Alcohols, Polyols and Phenols Manufacture and Derivatives

Marshall Sittig

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Thirty-Five Dollars

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INTRODUCTION

It takes two to make an ester - and one of the pair is an alcohol, polyol or phenol. In combination with either organic acids or inorganic reactants, the alcohols, polyols, and phenols produce esters which have tremendous impact on the consumer market in the form of:

- flame retardants
- synthetic resins
- plasticizers
- hydraulic fluids
- solvents
- synthetic lubricants
- surface-active agents

In addition to their use as chemical intermediates, the alcohols find broad utility as solvents for protective coatings, dyes, inks and many specialty applications.

The glycols and triols are used as intermediates in resin manufacture but are also widely used as solvents for dyestuffs, gums, resins and essential oils; they are also used as coupling agents for cutting oils, dry cleaning soaps and soluble oils. The diols and triols are also used as antifreezes and humectants.

Phenol is used as the starting material for phenol-formaldehyde resins, for epoxy resins and for polycarbonate resins. The new polyphenylene oxides are phenol derivatives. The phosphate esters of phenols are widely used as gasoline additives and non-flammable hydraulic fluids.

MANUFACTURE OF ALCOHOLS

The production of alcohols of various chain lengths to fit various special needs covers an almost encyclopedic range of operations in the chemical industry. Alcohols may be produced from natural or synthetic raw materials. Their production may involve simple reduction, hydration, hydrolysis or oxidation of hydrocarbon chain materials of approximately the same chain length as the product alcohol. Alternatively, the alcohols may be products of chain-building processes ranging from the older hydrocarbon synthesis and oxo reactions to the newer ethylene growth reactions for the production of long chain linear alcohols.

METHANOL FROM SYNTHESIS GAS

The production of methanol from synthesis gas according to the equation:

$$CO + 2H_2 \longrightarrow CH_3OH$$

is indeed old in the art, having been operated for half a century, since 1927.

In this, as in other areas of organic chemical technology, however, new developments are constantly appearing. Thus, as described in Chemical Week for January 6, 1968, pp. 34-36, Imperial Chemical Industries in England has developed a new low-pressure synthesis process which makes smaller plants much more economic than was previously the case.

Feed Materials: The feed is a sulfur-free gas mixture containing at least the stoichiometric quantity of carbon monoxide and conveniently up to a five-fold excess of hydrogen, according to P. Davies and F.F. Snowdon (to Imperial Chemical Industries, Ltd.) in U.S. Patent 3,326,956 (June 20, 1967).

A mixture of hydrogen, carbon monoxide and carbon dioxide is often used in the practical conduct of the synthesis of methanol. In this case, a second synthesis reaction occurs, this one involving carbon dioxide as follows:

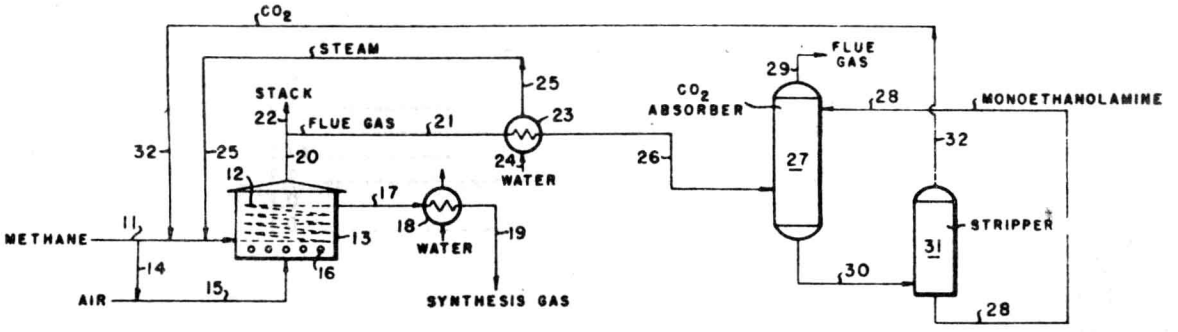
$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$$

The presence of carbon dioxide increases the duration of activity of at least some methanol synthesis catalysts. The water formed by the hydrogenation of the carbon dioxide is

readily removed from the product.

The production of synthesis gas may be carried out as described by N.P. Peet (to Esso Research & Eng. Co.) in U.S. Patent 2,904,575 (September 15, 1959) and as shown in Figure 1.

FIGURE 1: FLOW DIAGRAM FOR THE PRODUCTION OF SYNTHESIS GAS FOR METHANOL MANUFACTURE



Source: U.S. Patent 2,904,575

A methane feed stream is divided into a first portion and a second portion. The first portion is contacted in admixture with steam and carbon dioxide obtained in a later step of the process at an elevated temperature in a conversion zone with a catalyst to produce synthesis gas. The second portion of the methane feed stream is burned in the conversion zone to provide the elevated temperature and to form a combustion gas containing substantial amounts of carbon dioxide. The combustion gas is cooled with water to generate steam and reduce the temperature of the combustion gas. Carbon dioxide is recovered from the cooled combustion gas, and the steam and recovered carbon dioxide are admixed with the first portion. The synthesis gas comprising carbon monoxide and hydrogen is recovered from the contacted mixture.

The temperature at which the first portion is contacted with the catalyst to produce synthesis gas may suitably range between about 595° and 1010°C. with satisfactory operations obtained at a temperature of about 815°C. Pressures for the production of synthesis gas may range from about 0 to about 300 pounds per square inch gauge, with suitable operations conducted at a pressure of about 150 pounds per square inch gauge. The catalyst employed in the production of the synthesis gas is suitably a nickel catalyst, such as reduced nickel oxide, nickel-thoria magnesia, nickel-alumina-magnesia, nickel-magnesia, nickel on carbon, or nickel on alumina. Other suitable catalysts may include cobalt molybdate supported on alumina, a group VIII metal or metal oxide on a suitable support, nickel and iron on a support or carrier, and the like.

In Figure 1, the numeral 11 designates a charge line by way of which a methane-containing feed stream such as natural gas is introduced into the system from a source not shown. The methane feed stream is divided into two portions, with one portion being introduced into a conversion zone 12 arranged in a furnace 13, while the second portion is fed by way of line 14 into line 15 for admixture with air for charging to furnace 13 to be burned in burners 16 to raise the temperature of the methane introduced into reaction zone 12, which is in the form of a coil containing a suitable synthesis gas catalyst of the type illustrated. By virtue of the burning or combustion operation in zone 13, a synthesis gas having a composition as shown below may be formed.

Synthesis gas

	Percent
CO	25.3
CO_2	5.7
H_2	67.5
H_2O	1.3
CH_4	0.1
N_2	0.1

This synthesis gas is recovered from zone 12 by line 17 and cooled in cooler 18 for introduction into the methanol synthesis operation by way of line 19, which will be described further hereinafter.

The flue gas issues from zone 13 by way of line 20 with from about 50 to 75% of the flue gas being recovered by way of line 21 while the remainder is discharged by way of line 22 into a suitable stack for venting to the atmosphere, the stack not being shown. The flue gas then passes through a suitable boiler 23 into which water is admitted by way of line 24 for generation of steam which is withdrawn by line 25 and which is recycled to line 11 for charging with the first portion of the methane to reaction zone 12.

The cooled flue gas is then introduced by line 26 into a recovery unit 27 which suitably may be an absorber for carbon dioxide such as a tower with internal baffling equipment or other suitable gas-liquid contacting means such as bell cap trays and the like. Introduced into the top of absorption zone 27 is a suitable absorbent, such as monoethanolamine, by way of line 28, but which may be any other suitable absorbents for carbon dioxide. The unabsorbed flue gas is discharged from absorption zone 27 by line 29, while the enriched solution containing absorbed carbon dioxide is withdrawn from zone 27 by line 30 into a stripping zone 31, where heat is applied to drive the absorbed carbon dioxide from the monoethanolamine. The carbon dioxide is recovered by line 32 and discharged into line 11 to form the feed admixture to the reaction zone 12.

Temperature: The methanol production process may be operated at 200° to 300°C. and preferably at 220° to 270°C., according to P. Davies and F.F. Snowdon (to Imperial Chemical Industries, Ltd.) in U.S. Patent 3,326,956 (June 20, 1967). Temperatures of 290° to 400°C. and preferably of 345°C. are quoted by N.P. Peet (to Esso Research & Eng. Co.) in U.S. Patent 2,904,575 (September 15, 1959). The reaction zone should be maintained at a temperature above 225°C. and usually between 300° and 375°C. according to T.C. White (to M.W. Kellogg Co.) in U.S. Patent 3,064,029 (November 13, 1962).

Pressure: The operating pressure in methanol synthesis may be from 1 to 350 atmospheres, is preferably from 10 to 150 atmospheres and more preferably from 40 to 80 atmospheres, according to P. Davies and F.F. Snowdon (to Imperial Chemical Industries, Ltd.) in U.S. Patent 3,326,956 (June 20, 1967). Operating pressures of 130 to 400 atmospheres have been quoted by N.P. Peet (to Esso Research & Eng. Co.) in U.S. Patent 2,904,575 (September 15, 1959). A reactor outlet pressure of 300 atmospheres is specifically cited as desirable. Pressures above 200 atmospheres and preferably from 270 to 400 atmospheres are specified by T.C. White (to M.W. Kellogg Co.) in U.S. Patent 3,064,029 (November 13, 1962)

Reaction Time: The space velocity at which the methanol synthesis is carried out is conveniently in the range from 10 to 30,000 reciprocal hours and is preferably in the range from 7,000 to 20,000 reciprocal hours. The values cited are calaulated at 20°C. and one atmosphere pressure and are expressed in liters of gas per liter of catalyst-filled reaction space per hour.

Reaction Medium: The synthesis of methanol is carried out in the vapor phase.

Catalyst: The catalyst for the reaction of carbon oxides with hydrogen contains copper, zinc and chromium preferably in a ratio falling within the area defined by the perimeter passing through the following points on a triangular phase diagram (Figure 2), according to P. Davies and F.F. Snowdon (to Imperial Chemical Industries, Ltd.) in U.S. Patent 3,326,956 (June 20, 1967):

Cu	Zn	Cr
95	4	1
15	84	1
20	70	10
20	30	50
45	5	50

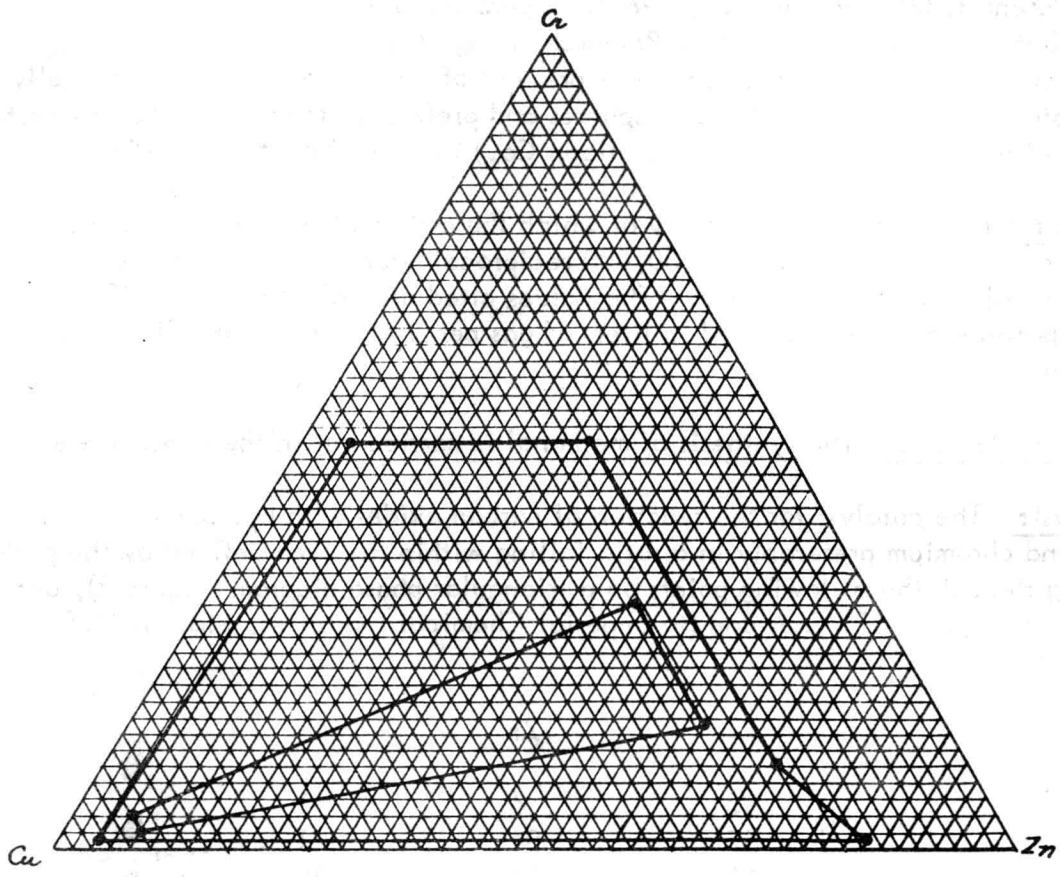
and especially by a second perimeter laying within the above perimeter and passing through the points:

Cu	Zn	Cr
90	8	2
25	60	15
25	45	30
90	6	4

These perimeters are illustrated in the triangular phase diagram shown on the accompanying drawing.

In the diagram the compositions represented are atomic percentages of the total content of copper, zinc and chromium. Where herein reference is made to a percentage copper, zinc or chromium content such a content is a percentage by atoms of the total copper, zinc and

FIGURE 2: DIAGRAM SHOWING PREFERRED COMPOSITION RANGES FOR CHROMIUM-COPPER-ZINC METHANOL SYNTHESIS CATALYSTS



Source: U.S. Patent 3,326,956

chromium. The preferred catalysts thus have a zinc to chromium ratio in the range 1.5:1 to 4:1 and a copper content in the range 25-90%. The copper content of such catalysts is more preferably in the range 45-85%, especially 55-75%. Thus as examples of valuable catalysts for use in this process there may be mentioned those consisting of the product of reducing the mixed oxides of copper, zinc and chromium in the atomic ratio 30:60:10, 40:40:20, 80:15:5 and 72:21:7 in increasing order of preference: catalysts having the ratio 60:30:10 and 75:18:7 are similar to the 72:21:7 catalyst.

The catalyst is preferably produced by co-precipitating the three metals from a solution of their nitrates as one or more compounds readily convertible to oxides. For example the mixed nitrates may be added to a solution of a carbonate. Preferably the precipitation is effected at a temperature above 50°C., especially 80°-100°C. Preferably also the mixture has a neutral to mildly alkaline reaction up to pH 10, for example pH 8 (the pH value being measured at room temperature) at the end of the precipitation.

The precipitate when a carbonate is used is a mixture of carbonates, basic carbonates and

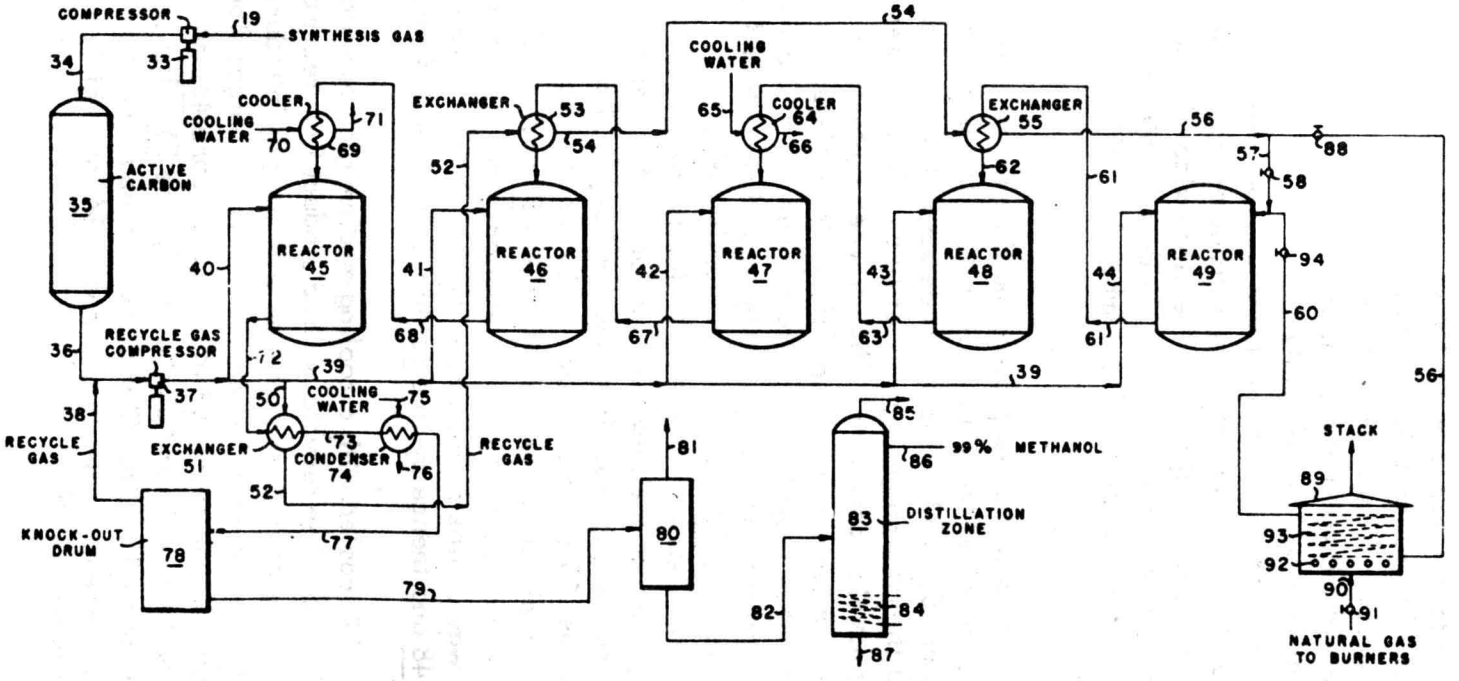
hydroxides. It is collected on a filter, washed substantially free of electrolytes, then dried and calcined at 200° to 400°C. to form the oxides of the metals present. The calcined material is formed into pieces by for example pelleting under pressure using graphite as lubricant. Before the oxide mixture can show its full activity as a catalyst it should be partly reduced. This may be effected conveniently by passing a mixture of hydrogen optionally with nitrogen as diluent at atmospheric pressure over the heated oxide mixture in the converter in which the catalyst is to be used. The catalysts may contain also support materials, diluents or binding materials, of types well known in catalyst-making, but these do not appear to be essential, very satisfactory results being obtained without them. The catalyst used in methanol synthesis may be zinc oxide-chromia or may be copper promoted with cerium oxide and containing zinc oxide according to N.P. Peet (to Esso Research & Eng. Co. in U.S. Patent 2,904,575 (September 15, 1959).

Reactor Design: A reactor system employing multiple reactors for methanol synthesis is shown in Figure 3 as described by N.P. Peet (to Esso Research & Eng. Co.) in U.S. Patent 2,904,575 (September 15, 1959). The synthesis gas in line 19 is suitably compressed in a compressor 33 and then discharged by way of line 34 into a tower 35 containing a bed of active carbon for removal of carbonyls. The scrubbed synthesis gas discharges from zone 35 by way of line 36 into a recycle gas compressor 37 in admixture with recycle gas introduced by line 38. The amount of recycle gas is approximately 2 to 3 parts of recycle gas per part of fresh feed. The total mixture then passes by way of line 39 and is introduced in parallel by way of lines 40, 41, 42, 43 and 44 into a plurality of reaction zones 45, 46, 47, 48 and 49, each provided with a bed of a methanol synthesis catalyst such as for example zinc oxide-chromia. A portion of the total feed mixture is then passed by way of line 50 into a heat exchanger 51 and the gas issues from heat exchanger 51 by way of line 52 and then passes into an exchanger 53 and thence by line 54 into another heat exchanger 55 and finally the recycle gas mixture is introduced by line 56 and branch line 57, controlled by valve 58, into line 60 for introduction into reaction zone 49, the recycle gas and product passing in series by way of line 61 from zone 49 through heat exchanger 55 and by line 62 into reaction zone 48 and thence by line 63 through a cooler 64 into reaction zone 47.

The cooler 64 is suitably cooled with a cooling medium such as water introduced by line 65 and withdrawn by line 66. The recycle gas and product from reaction zone 47 issues therefrom by way of line 67 and passes in heat exchange with the gas introduced by line 52 and thence into reaction zone 46, recycle gas and product being discharged from reaction zone 46 by way of line 68 and passing through cooler 69 into reaction zone 45, cooler 69 being cooled with water introduced by line 70 and discharged by line 71. The gas and product finally issues from reaction zone 45 by line 72 and passes in heat exchange with the gas introduced by line 50 and is discharged by line 73 into cooler 74 into which water is introduced by line 75 and withdrawn by line 76.

The cooled gas and product discharges from cooler 74 by line 77 into a knockout drum 78 with the recycle gas being withdrawn therefrom by line 38 and the cooled liquid containing the product being withdrawn by line 79 and introduced into a drum 80 wherein separation is made between the gaseous and liquid products, with the gases being withdrawn by line 81 and the product being withdrawn by line 82 for introduction into a suitable fractional distillation tower 83 provided with all auxiliary equipment including cooling and condensing

FIGURE 3: MULTIPLE-REACTOR PLANT DESIGN FOR METHANOL SYNTHESIS



Source: U.S. Patent 2,904,575

means and suitable reboilers and the like. For purposes of illustration only, the reboiler is shown as internal steam coil 84 for adjusting temperature and pressures in fractional distillation zone 83. Light products are withdrawn from fractional distillation zone 83 by line 85 with 99+% purity methanol being recovered by line 86 and heavy fractions by line 87.

During start-up operations it may be desirable to open valve 88 in line 56 and to allow a portion of the recycle gas to be introduced into a furnace 89 provided with line 90 controlled by valve 91 by way of which natural gas is introduced to burners 92 for support of a combustion operation, the recycle gas passing through coil 93 and being heated to a suitable temperature prior to passage through line 60 on opening valve 94 into reaction zone 49 as has been described.

Product Recovery: The effluent from the methanol synthesis converter contains, in addition to methanol, water, methane, dimethyl ether and relatively small concentrations of higher alcohols and other gaseous hydrocarbons. The reactor effluent is cooled to 25° to 50°C. to condense the normally liquid components. Condensed methanol contaminated with water is separated from the uncondensed gases and is further purified by standard procedures. The uncondensed gases, which are still at substantially reactor pressure, may be cooled further prior to being treated in an absorption zone as described by T.C. White (to M.W. Kellogg Co.) in U.S. Patent 3,064,029 (November 13, 1962).

Further cooling increases the efficiency of the absorption process. Where the uncondensed gases are further cooled, they are cooled to a temperature above the freezing point of the principal impurity, e.g., methane, and preferably a temperature above -45°C. Treatment of the uncondensed mixture of reactive and inert gases may therefore be carried out at a temperature between about -45°C. and about +50°C. The gas mixture is then treated in an absorption zone with an absorbent which has a high selectivity for the inert gases contained in the gas mixture. A gas stream containing hydrogen, carbon monoxide, carbon dioxide and a reduced quantity of inert gases is withdrawn from the absorption zone and is recycled to the reaction zone. As indicated, the absorption medium should have a high selectivity for the inert gases in the uncondensed gas stream.

In the reaction of hydrogen with carbon oxides, particularly where the principal product is methanol, the principal impurity will be methane. Therefore, a solvent or absorbent having a high selectivity for methane should be employed. (Also, the absorbent should not interfere with the synthesis reaction.) Such solvents include the lower aliphatic alcohols. Since methanol has the highest selectivity for methane, its use is preferred.

Since the efficiency of the absorption medium is decreased as the concentration of absorbed inert gases is increased, it is necessary to remove the absorbed inert gases if the absorption medium is to be recycled. According to the process, the absorbed inert gases are removed by withdrawing the rich absorption medium from the absorption zone, reducing the pressure and flashing off the absorbed impurities. In order to minimize loss of absorption medium the flashing operation is preferably carried out in at least two stages. As indicated, the reaction zone and the absorption zone operate at approximately the same pressure, i.e., above 3,000 psig and usually between about 4,000 and about 6,000 psig. In the first flashing zone, therefore, the pressure is dropped below the pressure prevailing in the absorption zone and usually to a pressure between about 300 and 5,000 psig.