5	C ₂ H ₆	000.00	1.00	000.00	00.00	30	0000.00	00.00
6	H ₂ O	601.36	1.00	601.36	85.94	18	1546.92	76.03
7	C ₃ H ₆	000.00	1.00	000.00	00.00	42	0000.00	00.00
8	C ₃ H ₈	000.00	1.00	000.00	00.00	44	0000.00	00.00
9	DME	18.67	1.31	14.25	2.04	46	93.66	4.80
10	C ₄	000.00	1.00	000.00	00.00	58	0000.00	00.00
11	C ₅	000.00	1.00	000.00	00.00	72	0000.00	00.00
12	Other	000.00	1.00	000.00	00.00	--	0000.00	
13	MeOH	38.67	0.46	84.07	12.02	32	384.64	18.90
14	H ₂	000.00	1.00	000.00	00.00	2	0000.00	00.00

Σ=699.68

Σ=2025.22

Table 3. THE ESTIMATION OF HYDROGEN BY FORCING H₂ BALANCE

Compound	n_i IN	HN(i)	X_i	$n_i \cdot \frac{HN(i)}{IN}$	$X_i \cdot HN(i)$	Y_i	$Y_i \cdot HN(i)$
CO	0.000	0	0.0000	0.000	0.0000	0.0379	0.0000
CH ₄	0.000	2	0.0000	0.000	0.0000	0.0858	0.1716
CO ₂	0.000	0	0.0000	0.000	0.0000	0.0438	0.0000
C ₂ H ₄	0.000	2	0.0000	0.000	0.0000	0.1924	0.3848
C ₂ H ₆	0.000	3	0.0000	0.000	0.0000	0.0731	0.2193
H ₂ O	0.000	1	0.8594	0.000	0.8594	0.3108	0.3108
C ₃ H ₆	0.000	3	0.0000	0.000	0.0000	0.0374	0.1120
C ₃ H ₈	0.000	4	0.0000	0.000	0.0000	0.0650	0.2600
DME	0.000	3	0.0204	0.000	0.0611	0.0337	0.1011
C ₄	0.000	4	0.0000	0.000	0.0000	0.0000	0.0000
C ₅	0.000	5	0.0000	0.000	0.0000	0.0000	0.0000
Other	0.000	0	0.0000	0.000	0.0000	0.0000	0.0000
MeOH	0.463	2	0.1202	0.926	0.2404	0.1202	0.2404
H ₂	0.000	1	0.0000	0.000	0.0000	0.0000	0.0000
				$\Sigma = 0.926$	$\Sigma = 1.1609$		$\Sigma = 1.8000$

Moles of each component in the inlet and exit streams, the mole fractions and the partial pressures are calculated as presented in Table 4.

The average molecular weight of the

$$\text{gas product} = 27.3850 \text{ gm/gm.mole.}$$

$$\begin{aligned} \text{Weight of the gas product} &= 0.3262 \times 27.3850 \\ &= 8.9330 \text{ grams.} \end{aligned}$$

$$\text{Moles of methanol in} = 0.463 \text{ moles}$$

$$\text{Moles of methanol out} = 0.074$$

$$\text{Overall conversion of methanol} = 83.98 \%$$

Let

$$n_r = \text{Moles of methanol reacted} = 0.388$$

$$M_i = \text{Moles of component } i \text{ in the exit}$$

$$W(i) = \text{Molecular weight of component } i$$

$$YLPR(i) = \text{Yield percent by weight for component } i$$

$$CN(i) = \text{Number of carbon atoms per mole of component } i$$

$$CAR(i) = \text{Carbon yield of component } i$$

$$= \frac{\text{Moles of component } i \text{ formed} \times \text{Carbon number of } i}{\text{Moles of methanol reacted}}$$

$$NCAR(i) = \text{Normalized carbon yield of component } i$$

$$HPCT(i) = \text{Percentage composition by weight among hydrocarbons}$$

$$YLPR(i) = M_i * W(i) / \sum M_i * W(i)$$

$$CAR(i) = M_i / n_r * CN(i)$$

$$NCAR(i) = CAR(i) / \sum CAR(i)$$

Table 4. PRODUCT DISTRIBUTIONS OBTAINED BY FORCING H₂ BALANCE

Compound	n _i IN	Y _i	Moles out in gas	Moles out in liq.	Total moles out	Mole fraction	Partial pressure
CO	0.000	0.0379	0.0124	0.00000	0.01240	0.0202	0.802
CH ₄	0.000	0.0858	0.0279	0.00000	0.02799	0.0458	1.815
CO ₂	0.000	0.0438	0.0143	0.00000	0.01429	0.0234	0.927
C ₂ H ₄	0.000	0.1924	0.0628	0.00000	0.06280	0.1028	4.072
C ₂ H ₆	0.000	0.0731	0.0239	0.00000	0.02390	0.0390	1.546
H ₂ O	0.000	0.3108	0.1014	0.24410	0.34500	0.5654	22.401
C ₃ H ₆	0.000	0.0374	0.0122	0.00000	0.01220	0.0200	0.791
C ₃ H ₈	0.000	0.0650	0.0212	0.00000	0.02120	0.0347	1.376
DME	0.000	0.0337	0.0110	0.00563	0.01660	0.0272	1.078
C ₄	0.000	0.0000	0.0000	0.00000	0.00000	0.0000	0.000
C ₅	0.000	0.0000	0.0000	0.00000	0.00000	0.0000	0.000
Other	0.000	0.0000	0.0000	0.00000	0.00000	0.0000	0.000
MeOH	0.463	0.0392	0.0392	0.03500	0.07420	0.1215	4.813
H ₂	0.000	0.0000	0.0000	0.00000	0.00000	0.0000	0.000

$$\text{HPCT}(i) = \frac{M_j \cdot W(j)}{\sum M_j \cdot W(j)}$$

j=hydrocarbons

The above calculations are presented in Table 5.

Percentage of hydrocarbons in the exit including
the unreacted reactants = 29.708

The individual material balances in terms of atoms of carbon, hydrogen and oxygen in the input and exit are calculated as shown in Table 6. From the above results, the balances of carbon/hydrogen, and hydrogen/oxygen may be obtained.

The overall rate of reaction

$$\begin{aligned} &= \frac{\text{Moles of methanol reacted}}{\text{Time x grams of catalyst}} \\ &= 0.388 / 1. \times 110. \\ &= 0.003527 \text{ moles/hr. gm. of catalyst} \end{aligned}$$

The individual rates of each of the components are also calculated in a similar fashion.

Calculation of n_{HFG} by forcing oxygen balance

Using the results obtained in Table 7 for the calculation of n_{HFG} and the equation 6, we obtain

$$n_{\text{HFG}} = \frac{0.463 - 0.2847}{0.5921} = 0.3012$$

Table 5. YIELD CALCULATIONS BY FORCING HYDROGEN BALANCE

Compound	M_i	$W(i)$	$M_i * W(i)$	YLPR(i)	CN(i)	$\frac{M_i \cdot CN(i)}{n_r}$	NCAR(i)	HPCT(i)
CO	0.012	28	0.3360	2.809	1	0.0319	0.034	0.00
CH ₄	0.028	16	0.4480	3.633	1	0.0722	0.077	10.25
CO ₂	0.014	44	0.6160	5.103	1	0.0362	0.040	0.00
C ₂ H ₄	0.063	28	1.7640	14.265	2	0.3231	0.347	40.26
C ₂ H ₆	0.024	30	0.7200	5.803	2	0.1233	0.132	16.38
H ₂ O	0.345	18	6.2100	50.449	0	0.0000	0.000	0.00
C ₃ H ₆	0.012	42	0.5040	4.156	3	0.0938	0.101	11.73
C ₃ H ₈	0.021	44	0.9240	7.576	3	0.1644	0.176	21.38
DME	0.017	46	0.7820	6.205	2	0.0856	0.092	0.00
C ₄	0.000	58	0.0000	0.000	4	0.0000	0.000	0.00
C ₅	0.000	72	0.0000	0.000	5	0.0000	0.000	0.00
Other	0.000	--	0.0000	0.000	-	0.0000	0.000	0.00
MeOH	0.074	32	2.3680	0.000	1	0.0000	0.000	0.00
H ₂	0.000	2	0.0000	0.000	0	0.0000	0.000	0.00

$$\sum_{i \neq 13} = 12.3040$$

$$\Sigma = 0.9305$$

Table 6. INDIVIDUAL ATOM BALANCES BY FORCING HYDROGEN

i	CN(i)	HN(i)	ON(i)	M _{in}	M _{out}	C _{in}	C _{out}	H _{in}	H _{out}	O _{in}	O _{out}
1	1	0	1	0.000	0.0124	0.000	0.012	0.000	0.000	0.000	0.012
2	1	4	0	0.000	0.0279	0.000	0.028	0.000	0.112	0.000	0.000
3	1	0	2	0.000	0.0143	0.000	0.014	0.000	0.000	0.000	0.029
4	2	4	0	0.000	0.0628	0.000	0.126	0.000	0.251	0.000	0.000
5	2	6	0	0.000	0.0239	0.000	0.048	0.000	0.143	0.000	0.000
6	0	2	1	0.000	0.3450	0.000	0.000	0.000	0.690	0.000	0.345
7	3	6	0	0.000	0.0122	0.000	0.037	0.000	0.073	0.000	0.000
8	3	8	0	0.000	0.0212	0.000	0.064	0.000	0.170	0.000	0.000
9	2	6	1	0.000	0.0166	0.000	0.033	0.000	0.100	0.000	0.017
10	4	10	0	0.000	0.0000	0.000	0.000	0.000	0.000	0.000	0.000
11	5	12	0	0.000	0.0000	0.000	0.000	0.000	0.000	0.000	0.000
12	-	-	-	0.000	0.0000	0.000	0.000	0.000	0.000	0.000	0.000
13	1	4	1	0.463	0.0742	0.463	0.074	1.852	0.297	0.463	0.074
14	0	2	0	0.000	0.0000	0.000	0.000	0.000	0.000	0.000	0.000
				Σ=0.463		0.436		1.852	1.836	0.463	0.477

Table 7. THE ESTIMATION OF HYDROGEN BY FORCING O₂ BALANCE

Compound	n_i IN	ON(i)	X_i	$n_i * ON(i)$ IN	$X_i * ON(i)$	Y_i	$Y_i * ON(i)$
CO	0.000	1	0.0000	0.000	0.0000	0.0379	0.0379
CH ₄	0.000	0	0.0000	0.000	0.0000	0.0858	0.0000
CO ₂	0.000	2	0.0000	0.000	0.0000	0.0438	0.0876
C ₂ H ₄	0.000	0	0.0000	0.000	0.0000	0.1924	0.0000
C ₂ H ₆	0.000	0	0.0000	0.000	0.0000	0.0731	0.0000
H ₂ O	0.000	1	0.8594	0.000	0.8594	0.3108	0.3108
C ₃ H ₆	0.000	0	0.0000	0.000	0.0000	0.0374	0.0000
C ₃ H ₈	0.000	0	0.0000	0.000	0.0000	0.0650	0.0000
DME	0.000	1	0.0204	0.000	0.0204	0.0337	0.0337
C ₄	0.000	0	0.0000	0.000	0.0000	0.0000	0.0000
C ₅	0.000	0	0.0000	0.000	0.0000	0.0000	0.0000
Other	0.000	0	0.0000	0.000	0.0000	0.0000	0.0000
MeOH	0.463	1	0.1202	0.463	0.1202	0.0392	0.0392
H ₂	0.000	0	0.0000	0.000	0.0000	0.0000	0.0000
				$\Sigma = 0.463$	1.0000	0.5920	

Using equation 1

$$\begin{aligned}n_{H_2} &= 0.61084 - 0.28464 - 0.3012 \\ &= 0.0250\end{aligned}$$

The moles of each of the components is calculated using the moles of hydrogen free gas calculated. The product distributions calculated by forcing oxygen are presented in Table 8. The yield calculations and the individual balances are calculated similarly to that of hydrogen forcing.

Table 8. PRODUCT DISTRIBUTIONS OBTAINED BY FORCING O₂ BALANCE

Compound	n _i IN	Y _i	Moles out in gas	Moles out in liq.	Total moles out	Mole fraction	Partial pressure
CO	0.000	0.0379	0.0114	0.0000	0.0114	0.0187	0.741
CH ₄	0.000	0.0858	0.0258	0.0000	0.0258	0.0423	1.677
CO ₂	0.000	0.0438	0.0132	0.0000	0.0132	0.0216	0.856
C ₂ H ₄	0.000	0.1924	0.0580	0.0000	0.0580	0.0950	3.762
C ₂ H ₆	0.000	0.0731	0.0220	0.0000	0.0220	0.0361	1.429
H ₂ O	0.000	0.3108	0.0936	0.2441	0.3377	0.5528	21.901
C ₃ H ₆	0.000	0.0374	0.0113	0.0000	0.0113	0.0184	0.731
C ₃ H ₈	0.000	0.0650	0.0196	0.0000	0.0196	0.0321	1.271
DME	0.000	0.0337	0.0102	0.0056	0.0102	0.0258	1.024
C ₄	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.000
C ₅	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.000
Other	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.000
MeOH	0.463	0.0392	0.0118	0.03500	0.0468	0.1166	4.620
H ₂	0.000	0.0000	0.0250	0.0000	0.0250	0.0406	1.610

VITA

Mr. Balaji Bondili Singh was born to Bondili Jagath Singh and Late Mrs. Bondili Durga Singh in 1951. He had his secondary and higher secondary education at Hyderabad, India. He obtained his Bachelor of Technology degree in Chemical Engineering major and Manufacture of Fine Chemicals and Pharmaceuticals as minor from College of Technology, Hyderabad, India. During his undergraduate studies, he was recipient of National Merit Scholarship and State Special Merit Scholarship. He was the Literary Secretary of the College and represented the College in various activities including the National Cadet Corps.

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The author typed the dissertation himself and swears never to do it again.