METHANOL: SYNTHESIS AND USES AS A FUEL, AS A CHEMICAL AND AS A CHEMICAL PRECURSOR

Introduction:

We have mentioned two large-scale commercial processes for the synthesis of fuels and chemicals from syngas. The F-T and related reactions, just discussed, yield a wide molecular-weight spectrum of aliphatic hydrocarbons and oxygenated compounds in addition to either water and/or CO_2. The synthesis of methanol is the other large scale product made from syngas on a commercial scale. Over ten million tons of methanol per year are currently produced. Plant capacity for methanol is increasing and there is the psosibility that its use, chiefly as a fuel, will eventually require large additional amounts of methanol.

There are many reasons why methanol is an important key to a syngas based fuels and chemicals industry (see Figures II-1 and II-2 in the Summary). First, methanol is synthesized in over 99% or greater selectivity, in sharp contrast to the melange of products, from methane to waxes, obtained in the F-T reaction. Second, the weight retention of syngas ($2H_2$:1CO) as a feedstock for methanol is 100%. Syngas is a costly raw material for the production of the hydrocarbons obtained in the F-T reaction where oxygen is eliminated as water or CO_2. Third, methanol furnishes selective pathways to a number of important chemicals, including formaldehyde and the widely used two carbon oxygenated chemicals. This route to fuels and to two carbon chemicals from methanol is presently more attractive than their direct synthesis from syngas. In addition, although many more uses of this versatile compound, chiefly as a fuel, will be discussed, there is the exciting discovery that methanol can be converted to high octane gasoline by Mobil's methanol-to-gasoline (MTG) process using a shape selective zelolite (ZSM-5) (Meisel et al., 1976) catalyst. A plant which will produce some 14,000 barrels per day of high octane gasoline from methanol will go on stream in New Zealand in 1985. The MTG process will be discussed in the next section of this report.

To furnish a proper basis for discussion of the synthesis of methanol, it is relevant to state that there are presently two main processes for the manufacture of methanol from syngas: the so-called high pressure and low pressure processes. The high-pressure process:

$$CO + 2H_2 \xrightarrow[\substack{25\text{-}35\ \text{MPa} \\ 623K}]{ZnO/Cr_2O_3} CH_3OH \qquad \Delta H_{298K} = -21.68\ \text{kcal/mol} \tag{1}$$

and the low-pressure process:

$$CO + 2H_2 \xrightarrow[\substack{5\ \text{MPa} \\ 523K}]{Cu\text{-}ZnO\text{-}Al_2O_3} CH_3OH \tag{2}$$

There is also a moderate pressure methanol synthesis which operates at about 10 MPa (Rogerson, 1973).

Importantly, methanol can be and has also been synthesized by the hydrogenation of CO_2 with the same catalysts (Wade et al., 1981; Marschner et al., 1982).

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O \qquad \Delta H_{298K} = -11.83\ \text{kcal/mole} \tag{3}$$

All these reactions are exothermic and involve a contraction in volume. Highest yields and conversions of methanol are obtained at high pressures and low temperatures.

History of Methanol Production

The commercial source of methanol, prior to the introduction of the synthetic processes, was the destructive distillation of wood. In 1905, Sabatier and Senderens (1905) suggested that methanol could be synthesized from CO and H_2. In the following years, particularly after the successful high-pressure synthesis of ammonia, there were a number of patent applications by BASF in Germany and Patart in France covering the hydrogenation of CO to oxygenated compounds at elevated temperatures and pressures with catalysts made up of Cr, Co, and Mn in the metallic form, as oxides, or as other compounds (Woodward, 1967). In 1923, BASF built the first commercial methanol synthesis plant and, a few years later, started exporting synthetic methanol to the U.S. at a much lower cost and greater purity than that of wood-derived methanol. The process used a zinc oxide-chromium oxide catalyst operating at 673K and 20 MPa (Woodward, 1967).

At this stage, realizing that methanol could be manufactured more economically by the catalytic synthetic process, Commercial Solvents Corporation and DuPont started experimenting with methanol synthesis and, in 1927, the commercial production by the high-pressure process was inaugurated in the United States (Wade et al., 1981). In the Commercial Solvents process, CO_2 produced at the company's butanol fermentation plant was hydrogenated to methanol at 30.6 MPa with metal oxide catalysts.

In 1927, DuPont operated a plant at Belle, WV, that used coal as the source of the gaseous feedstock. Ammonia and methanol were manufactured, in tandem, in the same plant. The raw gas, a mixture of CO, CO_2, H_2 and N_2 was produced from coal or coke by the water-gas reaction, purified and passed over a methanol synthesis catalyst and subsequently over a methanation catalyst to remove CO. The remaining gases, N_2 and H_2 were used in the synthesis of ammonia. The DuPont process used syngas and catalysts made of zinc-chromium or chromium-copper (Woodward, 1967). The plant continued in the co-production of methanol and ammonia until the late 1940's (Stiles, 1977). At that time, a plentiful supply of natural gas became available and coal was abandoned as a feedstock. However, in the long run coal promises to be the preferred feedstock for the production of methanol. Actually, at present a commercial plant using coal is in operation in South Africa. Here, the syngas is produced by the Koppers-Totzek entrained-flow, atmospheric pressure gasification of coal and the synthesis is by the ICI methanol synthesis process (European Chemical News, 1976). BASF may be credited with the discovery of the zinc-chromium catalysts in Germany in 1913 (Kuo, 1984). This was a high temperature catalyst operating at 623-673K because of its low catalytic activity. These zinc-chromium catalysts must operate at higher pressures (25-35 MPa) because of low syngas conversion due to less favorable thermodynamic equilibrium limitations at these high temperatures. This class of catalysts is less active than the copper-zinc based catalysts but more tolerant towards poisoning by compounds containing sulfur.

ICI introduced the more active copper-zinc based catalysts in 1966 (Davies and Snowdon, 1967). These low temperature catalysts operate at 523-573K and 5-25 MPa. The use of these more active catalysts was made possible because more efficient syngas purification processes had become available. The copper-zinc catalysts are much more susceptible to poisoning by sulfur compounds; they also are easily permanently deactivated at high temperatures, so proper control of reactor temperature is necessary. But even with the most carefully prepared catalysts, small amounts of CH_4, dimethyl ether and, traces of higher alcohols appear among the products.

Chemistry of the Methanol Synthesis

An excellent review of the synthesis of methanol has been published by Natta (1955). This chapter summarizes the thermodynamics, kinetics and catalysis of the high temperature synthesis of methanol and mentions the possible use of the easily poisoned copper catalysts which are now used in most new methanol synthesis plants (the low pressure process).

The catalysts used in the synthesis of methanol from syngas, which usually contains some CO_2, are highly active and most importantly, very selective. Among the many products obtainable from the catalytic reactons of syngas, CH_4 is thermodynamically the most favored, longer chain hydrocarbons the next most favored and even longer chain alcohols are thermodynamically more favored than methanol. Thermodynamic limitations for the synthesis of methanol are severe so that methanol synthesis reactors must operate within narrow temperature ranges, set by too low activity at lower temperatures and a thermodynamic limitation at higher temperatures (Satterfield, 1980). The effect of temperature and pressure has been studied in detail and is reviewed by Strelzoff (1970).

It is particularly important to avoid contamination of the methanol synthesis catalyst by metals that are Fischer-Tropsch catalysts. Care is required in catalyst preparation so as to obtain pure methanol. Nickel, and especially iron, both of which form volatile metal carbonyls ($Ni(CO)_4$ and $Fe(CO)_5$, respectively), must not be allowed to come into contact with the syngas under reaction conditions. The carbonyls form at lower temperatures and decompose to the metal at higher temperatures, possibly in upstream heat exchangers, etc. The presence of F-T metals in the catalyst or on the reactor walls will result in the formation of methane as well as higher hydrocarbons and higher molecular weight oxygenated products. Methanol synthesis reactor shells are typically lined with copper, although internals may be constructed of 18-8 stainless steel (Satterfield, 1980).

The formation of higher alcohols (ethanol, propanol, etc.) can be suppressed by careful exclusion of alkalis from the catalyst. Dimethyl ether, formed by the dehydration of methanol or by the hydrogenation of CO:

$$4H_2 + 2CO \rightleftharpoons CH_3\text{-}O\text{-}CH_3 + H_2O \qquad (4)$$

may form in the presence of Al_2O_3. However, if the Cu-ZnO low pressure catalyst is employed with about 7.5% Al_2O_3 as stabilizer and promoter, ether formation is negligible (Marschner, 1982).

The Boudouard reaction (Eq. 5)

$$2CO \rightleftharpoons C + CO_2 \qquad (5)$$

which results in carbon laydown is not significant, despite a high favorable thermodynamic tendency, if the temperature is carefully controlled.

The copper-zinc catalysts vary in zinc-copper composition and contain different amounts of other metals such as Cr, Al, Mn, V, Ag, etc. A number of companies manufacture these catalysts which are used in almost all new methanol plants (Kuo, 1984).

In the high pressure process the reaction rate decreases with conversion because the synthesis of methanol is strongly inhibited both by approach to equilibrium and by the adsorption of methanol on the catalyst. The gas leaving the last reaction vessel will typically contain only about 3% of methanol. The unreacted gases are recycled. In the low pressure methanol synthesis, the gas leaving the reactor contains some 4 to 6.5 volume % of methanol (Satterfield, 1980).

In actual practice, syngas made from any source contains some CO_2. Syngas made by methane reforming has a stoichiometric ratio of H_2 to CO that approaches 3. It also always contains some CO_2, which, as shown in Eq. 3 can also be hydrogenated to methanol. CO_2 may be added to the syngas in order to convert some of the excess H_2 to CO via the reverse water-gas shift which is favored at higher temperatures.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (6)$$

The presence of 6% by volume of CO_2 in the syngas increases methanol yields by about 23% in the Lurgi methanol synthesis process (Stratton et al., 1982). In various operations, CO_2 levels vary from 2-6% and are usually specified by the various producers.

The heat of reaction in the converion of CO_2 to methanol (Eq. 3) is less than that of the conversion of CO to methanol (Eq. 1) so that less heat has to be removed from the reactor. Also, using CO_2 in the synthesis might avoid a CO_2 removal step, although most CO_2 is actually removed in industrial practice.

It is well known that methanol is made in numerous plants all over the world in greater than 99% selectivity when a mixture of CO, CO_2, and H_2 is passed over a $Cu\text{-}ZnO\text{-}Al_2O_3$ catalyst at elevated pressures and temperatures between 493 and 573K. Surprisingly enough for such a widely practiced process, however, there are few facts, other than that the reaction is exothermic, about which complete agreement exists (Chinchen et al., 1984; Kung, 1980; Klier, 1982).

One of the major questions bedeviling the mechanistic interpretation of the methanol synthesis is whether the methanol is synthesized from CO or from CO_2. Kagan et al. (1977), using $^{14}CO_2$, showed that the methanol synthesis proceeds through CO_2 rather than through CO:

$$CO + H_2O \longrightarrow CO_2 + H_2 \longrightarrow CH_3OH + H_2O \qquad (7)$$

Chinchen and coworkers (1984) at ICI recently confirmed Kagan's findings. Methanol appears to be formed from CO_2 and H_2 through a surface formate intermediate.

Baskirov et al. (1976) showed that the reduction of CO_2 to CO and methanol could not occur in consecutive reactions since they both took place when the contact time approached zero. Temkin et al. (1982) reported that the formation of methanol from CO decreased dramatically if CO_2 or water were completely eliminated from the feed gases. They concluded that the conversion of CO_2 to methanol went through a direct pathway to methanol while that of CO involved CO_2 via the water-gas shift reaction. Klier et al. (1982b) have proposed that the role of CO_2 in the feed gases is to retain the catalyst in a favorable oxidation state. CO_2 here plays an oxidative role, keeping some of the copper catalyst as Cu(I). The effect of water in the methanol synthesis is still not clear although Klier et al. (1982b) has suggested that water can help keep a Cu(I) surface species as an active catalyst.

Formyl and formate intermediates have been proposed as surface intermediates in the synthesis of methanol. Sneeden and Denise (1982) have proposed the intermediacy of formyl (M-CHO) and formate (M-OCHO) species. Deluzarche et al. (1977) by the technique of chemical trapping have provided evidence for formate intermediates in the synthesis of methanol.

In any event, comparative studies of the hydrogenation of CO_2 and CO has shown that CO_2 leads to methanol more rapidly, with greater selectivity, at a lower temperature and with a lower activation energy (Denise and Sneeden, 1982) than does CO.

The mechanism of the methanol synthesis is also discussed by Kung et al. (1984), Vedage et al. (1984) and Karwacki and co-workers (1984).

In any event, the hydrogenation of CO to methanol can be guided by catalysts that, unlike F-T catalysts, do not dissociate the CO molecule. It is known that Pd, Pt, Ir, and Cu catalysts chemisorb CO associatively and all are candidates for use in a synthesis of methanol from syngas. Copper-zinc catalysts are presently the catalysts of choice but there is active research on the synthesis of methanol using Pd (and Pt) catalysts (Poutsma et al., 1978; Deligeanni et al., 1984).

It appears likely that the active components in the copper-based catalysts are Cu(I) species in a solids solution of ZnO (Herman et al., 1979). As stated earlier, the catalyst loses its activity if the syngas is completely devoid of CO_2, H_2O and O_2. These gases evidently preserve copper in the Cu^+ state. In their absence Cu^+ is gradually reduced to inactive metallic copper. The copper-based catalysts, since they are more sensitive to poisoning and sinter more easily, have shorter life spans than the zinc oxide-chromium oxide base catalysts.

Kinetics

The kinetics of the methanol syntheses are very complex and are affected by a number of variables, such as the nature of the catalyst, the physical changes of the catalyst as the reaction progresses, the composition of the gas (which also is constantly changing in the reactor), temperature and pressure (Stiles, 1977). Natta and co-workers (1953) studied the kinetics of the high pressure synthesis. Their equation is complex and another term was introduced by Cappelli et al. (1972). In any case, modern methanol syntheses use copper-zinc low pressure catalysts and since the methanol synthesis reaction proceeds to thermodynamic equilibrium very rapidly (Kuo, 1984), the kinetic behavior of the catalyst is not so important. It must be realized that all commercial catalysts, and hence their kinetic behavior, are proprietary.

Feedstocks

The primary raw material as the source of syngas for producing methanol at present is natural gas, which, in 1980, accounted for 70% of worldwide production (Wade et al., 1981). Residual fuel oil; naphtha and coal are the other feedstocks. In 1980, they accounted for about 15%, 5% and under 2% of worldwide production, respectively. Steam reforming of natural gas gives syngas with one mole of H_2 over the stoichiometric requirement for methanol synthesis. The excess hydrogen can be purged and used as a fuel to generate steam. As mentioned earlier, by adding CO_2 to syngas, the excess H_2 can be converted to methanol. Steam reforming of naphtha gives the required ratio of H_2/CO. Partial oxidation of residual oil produces syngas with an H_2/CO ratio of 1:1; this must be shifted to achieve the required gas ratio. Nevertheless, this raw material is attractive, since the bottom of the crude oil barrel is profitably utilized. In the long run, syngas for methanol manufacture will be made from coal.

Process Technology and Reactors

The production of methanol is established commercial technology practiced worldwide. Nevertheless, constant improvements are being made in process technology and reactor design for better recovery, in lower compression costs, and in processing of the raw methanol. Marschner (1982) and Satterfield (1980) have summarized these subjects.

Liquid Phase Methanol Synthesis

A methanol synthesis process utilizing a liquid phase slurry reactor is under development. The initial work was on a laboratory scale (Sherwin and Blum, 1978). This concept is being further tested in a process development unit at LaPorte, Texas by Air Products and Chemicals, Inc. with the technical assistance of Chem. Systems. The project is jointly funded by the U.S. Department of Energy, Air Products, Fluor Engineers, Inc. and EPRI (Klosek and Mednik, 1984). The construction of a pilot plant based on this technology using syngas derived from coal is under consideration. The syngas will probably be made in a Texaco gasifier so that the H_2:CO ratio will be low.

The liquid phase reactor for methanol synthesis, in design as well as in operating procedures, is basically similar to that originally proposed by Kolbel for the Fischer-Tropsch synthesis. In laboratory scale experiments at Chem. Systems, and at La Porte, commercial and experimental methanol synthesis catalysts have been tested at 3.5-7.0 MPa in the temperature range of 488-523K. Because the equilibrium conversion is favored by low temperature and the temperature is well-controlled in the slurry reactor, a high single pass conversion is possible. About 20% conversion of CO to methanol with a feed gas of balanced composition can be expected (Klosek and Mednick, 1984).

The syngas in the Chem. System experiments as well as in the most recent work at La Porte, is a synthetic mixture of H_2, CO, CO_2, and CH_4, representing gas from conventional or high-temperature coal gasifiers. In the tests conducted so far, the tail gases are not recycled; instead they are used to generate power in gas turbines. But it is possible to enrich the exit gases from the reactor in hydrogen so that part of the tail gas can be recycled, by adding steam to the feed gas.

Other Routes for Methanol Synthesis

The production of methanol from syngas using the low-pressure Cu-ZnO based catalysts will be dominant in the methanol industry for at least another decade, whether natural gas or coal is the feedstock. However, there are other reactions that produce methanol. One route is through the synthesis of methyl formate and its subsequent hydrogenation to methanol. The equations for this two-step synthesis are given below:

$$CH_3OH + CO \xrightarrow{NaOCH_3} HCOOCH_3 \qquad (8)$$

$$HCOOCH_3 + 2H_2 \xrightarrow{\text{Cu Catalysts}} 2CH_3OH \qquad (9)$$

$$CO + 2H_2 \longrightarrow CH_3OH \qquad (10)$$

Methyl formate ($HCOOCH_3$) is prepared by reacting methanol and CO in the presence of a homogeneous sodium methoxide catalyst at 353K and 3.0 MPa; this is followed by the catalytic hydrogenation of methyl formate to methanol at 453K and 3.0 MPa. Recent work by Trimm et al. (1983) has shown that the temperature and pressure required for the hydrogenation of the formate to methanol can be lowered significantly. The net result is the synthesis of two moles of methanol per mole of starting methanol (Eq. 10).

A modified version of this process is described in a German patent (Brendlein, 1954) in which the catalyst, operating temperature, and pressure for the hdyrogenation reaction are copper chromite, 373-443K and 2-6 MPa, respectively. A pilot plant was built in Germany in 1945 (Woodward, 1967).

The method is seemingly attractive, since it uses lower temperatures and pressures than even the present low-pressure commercial processes. The route to methanol is from syngas and the yields are high in both steps, thus avoiding the equilibrium constraints in the presently practiced methanol synthesis.

Another route to methanol in the partial oxidation of methane and C_2-C_5 hydrocarbons. These compounds can be catalytically air oxidized at 3.0 MPa and around 723K to liquid oxygenated products. Commercial plants using these reactions were operated in the United States (Mitchell, 1956; Woodward, 1967) but were all phased out by 1973. Suitable catalysts for the process are iron, nickel and copper as metals, as oxides or as mixtures of metal and oxides. The catalysts are not selective; acetone and C_1 and C_2 aldehydes are produced in significant amounts along with methanol. The products could possibly be used as liquid fuels. But better technologies are available for processing natural gas to methanol or to methyl fuel. Moreover, the process requires petroleum-derived materials while the future points to the replacement of this feedstock by coal.

Methanol From Coal

Coal-based methanol plants will be more costly and complex than the natural gas plants because of the more complex and costly facilities needed to handle coal and solid residues and the cleanup of the resultant gas. The cost and complexity will also be influenced by the type of coal selected and the gasifier used (Buckingham et al., 1982). Some of the features of coal-to-methanol technology, in which syngas is derived from a second generation gasifier and the methanol synthesis, at least for the near future, is by one of the low-pressure processes, are:

The syngas from the new gasifiers:

1) is mainly H_2 and CO, with little CO_2 and is virtually free of methane
2) is at a much higher temperature than the synthesis temperature

3) is already compressed to 3-8 MPa, eliminating the cost of compression to the synthesis pressure

4) has a low H_2: CO ratio

The low level of CO_2 and CH_4 minimizes the buildup of inerts in the methanol synthesis loop, thus reducing the amount of purge gas required to control the buildup. The excess heat can be recovered in high pressure steam generators and the steam produced can be used to run compressors and to generate electricity. But the syngas is deficient in H_2, and additional units may have to be added to the plant. The H_2:CO ratio has to be adjusted to 2:1 or slightly higher by the water-gas shift reaction. However, the shift reaction is exothermic and the heat may be recovered to generate additional high-pressure steam. Because it is not economical to have excess CO_2 in the feed gas, and the copper-based synthetic processes specify low-levels of CO_2, the extra CO_2 produced in the water-gas shift reaction should be removed in a acid-gas scrubbing unit.

The gasifier is a vitally important part of a coal-to-methanol plant. It influences the synthesis pressure and thus the selection of the commercial synthesis process, to what extent the syngas has to be shifted and the plant design to optimize waste heat recovery at different stages. In spite of this complexity, a large coal-to-methanol industry will one day be a reality. Several conceptual plant designs with economic evaluations are already available (Buckingham, et al., 1983; Leonard, et al., 1979). Moreover, three units of a coal-to methanol plant, the shift converter, acid-gas removal units and methanol converters are well-proven processes. Among the second-generation gasifiers, the Texaco gasifier is commercially proven and is in operation in several plants.

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HYDROCARBONS FROM METHANOL AND OTHER SUBSTRATES USING SHAPE SELECTIVE CATALYSTS: THE MOBIL METHANOL-TO-GASOLINE (MTG) TECHNOLOGY

Introduction:

There are two main processes for the commercial production of fuels and chemicals from syngas: the Fischer-Tropsch (F-T) process and the synthesis of methanol. We have discussed the F-T synthesis and found that it produces a wide variety of products. The wide range of paraffins, olefins and oxygenated compounds must be upgraded in a series of some 26 different processing steps. If we endeavor to change the product distribution by changing operating conditions or catalyst formulation, we always must make some trade-off. The products almost invariable obey the Anderson-Schulz-Flory rule and if we make more of one product, other products change in yield.

On the other hand, methanol can be synthesized in over 99% yield from syngas.

Shape Selective Catalysts; The Mobil (MTG) Process

A remarkable discovery was made in the 1970s by the Mobil Research and Development Corporation. They discovered that methanol could be converted to high octane gasoline in excellent yields, using a shape selective catalyst (a zeolite) called ZSM-5. This catalyst has a long catalyst life. While Mobil has done considerable work on the conversion of methanol to gasoline, it has been found that many other compounds such as ethanol, acetone, ethylene, propylene, etc., and even the complex mixture of F-T products, since they have little branching, can be converted to high octane gasoline over the same ZSM-5 catalyst. A constraint is that the feed must be composed of essentially straight-chain compounds, bearing only occasional methyl groups. Compounds with ethyl and larger degrees of branching are too large to enter the pores of the ZSM-5 catalyst.

We shall confine most of our discussion to the Mobil methanol-to-gasoline (MTG) process since most work has been carried out using methanol as the feed. Indeed, in 1985, a plant will convert syngas, made from New Zealand's extensive Maui gas field (containing over six trillion cubic feet of natural gas) to methanol. The MTG process will then be used to convert the methanol into about 14,000 barrrels a day of high quality motor fuel. In the future, coal will undoubtedly be the source of the syngas used to make methanol for this process.

ZSM-5 is a synthetic zeolite discovered by Mobil in the 1960s (Argauer and Landolt (1972)). In a way, this route for the production of gasoline and diesel fuel from syngas is the first really new route to the production of transportation fuels discovered since World War II (Chang et al., 1975; Meisel et al., 1976; Chang et al., 1979).

ZSM-5 has a unique pore structure and unusual catalytic properties (Kokatailo et al., 1978). It is the key element in the MTG process. Its structure differs considerably from a wide-pore zeolite such as faujasite and a narrow-pore zeolite such as erionite (Chang, 1983b). ZSM-5 has two sets of intersecting channels with openings of about 6 Å. One set consists of elliptical 10-membered ring straight channels; the other is a set of tortuous sinusoidal channels. The channel opening is just large enough to allow molecules with ten or less carbons to wend their way through the crystalline structure. If the molecule is small, it moves rapidly through the zeolite and experiences less cracking. Molecules containing more than 10 carbon atoms are unable to leave the catalyst pores and eventually "reform" until they are of the right size to emerge from the catalyst.

Zeolites are crystalline, three dimensional aluminosilicates in which the building blocks are silica and alumina tetrahedra. The framework will have a net negative charge since every oxygen in the "infinite" lattice is shared by two tetrahedra, with silicon being tetravalent but aluminum only trivalent. The negative charge is balanced by exchangeable cations; a general structure may be written as (Chang, 1983a):

$$M_{p/n}(AlO_2)_p(SiO_2)_q \cdot xH_2O$$

where n is the charge on the cation and x is the water of hydration. The SiO_2/AlO_2 ratio varies in different zeolites; it is high in ZSM-5. The mouth of a particular zeolite channel consists of a ring of a fixed number of tetrahedra, which determines the diameter of the mouth or the pore size.

Over 30 natural zeolites are known and many more that number have been synthesized in the laboratory. While the central atoms of all natural zeolites are dominated by Si and Al atoms, chemically related atoms such as B, P, Ge, Ga, etc. can be incorporated into synthetic zeolites.

Molecular shape selectivity in these aluminosilicates was first reported by Weisz and Frillette (1960). Weisz and his coworkers (1962) defined two types of shape selectivity: reactant selectivity, where certain molecules enter into the zeolite and others are excluded by virtue of their shape and size; and product selectivity, where some of the products formed within the pores are too bulky to diffuse out. These latter molecules are either converted to smaller molecuels or eventually deactivate the catalyst by blocking the pores. Csicery (1976) has reviewed the modes of action of shape selective catalysts. The Mobil (MTG) process may be represented by the following equations:

$$2CH_3OH \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} CH_3OCH_3 \tag{1}$$

$$CH_3OCH_3 \xrightarrow{-H_2O} C_2\text{-}C_5 \text{ olefins} \tag{2}$$

$$C_2\text{-}C_5 \text{ olefins} \longrightarrow \text{paraffins, cycloparaffins, aromatics} \tag{3}$$

Selectivity to gasoline-range hydrocarbons is about 85% with virtually no compounds heavier than C_{10} formed. Liquefied petroleum gas (LPG) comprises most of the remainder of the product.

One hundred tons of methanol is converted to nearly 44 tons of hydrocarbons and .56 tons of water. The hydrocarbons produced contain 95% of the energy in the methanol feedstock; the exothermic heat of reaction contains the remaining energy (5%).

The catalyst, ZSM-5 has 10-ring pore openings through which molecules with only critical (kinetic) diameters of about 6 Å can pass.

Approximate distributions of products obtained from Sasol's fixed bed (Arge) and fluid bed (Synthol) reactors are compared with those obtained from Mobil's MTG process in Table II-3.

A normalized distribution of aromatics obtained in the MTG process is, in weight percent: benzene, 4.1; toluene, 25.6; ethylbenzene, 1.9; o-xylene, 9.0; m-xylene, 22.8; p-xylene, 10.8; trimethyl substituted benzenes, 14.1; other aromatics 12.4 (Chang et al., 1981).

An excellent review of the synthesis of hydrocarbons from methanol has been published by Chang (1983a, 1983b). The monograph and the review paper summarize most of the various mechanisms that have been proposed for the conversion of methanol to hydrocarbons in the MTG process. Essentially three steps are involved: the conversion of methanol to dimethyl ether (DME), then the initial formation of a carbon-carbon bond and finally aromatization with hydrogen transfer. Crude methanol containing 17% water may be used in this process. The final steps, consisting of olefin condensation, cyclization and hydrogen transfer over H-ZSM-5, proceed by well-known carbenium ion mechanisms (Venuto and Landis, 1968; Pines, 1981; Galway, 1970; Dejaifve et al., 1980).

The mechanism of the dehydration of methanol, which has only one carbon atom, differs significantly from the dehydration of higher alcohols. The weight of evidence (Chang, 1983b) indicates that surface alkoxyls (i.e., Si-OCH_3 may be intermediates in the formation of ethers from alcohols.

The manner in which initial C-C bond formation from methanol over H-ZSM-5 occurs is, in spite of much work, far from being resolved. There are numerous postulations in the literature, from the intermediacy of carbenes to free radical mechanisms. Postulated intermediates include surface alkoxyls

Table II-3

Product Distributions from Sasol (F-T)
and Mobil (MTG) Processes
(Mills, 1977; Dry, 1981; Roper, 1983)

Process	ARGE (Fixed Bed) F-T	Synthol (Fluid Bed) F-T	Mobil (Fixed Bed) MTG
Temperature, K	490-520	590-600	633-685
Pressure (atm)	26	22	14-24
Feed	$1.7H_2:1CO$	$3H_2:1CO$	CH_3OH
Product Distribution			
Light Gas C_1-C_2	11.00	20.1	1.3
LPG C_3-C_4	11.00	23.0	17.8
Gasoline C_5-C_{12}	25.4	39.0	80.9
C_{13}-C_{19}	14.0	5.0	0
Heavy Oil, C_{19+}	37.0	6.0	0
Oxygenated Compounds	2.3	7.0	0
Aromatics, % of Gasoline	0	5	38.6

(Topchieva and Ballod, 1950), carbenes and carbenoids (Chang and Silvestri, 1977); oxoniums ions and ylides (van den Berg et al., 1980); carbenium ions and superacid chemistry (Pearson, 1974; Ono and Mori, 1981); chain mechanisms (Anderson et al., 1980) plus other intermediates and routes to the initial carbon-carbon bond (Chang 1983b).

A good bit of controversy has been generated about the nature of the mechanism of formation of the "first" olefin. There is little doubt that ethylene is extremely reactive in the presence of various zeolites (Novakova et al., 1979; van den Berg, 1981). At low temperatures, water may retard or inhibit the reaction in ZSM-5 zeolites. But methanol conversion gives an ethylene to propylene ratio of less than one with most unmodified zeolites.

Chu and Chang (1984) have recently studied the critical questions involved in the conversion of methanol to olefins. They found that the distribution of olefins derived from methanol over ZSM-5 approached thermodynamic equilibrium at low conversion levels. However, as conversion increases, the olefin distribution becomes subject to kinetic control due to autocatalysis. This is particularly evident with propylene formation. Propylene shows a marked increase in a certain region of the reaction path, following this apparent induction period. This type of behavior is characteristic of C_3+ olefins from methanol (Chang et al., 1977) and is attributed to autocatalysis (Chen and Reagan, 1979) during early formation of C-C bonds (Kaeding and Butter, 1980). As a result, C_3+ olefin selectivities will be higher than that calculated by thermodynamics.

It is concluded that thermodynamic equilibrium is approached at low methanol conversion levels. As conversion increases, kinetic control due to autocatalysis and competitive sorption of water takes over. Ethylene is therefore the initial olefin formed from methanol over ZSM-5.

Operation of the MTG Process; Reactor Design in the MTG Process

The MTG reaction is highly exothermic (some 186.6 kcal/lb of reacted methanol) and the adiabatic rise in temperature could approach 866 K. Mobil experimented with the heat removal capabilities of both fixed bed and fluid-bed reactors.

Since the fixed-bed reactor is simple in design, Mobil was able to scale up bench-scale units to a four barrel/day fixed-bed unit quite quickly. In the first reactor, crude methanol (with 5-20 wt% of water) is dehydrated to an equilibrium mixture of methanol, DME, and water. Some 20% of the overall heat of reaction is liberated in this dehydration step.

Conversion of the methanol and DME takes place in the second reactor. The temperature rise across the catalyst bed is limited by recycle gas. It is necessary to regenerate the ZSM-5 catalyst periodically by burning off the coke.

A fluid-bed reactor system lends itself to facile removal of reaction heat so that it can be kept at isothermal conditions. In addition, the fluid bed process is better suited for scale-up to very large plants. A four barrel/day fluid bed unit was also built and operated by Mobil.

The fixed-bed unit operates at an adiabatic temperature gradient across the bed and needs gas recycle to control temperature rise. The fluid bed operates isothermally at about 683 K and no recycle is required. The fixed bed operates at 2.0 MPa while the fluid bed is run at about 0.2 MPa. While both types of reactors give essentially stoichiometric yields of hydrocarbons and water, with little by-product, the hydrocarbon mixture is influenced by the gas recycle. The fluid-bed process produces only 60% raw C_5+ gasoline while the fixed bed yields nearly 80% of this product (Lee, 1982). But large amounts of propylene and butenes, which can be alkylated with isobutane, are also produced in the fluid bed process, so that a final yield of 88% of gasoline is attainable.

Gasoline made by the MTG fixed bed process is of high quality and is similar to conventional unleaded gasoline. It does contain durene which, since it is a symmetrical compound (1,2,4,5-tetramethylbenzene) has a high melting point (353K). Since durene could cause problems in concentrations of about 4% or more, MTG gasoine is treated to lower its durene content to about two percent.

There appear to be no obstacles to scale-up the fixed bed unit which will begin operation in New Zealand in 1985. The 14,000 barrels per day of unleaded gasoline manufactured in New Zealand will average 92 to 94 research octane; the amount produced will be equivalent to about a third of New Zealand's gasoline use. The feed for the New Zealand plant will be provided by two 2,200 tons per day methanol plants. The MTG plant will consist of a single train (Penick et al., 1983).

The initial scale up of the fluid bed MTG process was to a four barrel a day pilot unit. More extensive studies are required before a commercial plant can be built and operated with the same confidence as the fixed bed scale up in New Zealand. As a result, a semi-works unit that will process 100 to 200 barrels a day of methanol has been built in Germany and has been operated so far with considerable success. Participants in this venture include the German government (BMFT), the U.S. Department of Energy, URBK as the operating and managing agents, UHDE having design and construction responsibility and Mobil as the technical advisor, providing the catalyst and technical know-how.

At present, the MTG process is aimed at the production of gasoline, producing high yields of isoparaffins and aromatics. Mobil and others have learned how to control the extent of reaction and to operate at conditions where the yield of either light olefins or of aromatics is increased. As an example, it is now possible to increase the olefin yield to about 30 percent of the hydrocarbons and this is likely the most promising path for producing ethylene from syngas.

The Mobil Two-Stage Fischer-Tropsch (MFT) Process

As stated earlier, syngas can be converted commercially to a mixture of fuels and chemicals via the F-T process or to pure methanol over a Cu-ZnO catalyst. The MTG process, as we have just seen, is used to convert methanol to high octane gasoline.

In Mobil's MFT process, the total F-T product mixture is passed into a second reactor containing ZSM-5 as the catalyst. The result is a high yield (~70 weight percent) of high octane gasoline plus about 20 percent of LPG and small amounts of light olefins. In this second step, the ZSM-5 catalyst has converted the multitude of hydrocarbons and oxygenates produced in the F-T step into high octane gasoline and LPG in a single step. This contrasts sharply with the large number of steps needed to upgrade the usual F-T products, eliminating the heavier F-T products without making more light gases (Huang and Haag, 1981; Kuo, 1977; Haag and Huang, 1979; Haag et al., 1981).

The key to the success of the MFT process is the use of a bubble column F-T reactor, a reactor pioneered by Kolbel over 25 years ago (Kolbel et al., 1955). Haag and his coworkers at Mobil (Haag, 1982) have shown, on a laboratory scale, that the F-T synthesis can be carried out with a low H_2:CO ratio if the reaction temperature can be maintained at a low level. To avoid catalyst deactivation by carbon in the highly exothermic F-T reaction, the reactor temperature must be controlled to within just a few degrees. The way had been paved by Kolbel's early work: carry out the F-T reaction in a <u>liquid</u> medium instead of in the gas phase. Liquids transfer heat from the inside of the reactor to the wall of heat exchangers with much greater efficiency--at least an order of magnitude better than gas phase transfer. And use of the liquid phase should eliminate hot spots and allow strict control of reaction temperatures.

The Mobil workers, under a contract with the U.S. Department of Energy, carried out laboratory experiments in stirred autoclaves and a bubble column reactor, using an iron oxide F-T catalyst and an H_2:CO ratio of 0.7. The temperature in their six-foot high bubble column was kept within 2°C. In addition, the Mobil workers verified reports (Satterfield and Huff, 1980; Kolbel and Ackerman, 1956) that use of low hydrogen content syngas allows the achievement of very high conversions (>79%) in a single pass, thus avoiding recycle of unconverted syngas.

The next stage of the MFT process study is being successfully carried out by Mobil with partial funding by the U.S. Department of Energy. In summary, the MFT process uses an advanced gasifier to produce low H_2:CO gas, converts this gas in a slurry F-T reactor and then simplifies upgrading using the ZSM-5 catalyst.

Use of Bifunctional Catalysts

Two separate "syntheses" are needed in the Mobil MTG process and in similar processes developed by other companies using various different shape selective catalysts (Flanigen et al., 1978; Nijs et al., 1979a and 1979b). In the MTG process, methanol is first manufactured and then, in a second synthesis, the methanol is converted to gasoline over a shape selective catalyst. In the MFT process, as another example, the feed to the zeolite is made via the Fischer-Tropsch process.

There has been a fair amount of research on combining these two separate syntheses by using what may be termed a bifunctional catalyst in one reactor, if possible, to make gasoline (and diesel fuel) directly from syngas. Indeed, a bifunctional catalyst made by intimately mixing an F-T type catalyst with H-ZSM-5 (the hydrogen form of ZSM-5) (Rao and Gormley, 1980; Pennline et al., 1984) yields products similar to the MTG process. In a like manner, a methanol synthesis catalyst such as Cu-Zn-Al_2O_3, may be mixed with a shape selective catalyst. Good yields of gasoline are obtained when these intimately mixed catalysts are used, especially when the combination is comprised of an F-T catalyst mixed with ZSM-5. But further work is required in this area of research. The optimum temperatures of operation of the F-T and the ZSM-5 catalysts differ by about 100°C, for example. Operation at intermediate temperatures results in yields of CH_4 which are too high. Catalyst life and methods of regeneration of each catalyst also pose problems.

The U.S. Department of Energy has funded the Union Carbide Corporation to study the direct catalytic conversion of syngas to transportation fuels. An objective is to obtain product selectivities and product quality superior to those provided by the usual F-T process. The system under investigation consists of an F-T metal plus a shape selective component to control selectivity and fuel quality. It is hoped that superior selectivity to gasoline, turbine fuel and diesel oil will result from lowering the yield of light hydrocarbons and a cutoff of products just above the diesel range.

One of the catalyst systems under study by Union Carbide has a catalyst composed of Co/Th/K on LZ-Y-82 to obtain good selectivity to motor fuel. LZ-Y-82 is the acid form of steam-stabilized Y zeolite. (Quarterly Technical Progress Report, Pittsburgh Energy Technology Center, 1984.)

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METHANOL AND HIGHER ALCOHOLS AS FUELS

Introduction:

Methanol has many uses as a chemical and as a chemical precursor (Figure II-2 in the Summary). However, the future of methanol will eventually rest primarily on its use as a fuel (Figure II-1, Summary) since the fuel industry deals in units of barrels per day rather than in pounds per year (Pruett, 1981). As with petroleum, methanol uses as a fuel may govern; chemicals from methanol, though now important, will probably be made from excess methanol or syngas manufactured primarily for fuel use.

Some of methanol's uses as a fuel are:

- as a gasoline extender
- as a neat fuel for automotive use
- in the synthesis of methyl tert-butyl ether (MTBE), an octane extender
- as a turbine fuel
- as a source of CO and H_2 for use as a transportation fuel.

Methanol was used as a clean fuel for cooking and heating in Europe in the middle of the nineteenth century (Hagen, 1976). It was also used as a fuel for lighting until replaced by the more luminescent kerosene (Reed and Lerner, 1973). Alcohols were used as transportation fuels in the early part of the 20th century until cheap gasoline made its appearance. By 1937, some 70,000 tons of synthetic methanol were used in vehicles in Germany (Nash and Howes, 1938). Methanol has been and still is used in racing cars because of the increased power obtainable over gasoline (Gonnerman, et al., 1975). Blends of ethanol in gasoline have been in commercial use in Cuba, South Africa and South America for some years.

There have been a number of surveys and reviews on the use of alcohols as automotive fuels (S.A.E. Special Public SP-254, June 1964; Kant et al., 1974; Pangorn and Gillis, 1974; Anderson et al., 1974; Cassady, 1975.)

Europe's great dependence on imported petroleum coupled with the 1973 embargo led Germany to sponsor a comprehensive study on the use of methanol and of H_2 as fuels (Hagen, 1976). Studies on the use of methanol in gasoline (Hagen, 1976) continued in 1975, often with U.S. government support. In 1976, the Swedish Methanol Development Co. sponsored the first international meeting on methanol (Royal Swedish Academy, 1976).

Methanol is now made from natural gas and various petroleum fractions. It may be made at a later date from remote sources of natural gas, then from coal and eventually perhaps from renewable resources (Duhl and Wentworth, 1974).

Electric utilities have been interested in methanol as a fuel on a large scale for peak loads in turbines. Methanol and ethanol are already in extensive use as gasoline additives. The use of neat methanol will probably be limited initially to fleets or to certain regions; hundreds of cars are being tested on neat methanol in California. Gasohol, a blend of 10% ethanol and 90% gasoline has been used in Nebraska for many years and has been sold throughout the U.S. Over a million cars fueled by neat ethanol or 10-20% ethanol-gasoline mixtures are used in Brazil.

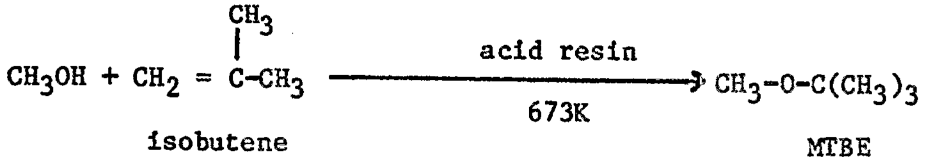
Methanol (CH_3OH) differs from a typical nonpolar gasoline component such as isooctane in that it is a polar molecule with oxygen constituting half of its weight. It thus picks up water easily. But it is a very attractive gasoline additive; it has a higher octane rating than isooctane and is manufactured all over the world from syngas obtainable from almost any organic resource. Phase separation (due to water pick-up), possible corrosion of certain engine parts and volatility considerations rule out the use of straight methanol or gasoline mixed with large amounts of methanol (> 5%) except for cars built specially for use of these fuels. (Sun Tech, Inc., 1983). Arco has received EPA approval for a methanol plus cosolvent mixture with gasoline and sells the product in parts of New York State and in Pennsylvania. Arco's additive consists of 4.75% methanol and 4.75% TBA (tertiary butyl alcohol) in 90.5% unleaded gasoline. Blending 5% methanol and 5% cosolvent into all gasoline used in the U.S. could reduce crude oil imports by over 200 million barrels per year. However no suitable system of distribution for such a methanol blend exists.

Two other points are pertinent. Emissions from the methanol-cosolvent-gasoline blend are lower than those from straight gasoline. And the cosolvent is not limited to tert-butyl alcohol; other alcohols and ethers may be used as cosolvents.

It is possible that methanol-gasoline blends will serve as a bridge between straight gasoline and straight methanol. EPA has indicated that a reduction in allowable addition of tetraethyllead to gasoline may be in the offing; octane enhancement due to added alcohols and ethers may therefore become necessary to retain octane ratings.

The methanol-gasoline blending picture is complex. Two articles that summarize the present situation have appeared recently (Chem. Eng. News, July 16, 1984). One of these article states that coal-based processes for the synthesis of methanol will eventually win out but methane will have the edge for a long time to come.

A rapidly growing use for methanol as a fuel is in the synthesis of methyl tert-butyl ether (MTBE), an effective octane enhancer,



$$CH_3OH + \underset{\text{isobutene}}{CH_2 = \overset{\overset{CH_3}{|}}{C}-CH_3} \xrightarrow[673K]{\text{acid resin}} \underset{\text{MTBE}}{CH_3-O-C(CH_3)_3} \qquad (1)$$

This ether was approved by EPA in 1979 as an octane enhancer for unleaded gasoline at concentrations of 7% or less by volume. MTBE capacity has grown from zero in 1970 to well over a million metric tons and its projected growth seems to be limited only by the availability of isobutene.

The MTBE-gasoline blend provides a number of advantages over methanol - gasoline blends. The MTBE-gasoline mixture has a lower oxygen content, has less severe water separation problems, less front-end volatility effects and also has a high octane quality. In addition, MTBE is usable in all proportions with gasoline, It is, however, more expensive than methanol as a gasoline extender.

Methanol as a fuel in stationary combustion turbines for peak load use for electric utilities has often been mentioned. But utilities are hesitant to rely too much on methanol. Large amounts of a reliable source of methanol would be needed and the possibility of brownouts must be avoided. And oil-based fuels have become more available and, presently are cheaper. But crude oil prices must eventually rise and if and when they do methanol's potential as a fuel "boggles the mind" (Chem. Eng. News, July 16, 1984, p. 16).

Methanol is an excellent gas turbine fuel although it might be necessary to modify turbines somewhat. The sodium content of the fuel in a gas turbine should be kept below 1 ppm. Methanol readily picks up water and the water could be contaminated with alkali salts. On the other hand, methanol as a gas turbine fuel has low pollutant emissions, good performance and good handling and storage properties (Hagen, 1976). In any case, supply and cost seems to be the main factors which influence the introduction of methanol as a turbine fuel.

Dissociated Methanol as a Fuel for Automobiles and Gas Turbines

It is well known that methanol dissociates into CO and H_2 (syngas) as the temperature is raised:

$$CH_3OH \underset{\text{high pr., low temp.}}{\overset{\text{low pr., high temp.}}{\rightleftharpoons}} 2H_2 + CO \qquad (2)$$

At equilibrium, for instance, over 80% of the methanol is dissociated at 1 MPa and 473K (Reed, 1976). It is for this reason that methanol's combustion characteristics are similar to syngas (Pefley, et al., 1971). The major difference in properties is caused by the heat of dissociation of methanol. It is 90.56 kJ/mol at 298K and one atm (13.4% of the lower heat of combustion) and 128.5 kJ/mol at 298K for liquid methanol (20.1% of the lower heat of combustion). It is possible, therefore, that a significant amount of exhaust heat to evaporate and dissociate methanol may be recovered and this is what is generally counted on in automotive use.

Dissociated methanol may offer higher efficiency than conventional liquid fuels for three reasons: (a) the just mentioned waste heat recovery, (b) extended lean misfire limits and (c) higher allowable compression ratios. Also, exhaust emissions are lower (Finegold, et al., 1982). At 573K, a temperature which matches available heat in engine exhaust, equilibrium favors 99.9% conversion of methanol to CO and H_2, although side reactions can occur. A number of catalysts, including Pt, Pd, Cu, Zn, etc. are known to be active for the dissociation of methanol.

Conoco has been cooperating with engine manufacturers in evaluating the methanol dissociation concept in automotive and diesel engines (Yoon and Burke, 1984).

The application of methanol dissociation in combustion turbine uses has also been discussed by Finegold et al., (1982). Woodley et al. (1982) have compared some advantages of burning liquid methanol, dissociated methanol and steam reformed methanol.

Ethanol as a Transportation Fuel

Methanol, CH_3OH, is a polar molecule toxic to humans. Ethanol (ethyl alcohol, CH_3CH_2OH), is somewhat less polar than methanol but that additional CH_2 group converts it into a beverage made and consumed in a great variety of forms all over the world. That CH_2 group also greatly influences the properties of ethanol as a transportation fuel. Ethanol is more hydrocarbon-like than methanol and is therefore more soluble in paraffins and in gasoline, as expected. Ethanol has a higher boiling point than methanol (351.3K versus 337.7K), while their specific gravities are essentially the same. The oxygen atom in methanol comprises half of its molecular weight while in ethanol, only 34.7% of the molecular weight of the molecule is due to oxygen. Ethanol is thus less hygroscopic than methanol. The lower heating value of methanol is 56,560 BTU/gallon (8,600 BTU/lb); that for ethanol is considerably higher: 75,670 BTU/gallon (11,500 BTU/lb). Both have excellent research octane ratings (106-108).

The chemical and physical properties of ethanol make it a better gasoline extender. A 10-90% ethanol-gasoline mixture termed "GASOHOL" has been used in the U.S. and other countries for many years, with little or no vehicle modification.

The manufacture of ethanol has an interesting history - one that is presently in rapid change. Ethanol for human consumption has been made by the fermentation of naturally occurring carbohydrates since prehistoric times. Such ethanol is still made by fermentation.

The first synthetic ethanol, for industrial use, was producted in about 1930 in the U.S. (Margiloff et al., 1981). It involved the hydration of ethylene with water in the presence of sulfuric acid. More recently, industrial ethanol has been synthesized by passing ethylene and steam under pressure (6-7 MPa) over a supported phosphoric acid catalyst at 573 K. Recycling is necessary, since the equilibrium formation of ethanol is low.

From almost complete dependence on fermentation processes up until the late 1920s, over 95% of ethanol (for industrial consumption) was made synthetically from ethylene in the 1970s. But, with the growing use of ethanol in transportation fuels initiated as a result of the 1973 oil embargo, the production ratio of fermentation ethanol to synthetic ethanol has grown rapidly and the future of fermentation alcohol seems bright.

The use of alcohol fuels has been studied for many years in a number of countries. In 1907, for instance, the U.S. Department of Agriculture published a report on the use of alcohol-gasoline mixtures in farm engines (Lucke and Woodward, 1907). Interest in grain alcohol was given impetus by the oil embargo and, in 1974, a gasoline-ethanol blend program for use in fleets was started in the state of Nebraska (Tarr and Jones, 1981). Since then a great deal of work has been focused on the use of ethanol as a gasoline extender, octane enhancer or as an alternative fuel. There are many studies to evaluate the engine performance, emission characteristics and the advantages and also the problems due to ethanol's use in conventional spark ignition engines (Tarr and Jones, 1981; Lucke and Woodward, 1907). U.S. production of fermentation alcohol for fuel use was about 80 million gallons in 1979. A year later, production of ethanol by fermentation neared 300 million gallons and production by fermentation continues to grow. Gasohol and even neat ethanol is now used in many countries, especially by Brazil (J. Goldemburg, 1982; Luchi and Trindale, 1982).

Ethanol by the fermentation of grain has been seemingly made competitive as a transportation fuel in the U.S. largely due to federal and state subsidies aimed at reducing this country's dependence on imported oil. (It must be borne in mind that the U.S. is an energy rich country, lacking only a sufficient reliable supply of transportation fuels). It is possible that U.S. fermentation alcohol may rise to about a billion gallons by 1990 and might then invade the industrial market of more than 200 million gallons (Halberg, 1984).

This report deals with the use of syngas in indirect liquefaction so that we shall not further explore the production of fermentation alcohol for fuel use. It is enough to mention that questions as to the economic viability of arable land for the production of fuel rather than food, as well as other questions, are currently still under debate. (Hyland, 1982; Shah et al., 1984).

Ethanol Directly from Syngas

What are the possibilities for obtaining ethanol (and higher alcohols) from syngas? This would seem to be highly desirable because it might eliminate the need for subsidies and return some land to the production of food. In the long run, ethanol from syngas may be cheaper than fermentation alcohol and independent of ethylene made from (imported) petroleum. Ethanol and higher alcohols are better energy storage chemicals and are less toxic and corrosive than methanol.

Ethanol and other C_2 oxygenated compounds have been synthesized directly from syngas using Fischer-Tropsch catalysts and modified F-T catalysts. The equations for these reaction may be written:

$$2CO + 4H_2 \rightleftharpoons CH_3CH_2OH + H_2O \qquad (3)$$

$$2CO + 3H_2 \rightleftharpoons CH_3CHO + H_2O \qquad (4)$$

$$2CO + 2H_2 \rightleftharpoons CH_3COOH \qquad (5)$$

All these reactions proceed with a decrease in the number of moles so that an increase in pressure should lead to an increase in conversion. Ethanol, acetaldehyde and acetic acid have high equilibrium conversions (~ 80%) at pressures over 1 MPa. Methanol requires pressures of over 20 MPa for high equilibrium conversions. However, the formation of low molecular weight paraffins is thermodynamically favored over that of oxygenates at all pressures and temperatures. The synthesis of C_2 oxygenated compounds therefore requires kinetic control to minimize the formation of alkanes.

Studies of the selectivities of alcohols formed in the F-T reaction have shown that, as with hydrocarbons, there is a regular Anderson-Schulz-Flory (A-S-F) relationship among the alcohols (Dry, 1981). It is of great importance to note, however, that the distribution of C_2 oxygenated products is similar to those of n+1 hydrocarbons. Thus, where C_3 hydrocarbons are the most abundant hydrocarbons produced (other than CH_4), then ethanol is the most abundant alcohol produced. We therefore should be able to obtain yields of C_2 oxygenates far above that predicted for ethylene and ethane by the A-S-F equation. In effect, we should obtain products according to A-S-F predictions but ethanol is the first product with alcohols while methane is the first product with hydrocarbons. In other words, it appears that C_2 oxygenates could be considered the "equivalent" of methane using certain F-T catalysts.

It was pointed out earlier (Figure II-8), that metals that dissociate CO catalyze the F-T synthesis while metals that adsorb CO nondissociatively (Pd, Cu, Ir, Pt) catalyze the synthesis of methanol. Rhodium may be termed a "swing" catalyst since it is situated below cobalt (a good F-T catalyst) and just to the left of palladium (a metal which adsorbs CO non-dissociatively) in the periodic table. Rhodium should be active in the synthesis of ethanol. Thus we have the possibility of the formation of the CH_3 group via CO dissociation and the insertion of an associatively adsorbed CO group into a metal-acyl bond:

$$CH_3{-}M \xrightarrow{CO} CH_3COM \xrightarrow{H_2} CH_3CHO \xrightarrow{M-H} CH_3CH_2OH \qquad (6)$$

Rhodium as bulk metal does produce mostly hydrocarbons (Sexton and Somorjai, 1977). Katzer et al. (1981) showed that Rh in very small clusters on acidic supports also produces mainly hydrocarbons. However, on more basic supports, the selectivity to alcohols is enhanced. Katzer et al. offered an explanation for this effect in terms of the more basic oxides having a higher Fermi level, thus having greater electron-donating capabilities; they suggested that Rh on such oxides behaves more like Pd, which as mentioned earlier, does not dissociate CO at F-T synthesis temperatures. Bhasin et al. (1978) and Ellgen et al. (1982) have shown that rhodium-SiO_2 based catalysts show unusual abilities to convert syngas to C_2 oxygenates in one step at about 573K and 3-10 MPa. Manganese added to these catalysts increased the synthesis rate but had little effect on the distribution of products.

Watson and Somorjai (1982) used a $LaRhO_3$ (lanthanum rhodate) catalyst to hydrogenate CO at 0.6 MPa and 498-648K. At about 573K, the yields of ethanol and acetaldehyde exceeded 50 wt %. Ichikawa (1982) studied rhodium catalysts on several moderately acidic oxides such as La_2O_3, TiO_2, Nd_2O_3, CeO_2, and ZrO_2 as supports. They obtained large yields of ethanol and other C_2 oxygenated compounds such as acetaldehyde and some acetates. A heterogeneous catalyst prepared from a $Rh_4(CO)_{12}$-La_2O_3 catalysts yielded, using one atm of syngas at 473K, the following product distribution based on carbon efficiency (%): CH_3OH, 10; CH_3CH_2OH, 49; $CH_3CHO + CH_3COOR$, 2; CH_4, 14; C_2-C_4, 6; CO_2 + other products, 8.

This is a lucrative field for further investigation. A synthesis of ethanol directly from syngas with over 80% selectivity would be a great step forward in the manufacture of transportation fuels and chemicals directly from syngas.

The Homologation of Methanol to Ethanol

The homologation or reductive carbonylation of methanol to yield ethanol plus acetaldehyde and acetates has been much studied but has not yet been commercialized. Homogeneous transition metal catalysts have been used as catalysts (Wender et al., 1949; Fakley and Head, 1983; Piacenti and Bianchi, 1977). There is little doubt that acetaldehyde is the precursor of ethanol.

$$CH_3OH + 2H_2 + CO \xrightarrow[RuCl_3, I_2]{Co_2(CO)_8} CH_3CH_2OH + H_2O \qquad (7)$$

The methanation of methanol is the most thermodynamically favored reaction at 298K and 0.1 MPa but the formation of ethanol is almost as favorable. At higher temperatures, ethanol and CH_3CHO become less favored at the expense of dimethyl ether and CO_2. The synthesis of ethanol is thermodynamically more favored as the pressure is raised to 10 MPa but the chief problem is kinetic control over the number of possible reaction products (methane, acetates, acetic acid, dimethyl ether, acetals and CO_2) (Fakley and Head, 1983).

Cobalt complexes, first used, are still the best catalysts in their activity and selectivity for the conversion of methanol and syngas to ethanol and CH_3CHO. Rhodium, usually more active than cobalt in homogeneously catalyzed reactions involving methanol and syngas, produces acids and esters, with ethanol a significant product at rather high H_2 partial pressures (H_2/CO = 40:1) (Dumas et al., 1979).

Operating temperatures in the 450-485K range are usually used with cobalt. As the temperature rises, selectively to ethanol increases at the expense of acetaldehyde. Rise in pressure increases conversion of methanol while product selectivity remains almost constant. There is evidence that water produced during the synthesis poisons the reaction (Fakley and Head, 1983). At high CO partial pressures, the competing alcohol carbonylation dominates and over 70% selectivity to methyl acetate is observed. At high H_2 partial pressures, the catalyst tends to decompose to metal with accompanying loss of methanol to methane and dimethyl ether. Highest ethanol selectivity is obtained at H_2/CO ratios of one.

The most significant discovery in methanol homologation has been the rate enhancement associated with addition of iodine or iodide. This arises mostly from the in-situ formation of CH_3I which reacts with syngas much faster than does methanol.

By the use of co-catalysts, a selectivity to acetaldehyde above 60% can be obtained at 68% conversion. For the production of ethanol, ruthenium has been found to be by far the best co-catalyst since all the aldehyde is hydrogenated to ethanol. For instance, cobalt acetate, I_2, $RuCl_3$ and PPh_3, at 450K and 27.2 MPa were used to convert 43% of methanol to ethanol with a selectivity of 80% (Fiato, 1979; 1980). The addition of tertiary phosphine ligands to the catalyst has two desirable effects: greater catalyst stability and enhanced ethanol selectivity.

In conclusion, the cobalt carbonyl-catalyzed reductive carbonylation of methanol with syngas to produce acetaldehyde, ethanol and acetates is a complicated system which achieves a remarkably high degree of kinetic control over the thermodynamically favored product mixture; however, selectivities to ethanol of 80% are rare. While the chemical reactions and promoter effects are fairly well understood, it is difficult to see how the system can be perturbed to furnish higher activities or selectivities approaching the carbonylation of methanol, where over 99% selectivity to acetic acid is achieved.

The diverse mixture of products coupled with low activity makes methanol reductive carbonylation an unlikely source of ethanol. However, a possible use of the product mixture is as a fuel blend and this alternative is under serious consideration (Chem. Eng. News, April 7, 1980, p. 37).

Chen et al. (1982) have shown that iron or ruthenium, promoted by a tertiary amine, catalyzes the homologation of methanol to ethanol at syngas pressures near 30 MPa and temperatures about 475K. Carbon dioxide rather than water is the by-product and no alcohols higher than ethanol are formed, nor are acetates or acetals formed.

$$CH_3OH + H_2 + 2CO \longrightarrow CH_3CH_2OH + CO_2 \qquad (8)$$

This reaction calls for further study although reaction rates appear somewhat low.

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THE SYNTHESIS OF HIGHER ALCOHOLS

As noted earlier Fischer and Tropsch, in their earliest experiments in 1922-1923 (Fischer and Tropsch, 1923, 1924; Anderson 1984) used alkalized iron catalysts to obtain mostly oxygenated products from syngas; they called this the Synthol process. It was carried out at 460-500K and 2 MPa and the product contained up to 70 wt % of alcohols with carbon numbers up to C_{20}. The aim at that time, however, was to obtain hydrocarbons by the hydrogenation of CO. In 1953, Anderson found that iron nitrides were durable, unique catalysts for the F-T synthesis yielding about 40 wt % alcohols (Anderson, 1980). A systematic catalyst development program to explore the use of iron nitrides in the synthesis of higher alcohols was not conducted. Anderson (1984) has recently summarized F-T work using iron carbides, nitrides and carbonitrides.

It has long been known that methanol synthesis catalysts prepared by precipitation with alkali led to an increase in higher alcohol yields (Anderson et al. 1952). It was found that methanol synthesis catalysts promoted with alkali and containing up to three metal oxides yielded higher alcohols--1-propanol and 2-methyl-1-propanol (isobutanol) -- together with the expected methanol. The catalysts for this synthesis generally operated at about 675 K and 20 MPa and lower space velocities than for the usual methanol synthesis. Cesium, rubidium and potassium were the most active promoters with potassium obviously the most practical promoter (Morgan et al., 1932, Natta et al., 1957; Runge and Zepf, 1954).

Although higher alcohols (C_1-C_6 especially) are very desirable products for fuel use, there has been a paucity of reports dealing with the quantitative aspects of the kinetics and selectivity for these promoted methanol catalysts which did not contain copper. And the effect of promoting the more active, low-pressure, Cu/ZnO methanol synthesis catalysts has been reported only in the patent literature.

Smith and Anderson (1983) studied the effects of promoting commercial low-pressure methanol catalysts (Cu/ZnO) with K_2CO_3. They found the optimum K_2CO_3 concentration to be about 0.5 wt %. Interestingly, the ratio of H_2 to CO in the feed was found to have a large influence on the selectivity to higher alcohols. The isobutanol production rate varied as $p_{H_2}^{-0.7} \cdot p_{CO}^{2.2}$; both exponents were positive and less than 1.6 for methanol, ethanol and n-propanol. The selectivity to isobutanol was more than doubled when the H_2 to CO ratio was decreased from 2 to 0.5. Smith and Anderson (1983) derived chain growth schemes for predicting the selectivity to higher alcohols. These catalysts operated at much less severe conditions than had been used previously. The large selectivity to isobutanol was postulated to be the result of the termination of chain growth, due to the inability of β-addition to occur with this branched alcohol. While methanol was always the main product, significant selectivity (carbon atoms in $alcohol_i$ total carbon atoms in alcohols x 100%) to ethanol (~ 4%), isopropanol (~ 1.5%), 1-propanol (~ 8%), 1-butanol (~ 2.5%), 2-butanol (~ 1.3%), isobutanol (up to 18.8%), and pentanols (up to 14.8%) were obtained in one instance.

Smith and Anderson (1984) later described a scheme for the distribution of the alcohols obtained, assuming one or two carbon addition at the α or β carbon atom of the growing alcohol chain. It was shown that addition of alcohols to the syngas increased the yield of some of the alcohols, a finding consistent with their postulated growth scheme.

Work has lately begun to center on the use of methanol synthesis catalysts combined with F-T catalysts, often in the presence of alkali. Courty et al. (1982) at the Institute Francais du Petrole (IFP) have been studying the synthesis of higher alcohols. Their aims included finding a catalytic system that operated under conditions comparable to those used for the methanol synthesis, avoiding pressures above 15 MPa. They have been studying two systems using mainly coprecipitation preparation procedures: $CuO/CoO/Cr_2O_3$ and $CuO/CoO/Al_2O_3$ (or ZnO), both promoted with alkali. Basically, the reduced cobalt acts as an F-T catalyst, dissociating CO, while the action of the copper resembles its role in the methanol synthesis. Courty et al. (1982) found that, with special attention to the design of these catalytic systems, it is possible to reduce the F-T activity while enhancing selectivity to C_1-C_6 alcohols to 60-80%; the $C_{2+}OH/C_{2+}OH + CH_3OH$ ratio exceeded 60%.

Work is proceeding on understanding the nature of the active sites in these catalysts, their possible interactions, and the mechanisms involved in these complex catalysts. The procedures used in their preparation is critical, especially to avoid F-T active catalysts.

Hydrocarbons as well as alcohols are produced, with the amount of hydrocarbons generally greater than the amount of alcohols obtained. The Anderson-Schulz-Flory (A-S-F) distribution is obtained for both types of products. IFP is building a pilot plant to produce C_1-C_6 alcohols (Martino, 1984.

Sibilia et al. (1984) also have investigated a system composed of an F-T catalyst combined with a methanol synthesis catalyst.

It is common for copper to be used as a promoter in iron catalyzed F-T reactions (Kolbel and Ralek, 1980; Amelse et al., 1981). The copper evidently increase the activity of the catalysts by means of its redox properties during catalyst preparation (Kolbel and Ralek, 1980). It is usually found that more oxygenated products are formed at lower gas hourly space velocities (Zaman, et al., 1977)

Herman et al. (1979) and Dominiquez et al. (1983) used well-characterized Cu/ZnO (30/70 mol %) catalysts and incorporated small amounts of iron into the catalysts. The catalysts, as expected, yielded paraffins and olefins as well as alcohols. These workers found that both alcohols and hydrocarbons are primary products with Fe/Cu/ZnO catalysts. Two chain growth processes were indicated, one with short carbon chains for alcohols and the other with the usual F-T hydrocarbon chain length. The synthesis of C_2-C_5 alcohols was optimum over these catalysts when the amount of iron was small (~ 1%).

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CHEMICALS FROM SYNGAS

Introduction:

This report is mainly concerned with the area of syngas in the synthesis of fuels (Figure II-1, see Summary), for the fuel use of syngas will eventually overtake its present use in the synthesis of high-value-added chemicals. But syngas is a major and growing source of chemicals (Figure II-2, see Summary). Only methanol and methane are now made in high purity directly from syngas. In the entire world, the largest use of syngas (some five trillion SCF per year) is in the manufacture of hydrogen for the synthesis of ammonia; the CO in the syngas yields another mole of H_2 via the water gas shift reaction:

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \qquad (1)$$

The second largest use of syngas is in the manufacture of methanol (about one trillion SCF per year). Syngas, besides being the world's principal route to H_2 for hdyrogenation, hydrogenolysis, resid upgrading, hydrodesulfurization, direct coal conversion, etc. is also a source of CO for the synthesis of chemicals.

A good deal of research is being carried out on new syntheses of chemicals directly from syngas. The theoretical reaction stoichiometry for the synthesis of various chemicals (mostly oxygenated compounds) directly from syngas (raw material usage in pounds of feed per pound of product) is generally favorable. For instance, the H_2/CO ratio is 1.5 for the already discovered direct synthesis of the important chemical, ethylene glycol; here, just one pound of feed yields one pound of glycol (Aquilo et al., 1983). But the reaction pressure in this new route to ethylene glycol is very high since five moles of gas must be converted to one mole of liquid product, among other drawbacks.

Most of the presently used processes for the direct synthesis of chemicals from syngas use homogeneous transition metal catalysts because of their high selectivity to desired products. It is likely that this trend will continue.

At present, a large number of chemicals are made sequentially, that is, by first converting syngas to methanol and then carrying out a second reaction with methanol to yield the desired product. If the second step involves the reaction of methanol with CO (a carbonylation reaction) as in the synthesis of acetic acid, then the final product is derived solely from syngas. At this writing, sequential process technology is better than trying to carry out the several steps directly from syngas in one reactor. As pointed out, these reactions from methanol or formaldehyde are quite selective and operate under mild conditions. The one-step synthesis of ethylene glycol not only requires higher pressures but usually results in low selectivity to the glycol. Wender (1984) has recently reviewed the synthesis of chemicals from methanol.

Formaldehyde

About 40% of the methanol produced around the world is converted to formaldehyde (HCHO) by dehydrogenation in the presence of Ag or Cu catalysts or by oxidation of methanol in the presence of iron-containing MoO_3 catalysts. Formaldehyde has many uses of its own, mostly in the manufacture of resins. But a number of other chemicals, including ethylene glycol, butynediol and isoprene are made from HCHO.

Acetic Acid

Some three billion pounds of acetic acid were produced in the U.S. in 1983. All processes for the production of this important chemical have been or are being steadily replaced by processes based on the homogeneously catalyzed carbonylation of methanol:

$$CH_3OH + CO \xrightarrow[CO]{\text{Rh complex, } I_2} CH_3COOH \qquad (2)$$

In this process, discovered by Paulik and Roth (1968), methanol and CO react in the liquid phase at 420-470K at pressures below 3.4 MPa to yield acetic acid with a selectivity of over 90% (based on CH_3OH) and over 90% (based on CO) (Forster, 1982). So that syngas rather than ethylene or other hydrocarbon feedstocks is now the raw material of choice for the manufacture of acetic acid.

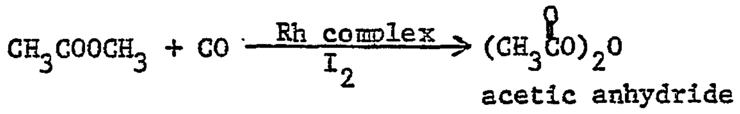
Acetic Anhydride

There is a real story here. The Tennessee Eastman Company is the first manufacturer to develop and commercialize chemical technology which uses coal as the raw material for the production of acetic anhydride. This chemical is used to manufacture cellulose acetate for use in making photographic film base; it has a number of other uses. Eastman started up this first integrated facility for the manufacture of chemicals from coal in 1984 using a Texaco gasifier to gasify 900 tons of high-sulfur bituminous coal processed daily (Chemical Engineering Progress, May 1984). About 500 million pounds of acetic anhydride will be produced per year; this would require the annual equivalent of one million barrels of oil using conventional technology. The reactions involved are given below:

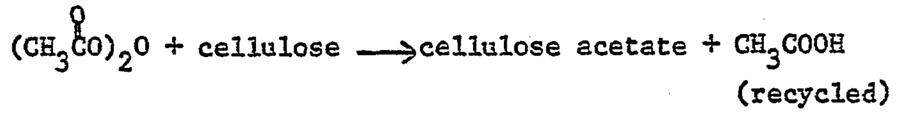
$$2H_2 + CO \xrightarrow{Cu/ZnO} CH_3OH \qquad (3)$$

$$CH_3OH + CO \xrightarrow[435K,\ 8\ MPa]{Rh-I} CH_3COOH \text{ (acetic acid)} \qquad (4)$$

$$CH_3OH + CH_3COOH \xrightarrow{H^+} \underset{\text{methyl acetate}}{CH_3COOCH_3} + H_2O \qquad (5)$$



$$CH_3COOCH_3 + CO \xrightarrow[I_2]{\text{Rh complex}} \underset{\text{acetic anhydride}}{(CH_3\overset{O}{C}O)_2O} \qquad (6)$$



$$(CH_3\overset{O}{C}O)_2O + \text{cellulose} \longrightarrow \text{cellulose acetate} + \underset{\text{(recycled)}}{CH_3COOH} \qquad (7)$$

All these reactions, except that in (4) are well known commercial reactions. The catalytic system developed for the conversion of methyl acetate to acetic anhydride was developed by Tennessee Eastman and Halcon International.

The current climate for coal conversion seems poor but Eastman feels this process is economically viable. The plant's location in Tennessee near substantial reserves of high grade coal is a positive factor. And perhaps the most encouraging part of this new development is the possibility that Eastman stands to be the first company to develop a whole series of important oxygenated chemicals from coal-derived syngas. The Tennessee Eastman process is diagrammed in Figure II-9. It appears that vinyl acetate can be manufactured by related catalytic reactions (King et al., 1982).

Methyl Formate, Formamide and Formic Acid

These chemicals are made from methanol and CO in the presence of a base catalyst rather than a transition metal catalyst. The equations are given below:

$$CH_3OH + CO \xrightarrow[\substack{343K \\ 2\text{-}20\ MPa}]{NaOCH_3} HCOOCH_3 \text{ (methyl formate)} \qquad (8)$$

$$HCOOCH_3 \xrightarrow{NH_3} \underset{\text{formamide}}{HCONH_2} + CH_3OH \qquad (9)$$

$$HCONH_2 \xrightarrow{H_2SO_4} (NH_4)_2SO_4 + HCOOH \text{ (formic acid)} \qquad (10)$$

World production of formic acid is about 100,000 tons per year.

Ethylene Glycol ($HOCH_2CH_2OH$)

Ethylene glycol is now made by the reaction of ethylene with oxygen over a silver catalyst; the ethylene oxide so formed is then hydrolyzed to ethylene glycol This chemical has now been produced directly from synthesis gas (Vida et al., 1978; Pruett, 1977).

$$3H_2 + 2CO \quad \underset{510K}{\text{Rh or Ru complexes}} \quad \underset{\sim 78\%}{HOCH_2CH_2OH} \qquad (11)$$

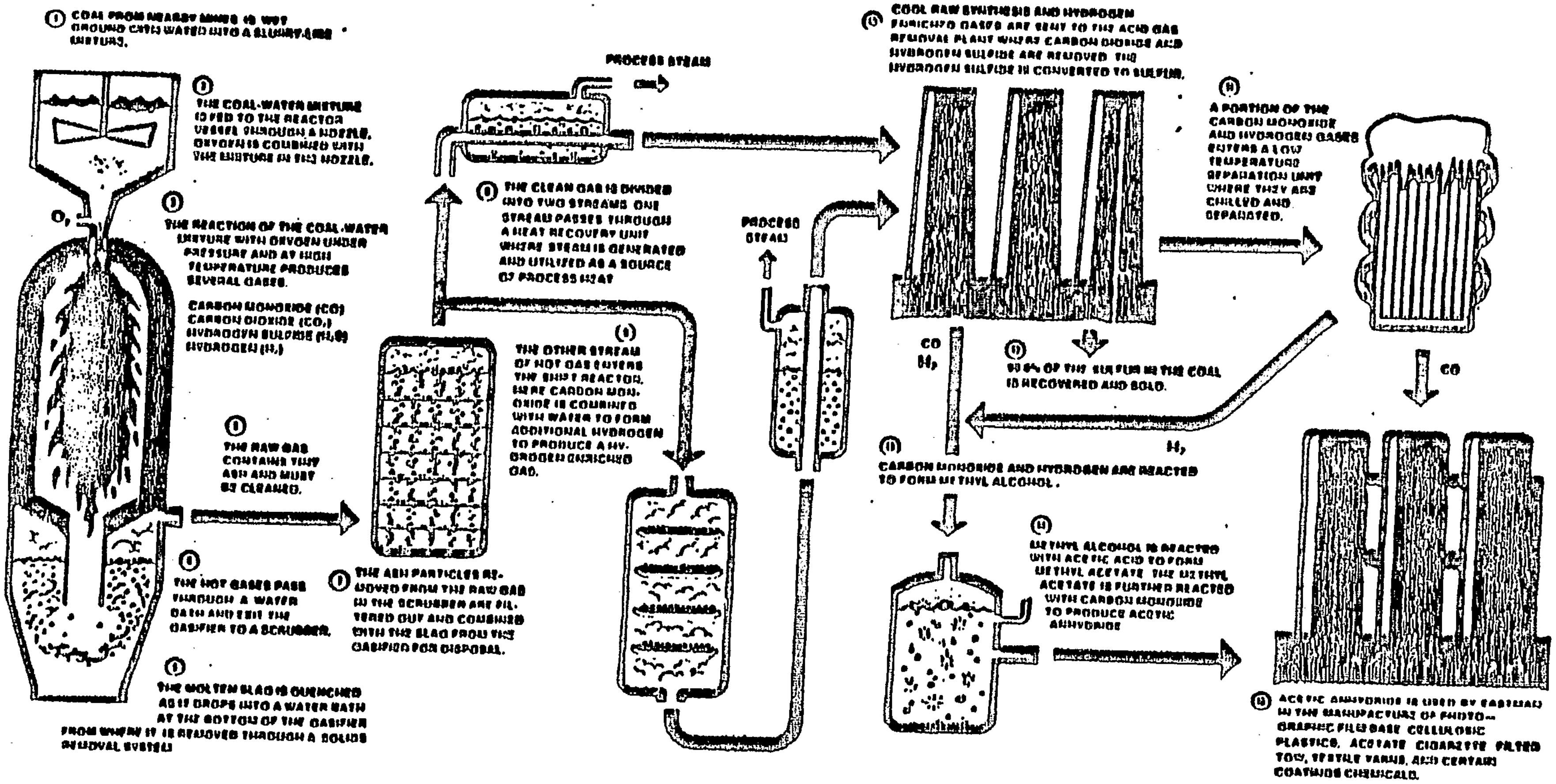


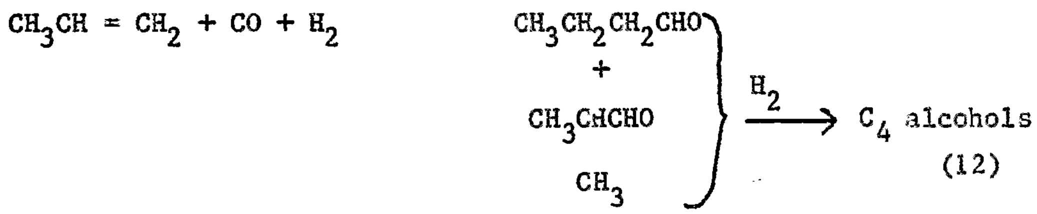
Figure II-9: Tennessee Eastman Company's Coal-to-Acetic Anhydride Plant

However, as noted earlier, pressures are too high, reaction rates too low and selectivity not good enough (methanol is a significant by-product) to make this route economic at present. There is evidence that the synthesis of formaldehyde is the rate-determining step in this direct synthesis (Fahey, 1981; Dombeck, 1980; Costa, 1983). By dividing the synthesis of ethylene glycol into at least two separate reactions based on methanol or formaldehyde, many kinetic and thermodynamic constraints to the synthesis of this glycol are removed. There are a number of processes being developed for the synthesis of ethylene glycol from either methanol or formaldehyde (Kollar, 1982a; 1982b; Chem. Eng. News, 1983; King et al., 1982).

Syntheses Using Syngas or CO Plus Another Chemical Not Derived From Syngas

The Hydroformylation (OXO) Reaction

This synthesis, the reaction of olefins of almost every kind with synthesis gas to yield aldehydes or alcohols, was discovered by Roelen (1943) in 1937, while he was studying the mechanism of the cobalt catalyzed Fischer-Tropsch reaction. About ten billion pounds of OXO alcohols are now produced per year around the world. The reaction with propylene, an important substrate, is given below:



$$CH_3CH = CH_2 + CO + H_2 \qquad \left.\begin{array}{c} CH_3CH_2CH_2CHO \\ + \\ CH_3\underset{CH_3}{C}HCHO \end{array}\right\} \xrightarrow{H_2} C_4 \text{ alcohols} \qquad (12)$$

First generation hydroformylation plants, most of which are still in operation, use the metal carbonyl, $Co_2(CO)_8$ or cobalt salts as the catalyst. New plants use tertiary phosphine complexes of rhodium as catalysts; these operate at lower pressures and temperatures. Unlike cobalt catalyzed reactions, easily polymerized olefins such as methyl methacrylate and styrene react cleanly with syngas over rhodium catalysts to yield alcohols or aldehydes having one carbon atom more than the original olefin (Pino et al., 1977; Pruett, 1979).

Important syntheses with CO have been reviewed by Falbe (1980).

Synthesis of Lower Olefins and Aromatics from Syngas

The Mobil (MTG) process for the conversion of methanol to gasoline has been discussed earlier in this report. A glance at Figure II-2, in the Summary indicates that C_2-C_4 olefins and aromatics (benzene, toluene and xylenes, termed BTX) can also be synthesized from methanol using ZSM-5 or modified ZSM-5 shape selective catalysts. The C_2-C_4 olefins and BTX essentially constitute what are known as petrochemical feedstocks so that the many chemicals and fuels normally produced in a petroleum refinery can be made from syngas in what may be termed a petroleum-less refinery.

The pathway from methanol to gasoline with ZSM-5 involves the conversion of methanol first to ethylene and then to higher olefins, some of which lose hydrogen and cyclize to aromatics. Light olefin yields can be improved by operating at high space velocities (King et al., 1981), adding diluents to the methanol or by increasing the shape selective reactions by reducing the pore size of the zeolites (Caesar and Morrison, 1978a; 1978b). Wunder et al. (1981) have used 13X molecular sieves plus manganese to obtain high yields of C_2-C_4 olefins. Anthony and Singh (1981) have used a small pore catalyst (>6Å) such as chabazite ion-exchanged with a mixture of rare earth chlorides to accomplish this result. Kaeding and Butter (1980) have obtained selectivities to C_2-C_4 olefins of up to 70% using ZSM-5 modified by treatment with trimethyl phosphite $(POCH_3)_3$. Mobil has also used an aluminosilicate zeolite labelled ZSM-34 to obtain high yields of C_2-C_4 olefins (Givens et al., 1978a; 1978b).

Yields of ethylene from methanol via these routes are constantly being improved and research will likely eventually lead to reliable catalytic processes possibly yielding over 70% yields of C_2-C_4 olefins from methanol (Hu, 1983). BASF is now operating a 15 ton/month pilot plant to produce olefins from methanol using a shape selective catalyst.

The Mobil (MTG) process, using a fixed bed reactor, produces about 39% of aromatics which helps to account for the high octane rating of the MTG gasoline. Aromatization of light olefins takes place in the strongly acidic media provided by the HZSM-5 catalyst. This is a type of conjunct polymerization wherein a condensation of an olefin with a carbenium ion is followed by a dehydrocyclization reaction to form benzene and methylated benzenes. This oligomerization of C_2-C_5 olefins takes place at zeolite channel intersections, where the stronger acid sites are found. It is logical, then, to expect that higher aromatic yields would be obtained with silica-alumina zeolites containing higher aluminum contents (Ione et al., 1984). Aromatic yields of about 65% have been claimed by Chang and Lang (1979; 1980). They used a methanol synthesis catalyst with a high (4:1) Zn to Cr ratio and a ZSM-5 zeolite catalyst.

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