Methanol, Past, Present, and Speculation on the Future

Methanol is overviewed from the standpoint of history: how the history relates to the present and how it could relate to the future. The overview includes ingredients (fuels, catalysts, etc.), synthesis gas generating procedures, processing techniques, and equipment and other considerations for the present and the near and more distant term future.

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SCOPE

The objective herein is to bring into a relatively abbreviated review form the story of methanol. Methanol has been manufactured by crude methods, such as destructive distillation of wood, and by sophisticated methods, consisting of the catalytic conversion of synthesis gases. The methods of deriving these gases, their purification and compression and the catalyst types, competitive reactions, specificity of the preferred catalysts, and purification of the product are included. Reactor types and synthesis conditions are also included. Product specifications, physical data, kinetics, and present and future uses are also presented.

Methanol is relatively easily synthesized once one has the synthesis gases. It consequently may be a major liquid fuel for internal combustion engines and as a clean burning fuel for turbines and even for an electric generating station based on steam.

Areas of future research and development are mentioned as imperative subjects, presuming methanol attains the status of a major liquid fuel.

CONCLUSIONS AND SIGNIFICANCE

Because methanol can be easily derived from basic building blocks carbon monoxide, carbon dioxide, and hydrogen, it is an attractive chemical for growth not only for increased application in the chemical industry but also in even greater volume as a liquid fuel for broad application. A review of the history and status is timely because of the implications of orders of magnitude growth in manufacture and use of this basic chemical.

Methanol synthesis is as old as wood fires; the earliest man-made methanol, at least on our instantaneous basis, must be ascribed to Adam and Eve if they burned wood to heat their home or to prepare their meals. Methanol is commonly referred to as wood alcohol because of its early commercial origin; that is, it was derived as a condensible by-product of the charcoal industry, charcoal being required in early ore smelters. In view of the present large synthetic methanol capacity it may seem anachronistic, but it is nonetheless true that the methanol required in World War I was derived from charcoal furnaces as a coproduct along with acetone and other chemicals from wood devolatilization and charing (destructive distillation).

Wood alcohol was first identified by Boyle in 1661, but it was not until 1812 that the difference between methyl and ethyl alcohols was discovered. If one reads some of the earlier references (about 1930), the differences were still considered minor, and wood alcohol was described as producing intoxication similar to that of ethyl alcohol. However, the major difference in toxicity between the two and the severe adverse physiological effects of inhaling or imbibing methanol is now well established (Bernstein and Sudborough, 1931; Manufacturing Chemists Association, 1970). Before about 1930, much of the toxicity of methanol was attributed to the large number of high concentration impurities in the product derived from the destructive distillation of wood and remaining after the refinement of pyroligneous acid, the condensate from the destructive distillation operation. The pyroligneous acid condensate contained, in addition to the methanol, other components such as acetic acid, acetone, methyl acetate, allyl alcohol, naphthalene, phenol, and guaiccols. The refining was difficult, and highly toxic materials tended to remain in the refined product. The crude product from modern methanol synthesis plants is probably much purer than the previously identified refined wood alcohol, and modern refined synthetic methanol is one of the purest of bulk chemicals.

SYNTHETIC METHANOL

It is possible both chemically and thermodynamically to produce methanol from carbon monoxide and hydrogen according to

$$CO + 2H_2 = CH_3OH \; \Delta H_R = -113 \times 10^3 J$$

This process was shown to be feasible by Mittasch and Schneider (1913), and German Patent 295787 (1913) was granted to Badische Anilin-und Soda Fabrik based on their work for the process, which simultaneously produced significant quantities of higher alcohols and saturated and and unsaturated hydrocarbons.

Modern methanol plants produce a crude methanol which is better than 97% methanol, considerably purer than that obtained by the original BAFS process. That this is a significant achievement in catalyst specificity is illustrated by the following reactions for well-established (by research if not by industrial application) processes for the conversion of carbon monoxide and hydrogen with or without carbon dioxide to various products:

1. $CO + 2H_2 \rightarrow CH_3OH$
2. $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$
3. $CO + 3H_2 \rightarrow CH_4 + H_2O$
4. $nCO + 2nH_2 \rightarrow$ Methanol and higher alcohols + H_2O
5. $nCO + 2nH_2 \rightarrow$ Straight chain hydrocarbons, methane, olefins, methanol, higher alcohols, waxes, oxygenated hydrocarbons + H_2O
6. $nCO + 2nH_2 \rightarrow$ Long, straight chain paraffins + H_2O
7. $nCO + 2nH_2 \rightarrow$ Long straight chain alcohols + H_2O
8. $nCO + 2nH_2 \rightarrow HOCH_2{-}CH_2OH + CH_3OH$ + other products + H_2O
9. $CO + H_2 \rightarrow HCHO$

The standard free energy change for higher hydrocarbon formation is zero between 380° and 460°C, with the temperature increasing with decreasing carbon chain length. Higher temperatures result in positive standard free energy changes. The free energy change for methane formation (reaction 3) is about 15 kcal/mole lower than that for ethane formation and becomes zero at about 620°C. The free energy change for alcohols formation is zero for 280° to 350°C; the temperature increases with increasing chain length. The standard free energy change is zero at a temperature considerably below 300°C and is positive for higher temperatures. Thus, in the hierarchy of products obtainable from $CO + H_2$ methane is thermodynamically the most favored; longer chain hydrocarbons are next followed by higher molecular weight alcohols and finally methanol. Thus, methanol production is entirely dependent on catalyst selectivity characteristics, since it is thermodynamically the least stable product which can be formed. In all cases high pressure favors increased equilibrium conversion because of the decrease in the number of moles upon reaction.

Reaction 1 is conducted with a mixed oxide catalyst usually consisting of zinc, copper, chromium, and alumina in varying ratios. Reaction 2 employs the same type of catalyst. Reaction 3 is carried out with a nickel catalyst ordinarily but may be performed with ruthenium or other of the iron and precious metals groups. Reaction of 4 is carried out with a catalyst similar to that used for methanol synthesis but with the addition of alkali and/or manganese. The fifth reaction is conducted with an iron or cobalt catalyst and is designated the Fischer-Tropsch reaction. Reactions 6 and 7 are with a ruthenium catalyst; at high pressures very high molecular weight linear products (23 000 mole wt at 1 000 atm) can be obtained. The eighth reaction is conducted at pressures above 2 000 atm with a Rh catalyst. The ninth reaction is reported by Berkman, Morrell, and Egloff (1940), but if the reaction, reportedly conducted over a copper catalyst, were ever actually observed, it has not attained commercial importance. This would certainly be a very economical route to formaldehyde; formaldehyde is probably thermodynamically less stable than methanol.

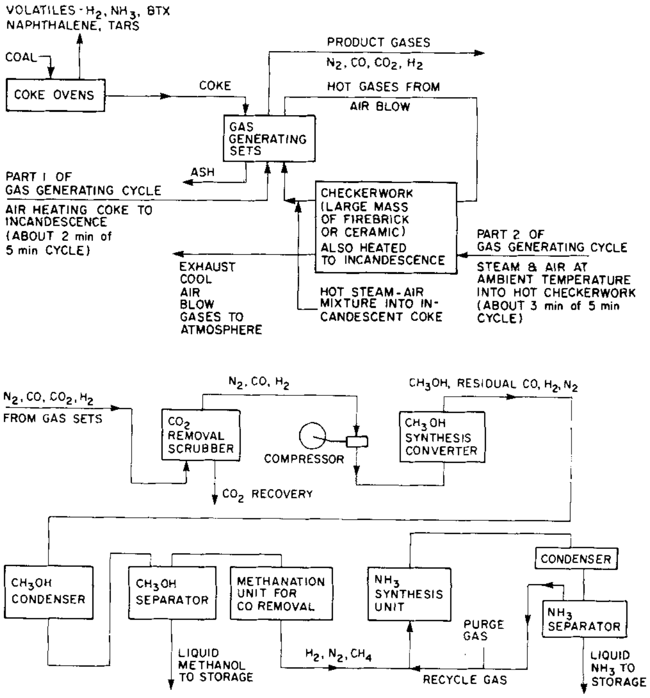


Fig. 1. Flow sheet for a plant sequentially making methanol then ammonia from carbon monoxide, nitrogen, hydrogen derived from coal, vintage 1920's.

Because of the vast array of primary products which can be obtained from carbon monoxide, carbon dioxide, and hydrogen, and because most are thermodynamically more stable than methanol, specific catalysts for methanol synthesis must be of carefully selected composition (and manufacturing procedure) and also must be free of contamination. The nine listed reactions are usually conducted under conditions of temperature and pressure which are not so different from those for methanol synthesis as to avoid completely other products if the catalysts are intermixed or contaminated.

EARLY HISTORICAL FACTORS AS THEY RELATE TO THE PRESENT

It is frequently desirable to look at the historical background of a process to see why the present operating conditions have been selected, but it is also important to look at these factors because there may be reasons for again adopting or adapting these early conditions. It is the purpose of this section to review briefly the historical base of methanol production as it may relate to present or future processing. For example, the earliest synthetic methanol was synthesized from carbon monoxide, carbon dioxide, and hydrogen which were derived from coal by the water-gas reaction. Our approaching increased dependence on domestically produced coal as a source of organic building blocks makes a review of this old coal technology a necessity. Other examples will follow as we proceed with this section.

From the earliest days of methanol and ammonia synthesis, the interrelationship between adjacent ammonia and methanol plants was evident. In some of the very earliest methanol plants, the synthesis gas was most con-

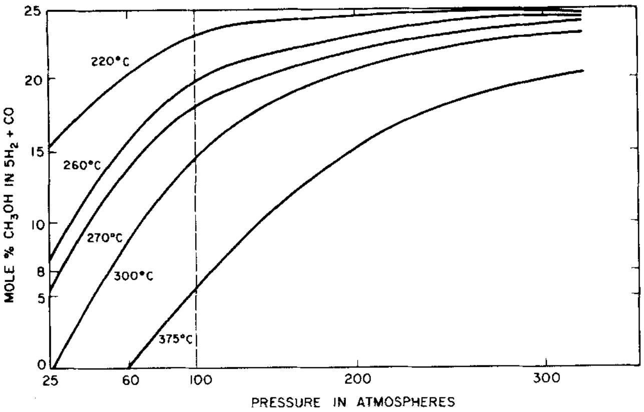


Fig. 2. Temperature—pressure relationships for methanol equilibrium for methanol in a 16.6% carbon monoxide in 83.4% hydrogen mixture.

veniently and economically produced as a carbon monoxide, carbon dioxide, hydrogen, and nitrogen mixture. This gas was produced in gas sets in which coal or coke, preferably the latter, was first heated to incandescence in a converter; then steam or steam plus air was passed over the incandescent coke to produce the aforementioned gases. This gas contained ash as well as sulfur compounds and other contaminants.

The purification procedure consisted of removal of the ash by scrubbing with water and removal of the sulfur compounds by scrubbing with alkaline solutions. Some or all of the carbon dioxide was simultaneously removed with the sulfur compounds.

In this combination process shown in Figure 1, the cleaned gas containing carbon monoxide, hydrogen, and nitrogen was first compressed to operating conditions which could have been as high as $81 \times 10^6 N/m^2$ and was then passed over a methanol synthesis catalyst to remove the carbon monoxide and a part of the hydrogen so that the gas effluent which then passed into the ammonia converter would have the proper 1:3 ratio of nitrogen: hydrogen. The methanol was condensed from the gas stream before it passed into the ammonia converter, and any residual carbon monoxide was removed from the nitrogen-hydrogen stream by methanation ($CO + 3H_2 \rightarrow CH + H_2O$). The pure ammonia synthesis gas was passed over the ammonia synthesis catalyst in a downstream converter. There were many problems with this type of operation some relating to the seasonal nature of the sales demand for both methanol, used largely as antifreeze at this time, and ammonia, used as a fertilizer. These demands unfortunately were out of phase by almost 6 months so that large storage facilities were required. The seasonal nature of product demand resulted in the development of procedures and equipment which could be used interchangeably for the two operations.

When methanol is synthesized from synthesis gas containing nitrogen (nitrogen is almost always present), there is always the simultaneous synthesis of organic amines. These are objectionable because they give an objectionable basic property to the methanol and cause an offensive odor. Refining costs are consequently increased, and thus the nitrogen level is ordinarily minimized or compensated for by selection of the proper catalyst and/or operating conditions. Synthesis of amines was intentionally sought in some of the Fischer-Tropsch operations and was augmented by the addition of ammonia to the feed gas to the Fischer-Tropsch reactor.

In the earlier converters and operating conditions, both the pressures and temperatures were much higher than at present. The accompanying temperature-pressure relationship chart (Figure 2) shows that as the temperature is increased, the pressure must also be increased in order for there to be a reasonable amount of methanol synthesized at equilibrium conditions. There were several reasons why the operations were conducted at high temperatures, and these were first that a poison resistant or at least tolerant catalyst was required. These usually contained chromium oxide as a component and were as a result somewhat less active than in the absence of chromium. (They were designated chromites.) Furthermore, the synthesis gas contained sulfur compounds, sublimed solids, mist, and other chemical and physical poisons, interfering factors which dictated that temperatures used in the environment of the catalyst be in the 350 to 450 deg. range.

These high temperatures and pressures necessitated specialized equipment which could be fabricated only by those who had experience in and facilities for munitions manufacture. This resulted in alloys and design often showing the common parentage with the munitions of that period between WW I and WW II. Since then, specific fabrication techniques have been developed which have made it possible to fabricate the larger size converters and interconnecting piping and the more easily assembled and disassembled facilities now required.

These earlier facilities were also plagued by corrosion due to the sulfur compounds, to carbon dioxide (as carbonic acid solution), or to hydrogen embrittlement, or to iron carbonyl formation from the high pressure-low temperature carbon monoxide containing gases. These problems were for the most part solved, but the iron carbonyl problem remains and seems to defy an economic solution.

MODERN METHANOL SYNTHESIS

Synthesis Gas Preparation

This phase of methanol synthesis is presently the most in need of major innovations and developments. As natural gas and liquid hydrocarbons become more costly and less abundant, the less easily processed sources of carbon must be used. These will be discussed later, but first to be considered will be the sources which have been historically important, next the ones most widely utilized presently, and finally speculation as to the sources and processes of the future. There is much thought devoted presently to the use of methanol as a liquid fuel for automotive and other uses, so the possibility of huge methanol plants with attendent gas generation facilities looms large in the future.

As previously stated, methanol has been produced commercially as a coproduct since the 1920's, but the present preferred route to carbon monoxide, hydrogen, and carbon dioxide was not widely practiced until the 1940's. The earlier sources included fermentation by-product gases, (Commercial Solvents Corp.), coke oven by-product gas, and steel furnace off gases. The coke oven by-product gas is deficient in carbon monoxide and carbon containing molecules whereas the off gas from blast furnaces is high in carbon monoxide and deficient in hydrogen. These latter sources of hydrogen and carbon monoxide have been considered and to some extent used, but because of the many difficulties involved in their utilization, they both are of very minor importance presently. However, as the need intensifies for complete conservation of our energy resources, they may in the future be utilized rather than burned as is almost universally the present case.

The preparation of carbon monoxide and hydrogen from coke or coal by the blue-gas and blow-run gas techniques has previously been mentioned. This process was used by E. I. duPont de Nemours at the Belle, West Virginia plant when the plant was first placed in operation in the late 20's and continued as the source of synthesis gases for both methanol and ammonia until the late 40's. The procedure used and a diagram of the facilities are shown in Figure 3. In addition to the gas sets which were used for the gas generation, a complete set of coke ovens was also required for the conversion of the coal to coke. At one time the conversion of coal directly to synthesis gases was the basic procedure, but because of difficulties with compounds being volatilized from the coal which later condensed in the gas lines to plug them, the procedure was altered to using coke which avoided these problems. The duPont Company at that time advertised that the products of the plant were from coal, air, and water, which is something we find many people presently speculating about without realizing that this had as a matter of fact been an industrial process in the 20's. It could hardly be considered a viable process of the present, but there are certain features of the operation and process which present interesting backgrounds which we certainly must assess in the present light of needs to derive fuels and chemicals from domestically available fossil energy.

The procedure which is most frequently used for the generation of synthesis gases for methanol, hydrogen, and ammonia is shown in Figure 4. It is steam-hydrocarbon reforming, with the hydrocarbon being most frequently natural gas, and usually natural gas from which all components except methane and nitrogen have been almost completely removed. The steam-hydrocarbon reforming process is very highly developed and will operate for months or even years without interruption, except for normal outages scheduled for boiler inspection, routine maintenance, and other attention which is placed on a definable schedule. The heat balance and utilization are well engineered ordinarily so that there is little waste, and what heat is unused on the furnace side of the reformer is subsequently recovered for use to generate steam for an ingredient in the inlet gas mixture or for other operations such as methanol refining or driving compressors.

The basic procedure and equation is:

$$CH_4 + H_2O = 3H_2 + CO$$

but for methanol synthesis the following relationship between the hydrogen and carbon monoxide is necessary:

$$2H_2 + CO = CH_3OH$$

Therefore, the following simultaneous operation is performed in the reformer by adding carbon dioxide into the feed gas:

$$CO_2 + CH_4 = 2CO + 2H_2 + H_2O$$

The latter reaction, of course, produces excess carbon monoxide relative to that needed for methanol, and as a consequence, in practice, the feed to a reformer comprises natural gas, steam, and carbon dioxide. Because the conversion of the carbon of both the methane and carbon dioxide involves an equilibrium relationship relative to the steam and temperature environment, the steam, methane, and carbon dioxide are mixed in a ratio which will be satisfactory from the standpoint of carbon monoxide plus carbon dioxide to hydrogen ratio in the product gas. The steam ratio and temperatures must also be considered from the viewpoint of carbon (soot) deposition in the reformer equipment and disintegration of the catalyst used for the reforming operation.

The steam-carbon dioxide-hydrocarbon conversion is conducted over a catalyst such as nickel (oxide) on alumina. This type of catalyst can be purchased in quite similar composition from a number of catalyst vendors who have some variations in manufacturing procedure or composition which are purportedly of advantage in life, avoiding carbon deposition, avoiding disintegration, giving more rapid approach to equilibrium (which means, in simple terms, that it is more active), and freedom from components which volatilize or sublime from the catalyst and condense downstream in heat exchange equipment or in other facilities or in or on catalyst where the damage can be very severe.

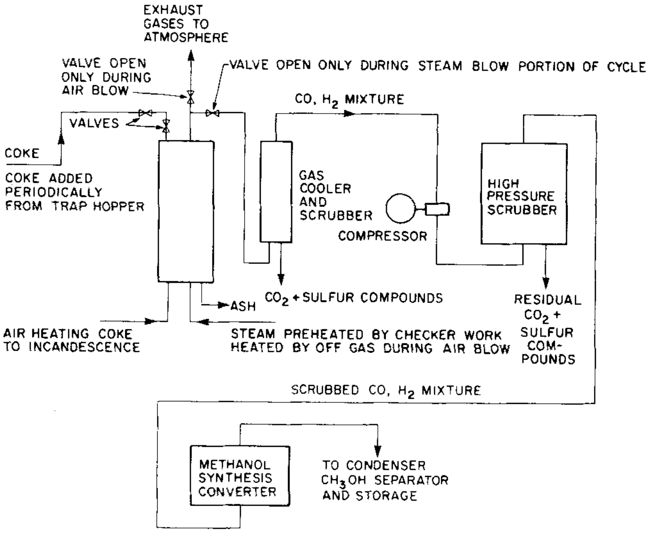


Fig. 3. Flow sheet for a plant producing methanol from carbon monoxide, hydrogen mixtures derived from coke by the old blue gas process.

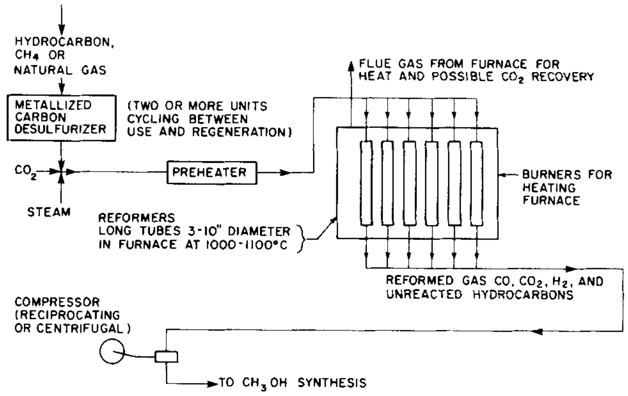


Fig. 4. Flow sheet for a plant producing methanol from carbon monoxide and hydrogen derived from the steam-hydrocarbon reforming process.

Referring again to Figure 4, one can see that the reactor in which the steam-hydrocarbon reaction is performed is multitubular and that the tubes are very long with respect to diameter. Several very important observations should be made at this time. First is that because of the length of the tubes, the gases must pass through a relatively great depth of catalyst producing costly pressure drop. Furthermore, the operation is most economical when performed at elevated pressure, which puts an added load on the design of the tubes which must be resistant not only to pressures up to 600 lb/in.^{2} but also to temperatures which in the furnace side of the tubes may be 1 050° to almost 1 100°C. This severe service requires high alloy tubes which are not only fabricated from expensive alloys but also are difficult to fabricate.

Other disadvantages must be pointed out such as the fact that in addition to the process gas requirements, there is a requirement for fuel gas or heating gas for the furnace side of the tubes which is as much as one volume of heating gas for each volume of process natural gas (methane). Additionally, as previously indicated, there is need for the providing of additional carbon source (carbon dioxide ordinarily) as feed to the reformer. This carbon dioxide may be derived from the furnace side of the reformers by suitable scrubbing and recovery procedures; if a source of discharge carbon dioxide is available from a companion operation (ammonia synthesis or hydrogen generation), then the carbon dioxide can be obtained from either of these sources. It was previously stated that methanol and ammonia syntheses are, in certain respects, ideal companion operations. The generation of hydrogen is similarly compatible because the carbon from the methane must be removed, usually by scrubbing, from the hydrogen stream before use in most hydrogenations. This makes the carbon dioxide available as a concentrated stream usually at elevated pressure.

HYDROCARBON PARTIAL COMBUSTION

Throughout the past decade or two there have been several shifts to and from steam-hydrocarbon reforming vs. hydrocarbon partial combustion as the more economical procedure for synthesis gas generation. The advantages and disadvantages of the steam-hydrocarbon process have been previously described. This section will deal with gaseous and liquid hydrocarbon partial combustion to synthesis gases. The equation for the reaction is as follows:

$$H_2O + C_nH_{2n+2} + O_2 \rightarrow H_2 + CO + CO_2 + H_2O \text{ (Exothermal)}$$

The ratio of ingredients in the feed, that is, water, hydrocarbon, and oxygen, is adjusted so that the desired ratio of carbon monoxide plus carbon dioxide and hydrogen are obtained in the effluent gas. The temperature and pressure, of course, influence this ratio so that all of these factors must be considered when the feed gas ratios are established.

The equipment used for hydrocarbon partial combustion is shown in Figure 5, and it is evident from this schematic presentation that the complex tubular reactor and furnace system of the steam-hydrocarbon process are avoided. Not shown but of extreme importance is that the reaction is performed at a much higher temperature and pressure than is possible in the tubular reactor of the steam-hydrocarbon scheme. The simplification and the higher pressure and temperature possibilities are of substantial economic benefit in the investment and reaction considerations. However, there is one very severe economic drawback, and that is that a source of oxygen must be provided, and this axiomatically means an air liquefication plant. This entails additional substantial investment and operation costs which may more than compensate for other investment and complexity advantages inherent in the partial combustion method.

At the time of this writing (late 1976), the issue is not clear because of the escalating prices and uncertainty over natural gas availability (almost double the gas is required for a steam-hydrocarbon operation than is required for the partial combustion unit) and, on the other hand, for the electric or steam power required for a liquefication plant. Furthermore, high interest rates may make the oxygen plant investment unattractive so the comparison must be made with current conditions in mind and a very clear and accurate crystal ball.

Usually the need for additional carbon dioxide can be avoided as a component to the partial combustion feed, so this investment is avoided and because of the exothermicity of the reaction, there is surplus heat which can be recovered for steam and ultimately electricity generation.

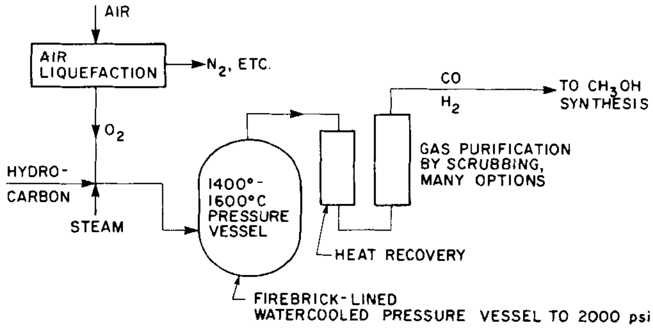


Fig. 5. Flow sheet for a plant producing carbon monoxide and hydrogen by the hydrocarbon partial combustion process.

It is evident in the equation for the partial combustion process that the types of suitable hydrocarbons were made more general than is true of the methane and lighter hydrocarbons used in the steam-hydrocarbon process. The purpose of this differentiation is to demonstrate the greater flexibility for usable carbon sources of the partial combustion system vs. the steam hydrocarbon system. I will hasten to add before critics point out that hydrocarbons higher than methane are regularly processed in the steam-hydrocarbon system that indeed this is true, but the flexibility of the steam-hydrocarbon system is substantially less in that the partial combustion system can handle heavy, even tarry hydrocarbons, but even more importantly, even coal and solid combustibles and fuel high in sulfur and ash. It is this latter solids partial combustion system that will be next described; it offers one of the most hopeful processes whereby coal can be utilized. It is not implied that such a scheme is on the shelf ready for use, but there has been much work, albeit about 20 yrs. old, which can be drawn on for background and for consideration of improvements. The basic system is shown in Figure 6.

In addition to the disadvantage of the requirement for an oxygen plant, in the coal partial combustion process there is the problem of erosion or corrosion of the refractory which must be designed against. Furthermore, there is the problem of removal of ash from the reactor effluent which, of course, means an added cost. It should be noted, however, that there is no catalyst requirement for the partial combustion scheme, so the effect of sulfur, ash halides, and other factors are avoided which so markedly adversely affect the steam-hydrocarbon procedure. The added flexibility of the partial combustion system is further demonstrated by the fact that it should be suitable for the use of such sources of carbon as wood or other vegetable scraps, waste paper, specific crops of brush, grasses, leaves, stocks, and the like. By-products from the timber, paper, and agricultural industries (corn stalks, wheat straw, sugar cane, etc.) should be usable. These, of course, represent a renewable resource, and these may ultimately be the carbon sources we or our progeny must rely upon.

OTHER SOURCES OF SYNTHESIS GASES

A few additional sources will be mentioned despite the fact that they will require much effort and development before they become applicable.

First is underground gasification of coal as is currently being investigated by ERDA at Hanna near Laramie, Wyoming. The procedure is similar to but more advanced than procedures used elsewhere previously in the United States and also in the USSR. The gases presently derived include hydrogen, carbon monoxide, and carbon dioxide together with high concentrations of nitrogen. The latter is owing to the use of air as the source of oxygen, whereas if pure oxygen together with steam or recycled carbon dioxide were used, the product gas would be higher in hydrogen and carbon oxides and lower in inerts.

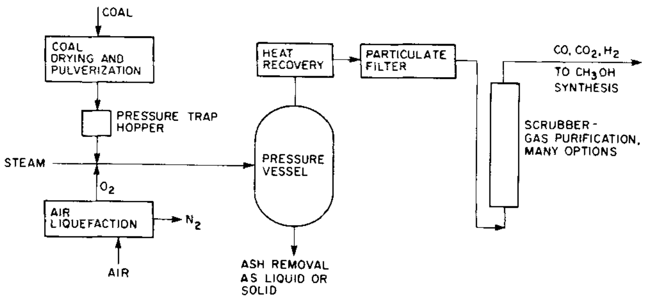


Fig. 6. Flow sheet for a plant producing carbon monoxide, carbon dioxide, and hydrogen by the solid carbonaceous (coal) partial combustion process.

There is simultaneously produced with the gas effluent from the underground partial oxidation a condensible liquid having a composition resembling the liquids derived from destructive distillation of coal. This side benefit presents an interesting possibility of deriving in one operation the highly desirable aromatic fraction of coal together with the excellent building blocks, carbon monoxide, carbon dioxide, and hydrogen (and nitrogen if wanted) in one single and potentially comparatively simple and inexpensive operation. The bringing of this procedure to successful fruition is probably not close at hand, but the potential is so great that the effort and cost are certainly justifiable in view of the potential for relatively simple lower cost conversion of coal to useful liquid and gaseous products.

A last procedure to be mentioned for synthesis gas preparation is through the roasting of limestone to produce carbon dioxide and the electrolysis of water to produce hydrogen. These procedures would come into play only when energy is comparatively inexpensive (let's speculate on atomic fusion) and organic or fossil sources of carbon are exhausted or insufficient. When this occurs, energy must be almost profligately expendable otherwise adjustments must be made to a less abundant life for the world's inhabitants. We have no time to waste in preparing for this eventuality.

GAS PURIFICATION

Two statements have been made previously which should be reiterated at this time. The first was that in earlier installations of methanol synthesis plants, there was little gas purification of the scale and effectiveness that is presently used, and as a result the catalysts or operating conditions that were used were necessarily more rugged and severe than is presently the case. In other words, the fact that recent methanol installations operate under milder temperature and pressure conditions is attributable not only to improved catalysts but also to the fact that the synthesis gases presently employed have been detoxified to the extent that catalysts that have long been known are now practicable.

The second comment is that gas purification can be performed either prior to the conversion of the feed stock to synthesis gas or afterward. In the case in which the feed stock is processed over a catalyst as in steam-hydrocarbon reforming, it is essential that the gas be purified, at least to some extent, prior to its passage over the reforming catalyst, particularly if the catalyst is of the typical composition of supported and promoted nickel (oxide). By contrast, if the synthesis gas is produced by partial combustion, no catalyst is used in this step so the purification prior to partial oxidation is unnecessary. As a result, depending on the process used for its generation, synthesis gas is purified by various procedures later to be described.

If we first consider the synthesis gas process now most frequently used, that is, steam hydrocarbon reforming, the methane (natural gas) is usually detoxified using an adsorbent such as carbon on which is impregnated suitable chemical adsorbents such as elemental iron or copper. These are shown as metallized carbon desulfurizer in the overall diagram (Figure 4). There are two of these in parallel, with one on the line while the other is being regenerated. Regeneration is effected by passing steam or steam plus a small amount of oxygen (parts per million range) over the adsorbent in such a way that the sulfur is removed as sulfur dioxide or hydrogen sulfide; heavy hydrocarbons simultaneously adsorbed by the carbon are removed as such to be flared, or if there is sufficient, to recover for sale or combustion to derive useful heat. If there are solids such as sodium chloride and its associated minerals entrained with the natural gas, obviously these impurities must be removed; water scrubbing can be used.

Steam used in the operation must be free of solids. This, too, seems like an obvious statement, but the entrainment of solids in the mist from boilers is not an infrequent cause of physically poisoning the reforming catalyst at least in the upper (upstream) part of the reformer tubes.

It may seem anomalous that hydrocarbons themselves can be troublesome, but this fact arises from two causes both resulting in carbon depositions. First, the steam-to-carbon ratio must be kept above an experience range, and second, unplanned for higher hydrocarbons must be avoided because higher hydrocarbons are more susceptible to dehydrogenation (cracking, causing carbon deposition) than are the lower ones such as methane, ethane, and even propane.

If, for some reason, the natural gas has a surge in higher hydrocarbon content, the effect can be disastrous in that the nickel catalyst will quickly become coated with a sooty carbon, which quickly deactivates it. A second result is that the carbon may be deposited interstitially in the catalyst body causing it to disintegrate to powder, which of course stops flow through the tube. This can have the immediate effect of eliminating the endothermal reaction in the tube, which is relied upon to keep the tube walls well below the furnace temperature (850°C vs. 1 050° to 1 100°C). If the tube metal is permitted to reach this higher temperature and remain under elevated pressure, there may be a distortion of the tube or even rupture.

It is essential that adequate monitoring of the natural gas be conducted so that compensating action can be taken. This compensating action may be more frequent regeneration of the desulfurization drums (which should be also thought of as scavengers for higher boiling hydrocarbons) or increasing the steam-to-gas ratio, increasing the firing temperature of the tubes, particularly at the inlet part of the tubes, or, last, a complete shutdown of the reformer until the natural gas composition returns to normal.

When naphtha is used instead of natural gas, the problems are similar but more severe, and proper modifications are made in the catalyst to make it resistant to severe poisoning and carbon deposition conditions. These catalysts usually contain lower amounts of nickel and may contain such promoters as uranium, potassium, or other alkali or alkaline earth oxides. Inasmuch as it was previously pointed out that alkali metal oxides migrate from the catalyst at higher temperatures and pressures, it is necessary to operate the naphtha reformers at milder conditions than when natural gas is the feed. In such cases, it may be desirable to operate two reformers, one for the conversion of naphtha to lighter hydrocarbons, following this with a converter designed and operated more like the natural gas reformer previously described.

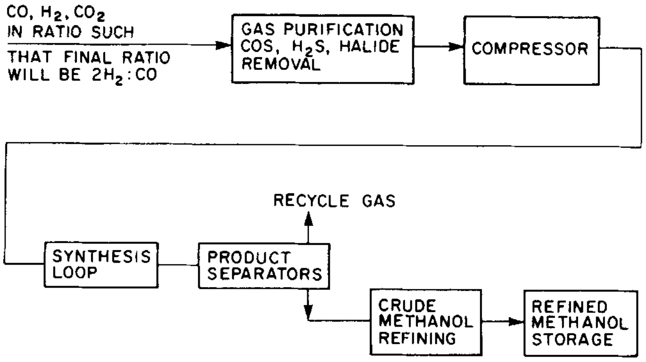


Fig. 7. Flow sheet for the synthesis of methanol from carbon monoxide, carbon dioxide, and hydrogen derived from any of foregoing generating processes.

Gas purification, in the case of hydrocarbon partial combustion, is effected after the conversion of the hydrocarbon or other carbon source to synthesis gas. The usual impurities (after the partial combustion) are less varied than is the case of the natural gas which may contain sulfur in several forms other than the typical hydrogen sulfide, mercaptans, and CS_2. By contrast, in the partial combustion systems, all of the sulfur compounds in the feed, whether natural gas or other ingredient, will be converted almost 100% to hydrogen sulfide with only traces of COS and CS_2. These can very readily be removed by scrubbing with water under pressure or even more efficiently with an alkaline solution such as ethanol amines or potassium carbonate.

These solutions are also effective for the removal of carbon dioxide, and when it is desired to have a carbon dioxide free synthesis gas, the carbon dioxide and sulfur compounds can simultaneously be removed. If sufficient sulfur compounds are present, the sulfur can be recovered as elemental sulfur or can be oxidized to sulfur dioxide and then to sulfur trioxide for sulfuric acid synthesis. It accordingly becomes apparent that a sulfur containing feed may be a boon in such a synthesis and with such a feed if the geography-economics are favorable, that is, for the sale of the sulfuric acid within economical delivery distances.

The carbon dioxide could be recycled if needed for the proper hydrogen:carbon monoxide balance, but usually, in the partial combustion units, more than adequate carbon oxides are produced normally and any excess carbon dioxide can be used for urea or carbon dioxide sales.

If there are ash or other solids in the gas stream, these should be removed with a separate water wash to prevent fouling the scrubbing liquid used for the carbon dioxide and sulfur compound removal. Inasmuch as any scrubbing must be performed at a relatively low temperature, the heat content of the gases following the partial combustion unit must be conserved by exchange to incoming gases or recovered in a waste heat boiler. This means additional investment and because the volumes of gases are greater than before conversion to synthesis gases, the investment is likely to be higher than for the removal procedure utilized in the steam-hydrocarbon reforming process. To compensate, however, for this added cost, the efficacy of scrubbing at the carbon monoxide plus hydrogen stage is usually such as to produce a purer gas stream having advantages in catalyst and equipment utility.

Gas purification following partial combustion is even more complex than that employed for the gases effluent to the naphtha type of reformers which are in turn more complex than when natural gas or LPG's are used. Because there may be orders of magnitude more ash in the effluent, special scrubbing or cyclone facilities may be necessary. Additionally, it may be necessary to utilize bag filters or other filtration means for adequate cleanup. Avoidance of carryover to the downstream operations is absolutely essential. This statement becomes axiomatic when one considers that downstream there may be compression equipment with close clearance tolerances, turbines with blades which would erode, or catalysts which would quickly become coated and inoperative.

In the partial combustion procedure for synthesis gas preparation, there may be additional poisons or problems introduced by nitrogen oxides or ammonia being synthesized in very small equilibrium quantities (parts per million or parts per billion) which cause corrosion or other problems downstream (ammonia + carbon dioxide = carbonate solids).

A final consideration is now given to the purification of gases to be used in bench scale or semiworks in which the hydrogen and carbon monoxide are derived from cylinder supplies. The poisons in the so-called pure cylinder hydrogen comprise the typical catalyst poisons of halide, sulfur, and lubricating oil. These impurities vary with the source of the hydrogen and with the type of equipment used for compression by the vendor of the cylinder gas. An entirely different problem and one that may be overlooked for the carbon monoxide is that it is capable of reacting with the iron cylinders to produce surprisingly large quantities of iron carbonyl which will decompose on or in the catalyst under test. The removal of the poisons in both cases is via chemisorbents such as zinc oxide and an alkali such as alkali earth or alkali metal oxide. The carbonyl can be removed with a low temperature (−60° to −120°C) activated carbon trap. Cylinder gases must not be considered pure gases, at least not pure enough for tests of methanol synthesis catalysts or operating conditions.

GAS COMPRESSION

Let us begin with a consideration of the compression of small quantities of gas required for bench or semiworks scale test facilities. These must produce pure gases at a constant pressure; the method of choice is a metal diaphragm pump with a reservoir of sufficient size to damp out pulsations. Pulsations can have adverse effects on the mechanical stability of the catalyst by causing abrasion of the surface of the catalyst particles; the pulsations of the catalyst cause slight movement of the particles which rub against and abrade each other. The result can be faulty data in that the catalyst is decreasing in volume and thus shorten life and lower productivity or by contrast it can increase activity by abrading away the surface which may otherwise be gradually poisoned and deactivated. A false indication of longevity may be obtained.

For plant installations, the older plants used the typical reciprocating compressors, usually of multistage design, so that the gas might enter one stage at 2.7×10^6 N/m^2, exit at 5.4×10^6 N/m^2, then enter another stage at this pressure and leave at 10.8×10^6 N/m^2, then a third or even fourth stage to approximately 20 or 60 $\times 10^6$ N/m^2. These were necessary when pressures above 13.5×10^6 N/m^2 were required, but they were fraught with problems to the catalyst downstream in that they caused pulsations with results described above but with the additional effect that the powdered catalyst emerged from the converter to contaminate the crude alcohol or to collect in interconnecting piping, heat exchangers, and circulating pump valves and cylinders.

Most modern plants of high capacity, that is, 450 × 10^3 kg/day or above, use centrifugal compressors. (A flow sheet for a modern methanol plant is shown in Figure 7.) These may be driven with steam generated from waste heat from the hydrocarbon-steam reformers or from heat derived from the gases effluent from the methanol synthesis converter. As mentioned above, there is a limit of maximum pressure that the centrifugal compressor may be capable of producing, but instead of the 13.5 × 10^6 N/m^2 formerly limiting, they are now designed for about 33.75 × 10^6 N/m^2. They are relatively free of the lubricating oil contamination problems mentioned for the reciprocating compressor, and also they avoid the pulsations and problems caused by pulsation. However, they have problems of their own as follows.

Primary in the objections is the relative nonflexibility of operation of the centrifugal compressor. They are designed for a certain capacity, and departures from this rate cause rapid drop in efficiency. Furthermore, they are designed for gas of certain density, which means that the composition cannot easily be changed, the inlet and exit pressures cannot be changed, and the temperature of the gas must be maintained relatively constant. Consequently, recycling the gas to accommodate the compressor to lower production demands whould require a means of cooling the gas that is being recycled. Despite these drawbacks, however, the centrifugal is presently the compressor of choice because of its high efficiency and other advantages mentioned above.

CONVERTER LOOP DESIGN

The converter loop is shown in Figure 8. Reference to this figure should indicate it to be self-explanatory, so no additional explanation will be given here. A photograph of a recently constructed methanol plant is shown in Figure 12.

CONVERTER DESIGNS

The two designs most frequently used for gas phase reaction are shown in Figures 9 and 10. Figure 9 shows the older scheme which involves heat exchange between the reaction zone and the incoming gases as well as heat exchange external to the reaction zone. Facilities permit cold gas bypassing the external heat exchanger.

The second design shows the scheme most frequently used presently in one of its many forms. The basic principle is for the reaction to be conducted in a multistage or multitray reactor, with cold gas being mixed with the reacted gases as they emerge from all of the trays except the last.

In all of these designs, the purpose is to attain as close to an isothermal reactor and reaction as possible. This is also aided by controlling the carbon monoxide content of the incoming gas and by effecting the reverse shift of carbon dioxide to carbon monoxide in the catalyst bed. In other words, by feeding to the converter a mixture of hydrogen, carbon monoixde, and carbon dioxide, the reverse shift of the carbon dioxide to carbon monoxide and water, being endothermal, will, if conducted in the same environment as the exothermal methanol reaction, compensate for some of the heat generated by the methanol reaction. It becomes obvious that the catalyst used for the methanol reaction must be equally effective for the carbon dioxide shift ($CO_2 + H_2 \rightleftarrows H_2O + CO$). As one skilled in the art of catalysis is well aware, this is not an easy condition to accomplish. However, some catalysts are reasonably effective, and a well-designed catalyst will effect the two reactions almost equally well at similar conditions of temperature and pressure.

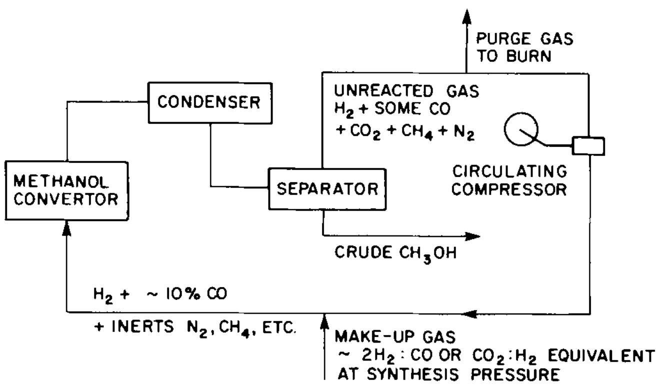


Fig. 8. Schematic diagram showing a typical methanol synthesis loop.

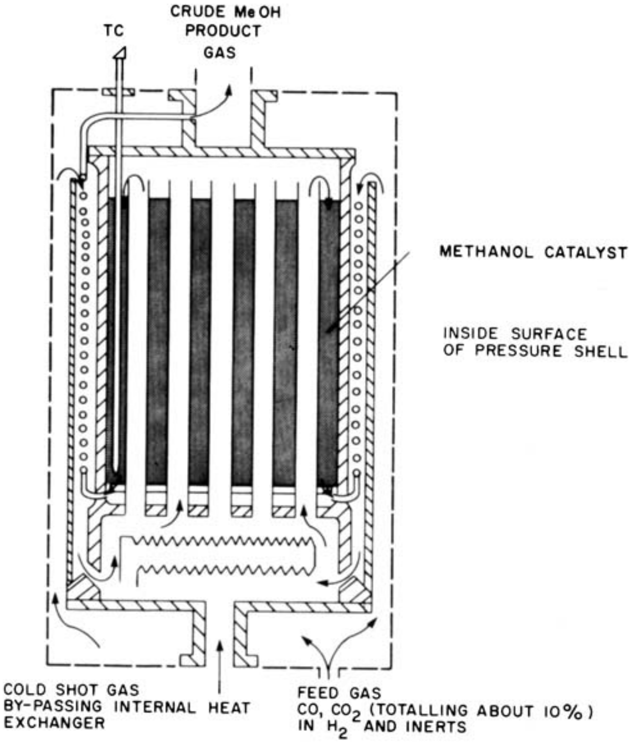


Fig. 9. Tubular type methanol synthesis converter.

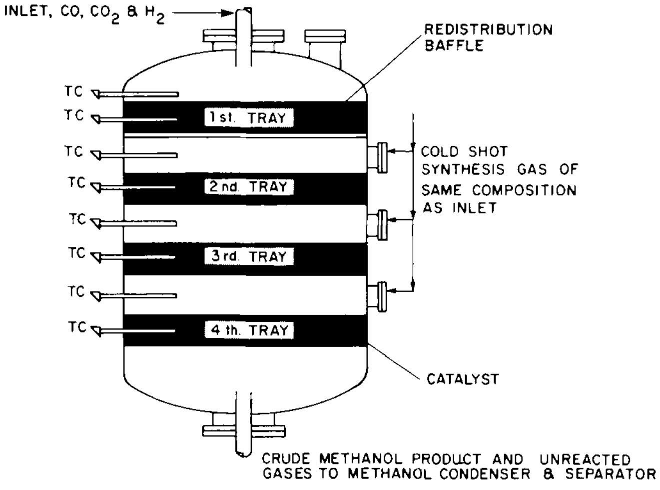


Fig. 10. Tray type of methanol synthesis converter.

There are two other converter designs that will be only mentioned but have found some application. The first is one in which the methanol reaction is conducted in a tubular reactor as shown in Figure 9, but instead of exchanging the heat to incoming gas, the tubes are cooled with water at sufficient pressure so that when it is at the boiling point, the reaction efficiency is at its maximum on the methanol synthesis side of the tubes. The steam generated can be used for process or distillation (crude methanol) applications.

Much research work and possibly some industrial application have been devoted to a procedure in which the methanol is synthesized at low pressures, 2×10^6 N/m^2 to 6.3×10^6 N/m^2 in liquid phase. The reaction is as follows:

$$CH_3OH + CO = HCOOCH_3$$

$$HCOOCH_3 + 2H_2 = 2CH_3OH$$

with the net being $2CO + 4H_2 = 2CH_3OH$, one of which is recycled. The reaction is really two steps, with the first being base catalyzed and the second a typical hydrogenolysis. The major problems associated with the scheme relate to maintaining the activity of the two types of catalyst without mutually being antagonistic. The basic catalyst usually is deactivated with carbon dioxide, water, or other acidic components in the feed stream.

One may reasonably ask why it is desirable to have an isothermal or nearly isothermal reaction environment. The answer probably is obvious, but it can be demonstrated or reinforced by reference to the many product possibilities from the two building blocks, carbon monoxide and hydrogen. To obtain the greatest specificity from a specific and efficient catalyst, the temperature and pressure conditions must be maintained in a specified and sometimes fairly narrow range. Otherwise, methane, dimethyl ether, and higher alcohols will be produced to reduce efficiency and present refining problems.

CHEMISTRY AND KINETICS OF METHANOL SYNTHESIS

The synthesis of methanol and its coproducts are very complex operations and reactions. Beginning with the accepted and known facts of methanol synthesis with the common zinc-chromite catalyst, the products from a reaction under the typical conditions of 10×10^6 N/m^2 to 33.3×10^6 N/m^2 at 300° to 400°C are as follows:

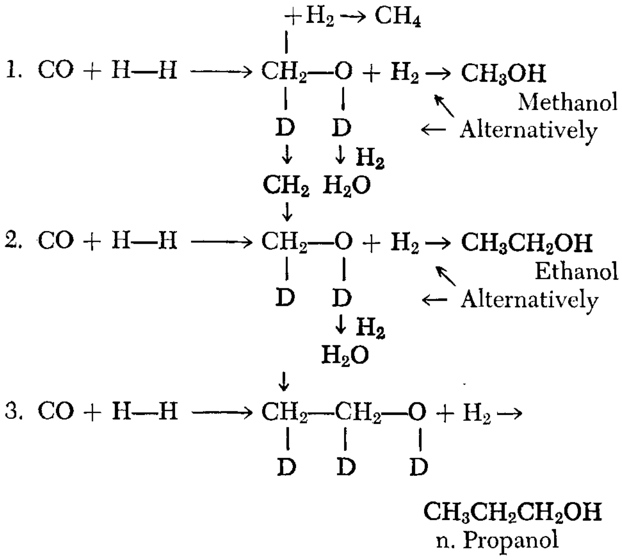
Methanol
Methane
Dimethyl ether
Ethanol
Propanol
Isobutanol
Hydrocarbons (cloud producers in aqueous dilution test)
Water
Traces of aldehydes and ketones

To explain these products, it is necessary to visualize that varied types of adsorption (sorption), reaction, and free radical or ion formation are occurring. I do not propose to offer any single type of mechanism which will reconcile with all of the reactions and products. There have been proposals that the carbon monoxide is adsorbed at a site and is hydrogenated to form formaldehyde which is further hydrogenated to methanol which is desorbed. For methane to be synthesized, it is more logical to visualize an intermediate formation of a methylene radical which is hydrogenated to methane or higher hydrocarbons with the methylene radical being incorporated into the chain via a mechanism similar to that proposed for polyethylene synthesis on the chrome-alumina heterogeneous catalyst system (or on the titanium-aluminum organohalide of the homogeneous system for polyethylene).

The ethanol and higher alcohols would be derived via the same route as the hydrocarbons, except that the methylene radical would be incorporated into the formaldehyde while loosely sorbed (in labile condition) on the catalyst surface. The methylene would be formed and sorbed loosely on a site adjacent to a formaldehyde sorbed species and would swing into the formaldehyde to produce acetaldehyde which would be immediately hydrogenated to ethanol which would desorb.

If it were in a position where it would remain loosely adsorbed as acetaldehyde and there were an adjacent methylene, the same mechanism could be used to explain the propanol. The isobutanol would require a more complex explanation such as a simultaneous sorption of two methylene radicals into a loosely sorbed acetaldehyde. In all of these reactions, water would be formed simultaneously with each methylene radical produced. Pure methanol would not produce any water, but inasmuch as there is always water (even when there is no carbon dioxide in the synthesis gas) in the crude methanol, the methylene intermediate is evidenced by this product. The fact that dimethyl ether is formed is most easily explained by the fact that two methanols are dehydrated during the desorption step at adjacent sites. This is circumstantially indicated by the fact that the proportion of dimethyl ether can be enhanced by incorporating dehydrating agents into the catalyst composition.

A diagram of the proposed schemes and mechanisms is as follows. (D is used for catalyst site instead of M because of my belief that the reaction site is a lattice deformity site rather than a metallic site.) The deformity site may be a metal, suboxide, or lattice nonconformity site. Perhaps there are combinations of each contributing to the different types of reactions required in the above or any other explanation of the chemistry.



$$\begin{array}{lcccl}
 & +H_2 \rightarrow CH_4 & & & \\
 & | & & & \\
1.\ CO + H{-}H \longrightarrow & CH_2 & {-}O & & + H_2 \rightarrow CH_3OH \\
 & | & | & & \nwarrow \quad \text{Methanol} \\
 & D & D & & \leftarrow \text{Alternatively} \\
 & \downarrow & \downarrow H_2 & & \\
 & CH_2 & H_2O & & \\
 & \downarrow & & & \\
2.\ CO + H{-}H \longrightarrow & CH_2 & {-}O & & + H_2 \rightarrow CH_3CH_2OH \\
 & | & | & & \nwarrow \quad \text{Ethanol} \\
 & D & D & & \leftarrow \text{Alternatively} \\
 & & \downarrow H_2 & & \\
 & & H_2O & & \\
 & \downarrow & & & \\
3.\ CO + H{-}H \longrightarrow & CH_2 & {-}CH_2 & {-}O & + H_2 \rightarrow \\
 & | & | & | & \\
 & D & D & D & \\
 & & & & CH_3CH_2CH_2OH \\
 & & & & \text{n. Propanol}
\end{array}$$

4. Isobutanol same as above with CH_2's at a triangular group of sites.

KINETICS

This phase of the discussion is probably the most difficult to get a handle on. The kinetics are influenced by the gas composition which varies constantly in a reactor, the catalyst shape, pore characteristics, age, sintering, internal depositions within the catalyst particle, temperature, pressure, and many other factors. Because of this, the following are presented as a compilation of data derived from several investigators melded in such a way that it will give a working arrangement, whereby another investigator can at least begin his work with the knowledge available which has been published and has become available in search and inquiry by this author.

The basic work was done by Natta. However, Natta did not include the presence of carbon dioxide, nor did he consider catalyst particles of the size used in heterogeneous systems of methanol synthesis. His rate equation is as follows:

$$R = \frac{f\text{CO}\, f^2_{\text{H}_2} - f\text{CH}_3\text{OH}/K_a}{(A + B_{f\text{CO}} + C_{f\text{H2}} + D_{f\text{CH3OH}})3}$$

where f_c = fugacity of component C, atmospheres. (These relationships were fitted to the data using the f/p correlations of Newton (1935). While more accurate f/p correlations are now available, Newton's relationship should be used to regenerate data using these equations.)

A, B, C, and D are temperature dependent parameters which are shown by Natta in graphical form. Some investigators have fitted these by the following:

$$A = 216.07 - 10^{[3.50192 - 1.292 \log 10(0.1T - 50)]}$$

$$B = A[10^{(-9.911 - 5\,180/T)}]$$

$$C = A[10^{(-13.942 - 7\,230/T)}]$$

$$D = A[10^{(-11.901 - 6\,780/T)}]$$

The tabulated references include two to Cappelli and Dente (1965) who incorporate the expression necessary to include the effect of carbon dioxide. The equation then becomes the following:

$$R = \frac{f_{\text{CO}} f^2_{\text{H}_2} - f_{\text{CH3OH}/K_a}}{A^3(1 + Bf_{\text{CO}} + Cf_{\text{H}_2} + Df_{\text{CH}_3\text{OH}} + Ef_{\text{CO}_2})^3}$$

where R = reaction rate, Kg × 10^{-3} CH_3OH/Kg × 10^{-3} catalyst/hr.

$$A = \frac{2.78 \times 10^{-5}}{S^{1/3}} \exp(-8\,280/RT) \quad (S = \text{specific catalyst surface})\ \text{m}^2/\text{g}$$

$$B = 1.33 \times 10^{-10} \exp(23\,850/RT) \quad f[=]\ 1.58987 \times 10^5\ \text{N/m}^2$$

$$C = 4.72 \times 10^{-14} \exp(30\,500/RT)$$

$$D = 5.05 \times 10^{-12} \exp(31\,250/RT)$$

$$E = 3.33 \times 10^{-10} \exp(23\,850/RT)$$

Even this equation is not complete in describing a plant operation because the effectiveness factor is not included. This factor is defined as follows:

$$\text{Eta}, \eta = \frac{\text{Reaction rate with pelletized catalyst}}{\text{Reaction rate with powdered catalyst}}$$

(not diffusion limited)

Pasquon and Dente have shown that η is in the range of 0.52 to 0.95 for methanol synthesis on a zinc oxide-chromic oxide catalyst. Thus, if the equation for R is modified by the factor η, then the equation becomes more meaningful, but still the effect of age and catalyst composition are not taken into account. Furthermore, the effect of changes in gas composition brought about by nitrogen, methane, and other diluents in the recycle gases and the effect of solids, lubricating oil, and decomposed carbonyls on and in the catalyst surface and pores are not taken into account here; they are believed to be small in most important applications. It is here that the author only points the direction and tells the future investigator that these are characteristics of his individual operation which must be considered and properly added to the kinetic factors. The questions are very complex, and experience factors alone may be the only way to obtain the answers.

CATALYST TYPES AND CHARACTERISTICS

The earliest methanol synthetically produced was a coproduct of what is similar to what we now refer to as the Fischer-Tropsch process. The transition was gradual over the years to the current procedure, whereby the principal product is methanol. The cause of the transition was that the methanol was a commercially viable product, whereas the majority of the coproducts were useful only as fuels; with the competition of very cheap petroleum products, the route to fuels via the carbon monoxide plus hydrogen route was uneconomical and as previously reported was practiced only in times of dire need such as in Germany during WW II. However, even in Germany, reliance for most of their fuel for their war machine was upon the Rumanian oil fields which were taken early as part of the strategy of self-sufficiency for Germany.

The early history of methanol finds the types of catalyst quite diverse and the inventors' names those of well-known early workers in the field. A few are tabulated below:

Catalyst	Inventor or assignee
Oxides of Ce, Cr, Mn, Mo, Ti, Zn or their mixtures together with alkali oxides	Badische Anilin-und-Soda Fabrik (Mittasch and Schneider) G.P. 293,787 (1913)
Ni, Cu, Ag, Fe Fe + Cs (Rb)	F. P. 540, 543 (1921) Fischer and Tropsch
$\text{CuO} + \text{Cr}_2\text{O}_3$ (ZnO, MnO) 2-10 $\text{ZnO} + \text{CrO}_3$ $\text{ZnO} + \text{Cr}_2\text{O}_3 + \text{Mn}_2\text{O}_3$ $\text{ZnO} + \text{Cr}_2\text{O}_3$	Badische Anilin-und-Soda Fabrik (Mittasch, Pier and Winkler) F.P. 571, 356 (1923) Also counterpart patents in Germany

The Mittasch, Pier, and Winkler compositions for the methanol catalyst are described as producing pure methanol. It is noteworthy that the catalyst sold commercially for most of the present methanol plants is made by one of these reactions, that is, the mixing of zinc oxide with chromium trioxide to obtain a reaction resulting in zinc chromate. The resultant chromate is pelleted and then reduced to zinc chromite either in situ or as a precharging operation. The reduced catalyst (all chromium reduced from 6 to 3 valence) becomes the catalyst. This is the present so-called high temperature, high pressure catalyst.

Through the years to the past five or ten, there were many other catalysts and names appearing such as Larson, Lazier, Frolich, Fenske, Cryder, Molstad, Dodge, Storch, Karpen, and many others. Companies which are prominently mentioned are, in addition to the above, British Celanese, Ltd., Companie de Bethune, Synthetic Ammonia and Nitrates, Ltd., Roessler and Hasslacher, Inc., duPont, I. G. Farbenindustrie A. -G., Commercial Solvents, Selden, Imperial Chemical Industries, Montecatini, and Ammonia Casale. Catalysts described include oxides and their mixtures such as those mentioned by Larson (1936) and prepared as fused, crushed, and sized granules. Magnesium, aluminum, zirconium, vanadium, titanium, thorium, and silicon as oxides are mixed as two or three component compositions which are described as being effective at pressures of 40.5 × 10^6 N/m² to 101.3 × 10^6 N/m² and at temperatures of 250° to 500°C. Earlier, Dodge (1933) described a catalyst comprising copper and zinc oxides precipitated from the nitrate salts using a solution of potassium or sodium carbonate as the precipitant. The desirability of having the precipitate as carbonate and the utility of the zinc oxide as stabilizer is pointed out. The catalyst is described as being effective at 10.6×10^6 N/m^2 and at temperatures as low as 200°C.

The Dodge catalyst appears to be the earliest of the so-called low temperature, low pressure catalysts which were later described more fully in the Davies and Snowden patent (1967) which disclosed a copper-zinc-chromium oxides catalyst precipitated from the nitrates with an alkali carbonate. This patent also pointed out the desirability of having carbon dioxide in the gas stream to prolong catalyst life apparently by minimizing poisoning by sulfur or other offenders. The chromium content is added presumably for the same purpose, although this is not taught in the Davies and Snowden patent but is taught in other sources. This catalyst art is the basis of the present low temperature, low pressure methanol plants being offered and engineered by Power Gas or more recently by Davy Power Gas which was set up by ICI to market this technology.

The capabilities of the Davy Power Gas technology as described by them as vendors is probably as advanced as any offered commercially, but it is reasonable to expect that with the current upsurge in interest in massive quantities of methanol required for the future, there is much development which is not now disclosed in the available patent or other literature. There is much yet to be done, as pointed out in a subsequent section.

SPECIFICATIONS FOR METHANOL IN PRESENT MARKET

Methanol is one of the purest of commercial products and the following is a typical set of specifications for the commercial product:

Methanol, wt. %	99.98
Specific gravity	0.78891
Distillation range (1.013×10^5 N/m^2), First drop to dry, °C	0.40
Nonvolatiles, wt %	0.0001
Acetone, wt %	0.0006
Acidity, (as acetic acid) wt %	0.0010
Alkalinity (as ammonia), wt %	0.00000
Carbonizable substances, platinum cobalt scale (APHA)	11.
Permanganate test, min	70.
Color, platinum cobalt scale (APHA)	1.
Hydrocarbon test, clouding when diluted with 2 parts water	None

PHYSICAL PROPERTIES

A tabulation of the physical properties of methanol is as follows:

Formula weight	32.042
Boiling point, °C	64.70
Freezing point, °C	−97.68
Specific gravity, liquid 25/25°C	0.78891
Weight per gallon (15.6/15.6°C)	6.63
Coefficient of thermal expansion (15.6° to 25°C avg/°C	0.001194
Specific heat (C_p) at 25°C	
liquid, cal/(°C g)	0.6055
vapor, cal/ (°C g)	0.3274
Latent heat of vaporization, cal/*g*	257.
Critical temperature, °C	239.43
Critical pressure,	79.9
Critical density, *g/ml*	0.272
Heat of Combustion (AH_c°) at	
25°C liquid, cal./g	−5 416.3
vapor, cal./g	−5 699.4
Rate of evaporation (*n*-butyl acetate-100)	610.0
Solubility parameter (delta)	14.5
Hydrogen bonding index (gamma)	8.9
Dielectric constant (20°C)	33.58
Dipole moment (vapor or benzene sol.) Debye	1.68
Flammable limits (vol % in air)	
lower	6.7
upper	36.0
Flash point (TOC), °C	16.0
Flash point (TCC), °C	11.0
Ignition temperature, °C	385.0

USES FOR METHANOL

A tabulation of the major uses presently for methanol follows, decreasing in volume as one descends in the table:

Formaldehyde
Dimethyl terephthalate
Solvents
Methyl halides
Methyl amines
Methyl methacrylate
Inhibitor for formaldehyde
Ethylene glycol methyl ethers
Acetic acid
Miscellaneous

The present production capacity (late 1976) is approximately $2\,831 \times 10^3$ m^3 (1 billion gal) annually. This is equivalent to about 2 days' consumption of gasoline in the United States. Consequently, if the liquid fuel of the future is to be methanol or related alcohols, it is obvious that expansion of facilities by several orders of magnitude will be required. This will obviously be a major effort, and it is not too soon to intensify the preparative research and design.

A potentially very large outlet for methanol is represented by the utilization of methanol as the carbon source for food via bacterial action. Ammonia would be the source of the nitrogen for the bacteria. Inasmuch as the fossil fuels are presently the primary and probably the sole sources of both of these nutrients for the bacteria, it is obvious that we are placing still another burden on the limited and dwindling supplies of fossil fuels. It would appear that reliance on our current solar energy which, of course, is a renewable resource is much to be preferred as the area to research in our efforts to increase food supplies. Despite this factor, a protein from methanol plant was recently announced for England to produce animal feed.

PRICE OF METHANOL

The price of methanol has varied over the years as shown in Figure 11. The price declined to an unrealistic low of 10¢/gal, from which it recovered rapidly to 38¢ and currently is (late 1976) 42¢ a gallon.

QUESTIONS YET TO BE RESOLVED AND IMPROVEMENTS NEEDED

Ingredients and Procedures for Generating Carbon Monoxide and Hydrogen (Synthesis Gases)

Presently, these two problems are really one. There is general agreement that there is background engineering and process information that would permit us to build gas generating and methanol synthesis facilities which would be necessary for the conversion of coal and other solid fuels to methanol. This is, unfortunately, true only if one is to be satisfied with relatively small plants producing at most 5 100 m^3/day of methanol. What is needed are plants which have at least an order of magnitude greater capacity, and if these are developed, there would be required fifty to one hundred of these huge plants to produce the liquid fuels equivalent to our present consumption for vehicles alone.

Coal is the logical source of the carbon for the carbon monoxide and water the logical source of the hydrogen and some of the oxygen (supplemented with oxygen for the partial combustion), but the technology for the conversion of coal is either grossly inadequate from a volume process standpoint or is in a very embryonic stage of development. New and bold ideas are desperately needed; money alone cannot bring successful procedures from what now is on the horizon. What is needed is complete departures from the current research parameters which can best be described as sledgehammer technology. It is our patriotic duty to criticize, but it is even more our duty to present new and intelligent ideas.

The technology should include the recovery of the useful aromatics from the coal prior to its conversion to carbon monoxide and hydrogen and then the conversion of this devolatilized char to the carbon monoxide and hydrogen. Additionally, the technology should include the conversion of combustible farm products (trees, corn stalks and cobs, oat hulls, rapid growing brush, water hyacinths, wastepaper, etc.) because the cost and availability of coal are going to be ever intensifying problems. The agronomist must be an essential contributor to the solution of our long range energy problems.

It is no problem to stand back and observe the present efforts in deriving solutions to the utilization of coal and be critical and even sympathetic of those digging themselves deeper and deeper into what most must now feel are unsolvable problems. It is also easy to make a blanket statement that what are needed are bold new ideas and engineering innovations. It is time to face these facts and seek and examine new approaches; the old ideas perhaps have been given their chance.

Generating Low Cost Oxygen

It is possible that the generation of carbon monoxide and hydrogen will be by partial combustion of coal or other solid combustible; the combustion will be via a feed of this combustible plus oxygen and steam. Low cost oxygen is essential. Deriving the oxygen by the present mechanical means probably is the best, but one must ask are there possibilities of low cost chemical routes which would be preferable as the cost of energy increases. Certain solvents such as flurocarbons selectively dissolve oxygen from air and may be of commercial importance in the future. An oxide-peroxide cycle for barium, sodium, or other oxide or a heteropoly acid oxide-suboxide may be operable economically in the future economic environment; metallo-organic complexes with oxygen have been examined and may be applicable in the future.

What Products Should be Made Simultaneously with the Methanol?

Methanol can be made in high purity as a crude product utilizing known catalysts. This is in contrast to the Fischer-Tropsch process, which makes an extremely wide group of products from methanol to waxes. The question becomes can catalysts and operating conditions be developed which will make it possible to produce the desired methanol together with selected and needed products? Inasmuch as olefins, ketones, esters, and higher alcohols can be produced as previously described, the development of conditions necessary to produce these products economically with the methanol could be a worthwhile project.

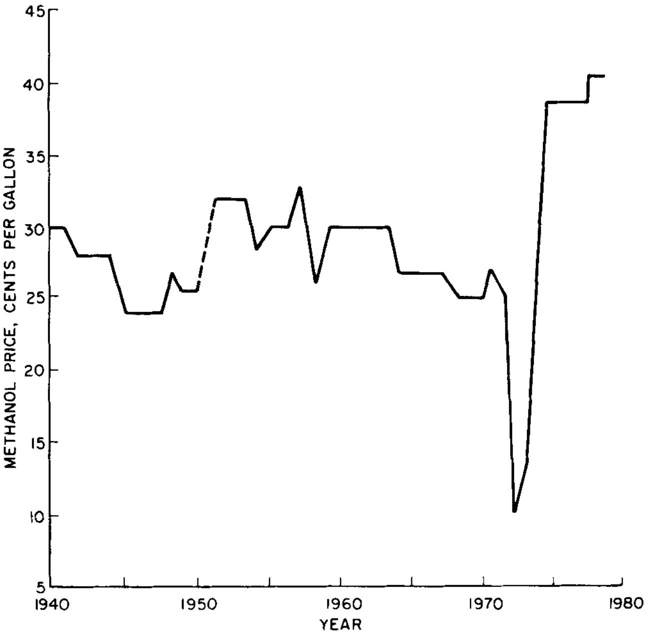


Fig. 11. Bulk methanol price range since 1940.

How Can Metals Carbonyl Formation Be Avoided?

Metals carbonyl formation in the equipment and deposition in or on the methanol synthesis catalyst are serious problems. Means of avoiding them should be a prime objective of research directed at the synthesis of methanol in large quantities.

How to Increase Productivity of Catalyst per Unit Volume of Converter

This relates both to the catalyst and the converter design, the former with respect to its ability to produce large quantities of methanol per unit volume and not be deactivated thermally or by the common poisons, and the latter with respect to its ability to dissipate and utilize the large quantities of heat generated from the methanol reaction. The catalyst must also be capable of operating at varying pressures efficiently because the optimum may under certain circumstances be as low as 5.2 to 6.9 × 10^6 N/m^2 to as high as 34.5 to 51. × 10^6 N/m^2 as dictated by equipment size and heat exchange.

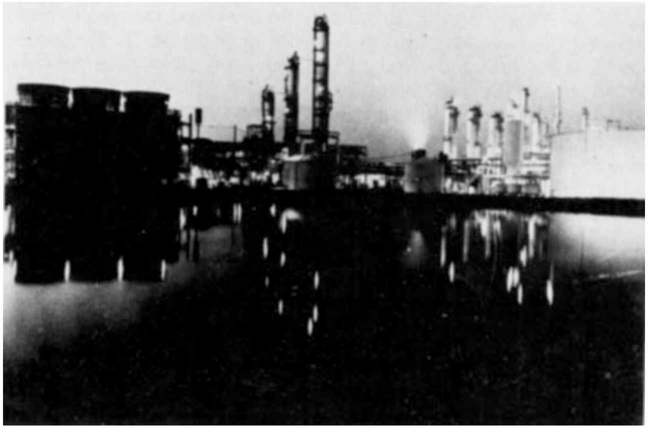


Fig. 12. Modern methanol plant.

Develop Catalyst Equally Effective for Methanol Synthesis and Reverse Carbon Monoxide Shift

Since it may in most cases be most economical to let the carbon dioxide remain in the gas stream, a catalyst is needed which will efficiently perform the methanol synthesis but be equally efficient in converting the $CO_2 + H_2 = CO + H_2O$ reaction. This catalyst probably will be essential for the greatest productivity per unit volume of a converter.

Miscellaneous Problems

Better methods and effectiveness are needed for the purification of synthesis gases.

A study is needed to determine the maximum optimum size for a methanol converter and the concomitant systems. Is a 12 500 m^3/day plant the maximum, or is it even feasible?

Can coal be converted underground to carbon monoxide and hydrogen of sufficient purity for synthesis gas?

How can one minimize the water requirements for a large gas generating system coupled with a methanol plant?

If there is excess heat generated, as there surely would be, can electric generating systems be made a part of the complex?

How can one minimize the very large capital investment requirements?

Comment

Our first statement was to the effect that methanol was a product of the first wood fire. Despite the early date of methanol synthesis and the high state of present development, it is apparent that there is a tremendous need for new ideas and developments. It is an area of major national concern and importance for our future, beginning almost at the present; it is necessary to emphasize and recognize it as such.

ACKNOWLEDGMENTS

I want to express my appreciation to Dr. A. B. Metzner, Chairman of the Department of Chemical Engineering of the University of Delaware, for initially suggesting the preparation of this paper and for his help in many ways since. Professors J. R. Katzer and B. C. Gates are also due many thanks for their careful review of the manuscript and many helpful suggestions and comments. Without the devoted work of the secretarial staff of the Department of Chemical Engineering, the efforts in preparing this paper would have been much more difficult. Especially to be thanked are Mrs. Rachel Rambo and Ms. Elizabeth Stewart.

There are many in the duPont Company over the past 45 years to whom I am deeply indebted for real world experiences and knowledge. Those to be especially mentioned in this regard are M. A. Naylor and S. T. Allen, who reviewed this paper and obtained the necessary approval for its publication. T. R. Keane and F. Miles Julian also have been especially helpful in providing kinetic data and comments thereon. R. W. Kropf has provided invaluable information on markets, forecasts, specication for refined methanol, safety features, and related subjects.

Last are those operators, supervisors, and managers who have been tolerant and understanding as well as helpful as exploratory catalysts have been developed, evaluated, and in a few cases adapted to plant operations.

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He engaged in both supervisory and scientific types of activities, but in the 1950's he was asked to devote all of his time to scientific and consulting activities. These led to his being designated Research Fellow in which capacity he was active until retirement in 1974, when he became Research Professor in the Department of Chemical Engineering at the University of Delaware. He continues to consult for duPont and others.

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Manuscript received November 12, 1976; revision received and accepted March 9, 1977.