

PATENT SPECIFICATION



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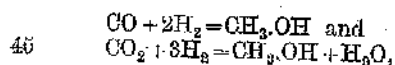
The Synthetic Manufacture of Methanol.

I, JAMES YATE JOHNSON, a British subject, of 47, Lincoln's Inn Fields, in The County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by the Badische Anilin & Soda Fabrik, of Ludwigshafen-on-Rhine, Germany, a company incorporated according to German laws) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

Hitherto it has not been possible to produce methanol successfully by the catalytic reduction of carbon monoxide, though several proposals have been made for this purpose.

My foreign correspondents have now found that methanol can be produced by the catalytic reduction of carbon oxides with very good yields and a good speed of the reaction so that an industrial utilization of the process is rendered possible, by employing at an elevated temperature and pressure contact masses which contain, besides one or more than one of the following elements: Copper, silver, gold, zinc, cadmium, and lead as hydrogenating elements also titanium, vanadium, chromium, manganese and the elements related to them namely, zirconium, cerium, thorium, niobium, tantalum, molybdenum, tungsten, uranium, or boron or compounds of these elements or more than one of these elements or compounds thereof.

It is of advantage to use gas mixtures of carbon monoxide, or dioxide, or both and hydrogen with quantities of the latter exceeding by volume the quantities of the oxides of carbon and preferably in the proportions calculated according to the equations:



or with even more hydrogen. Such exceeding quantities of hydrogen must be

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used when contact masses are employed consisting of mixtures of the oxides chromium, manganese, molybdenum, titanium, or cerium with zinc. A high excess of hydrogen may be present for example one and a half of the calculated volume or a multiple of the latter. The gas mixture may also contain hydrocarbons or nitrogen or other inert gases and it may be purified and dried, prior to the reaction.

With the beforementioned conditions, a very pure methanol is obtained at comparatively low temperatures.

The contact masses may be prepared in any suitable way and the proportions of the components may be varied within wide limits. *Inter alia*, the additional elements mentioned may be compounded, in the form of their higher oxides with an acid character, with the hydrogenating element to form a salt, and such salts, for instance vanadates, chromates, manganates, borates, may be subjected to reduction. Mixtures of such acids with the hydrogenating elements may also be used, and the contact mass may be prepared in any other way. Supports may also be employed and a great variety of substances may serve this purpose.

In order to produce a very pure methanol it has proved useful to employ catalysts of the aforesaid kind which contain as little alkali as possible and accordingly to purify thoroughly those contact masses which contain any alkali from their preparation prior to their use for the present process, or to exclude any alkali compounds when preparing the contact masses. When supports are employed such materials should be used as do not give off any alkali. Thereby the formation of oily products is prevented or greatly diminished.

The temperatures of the reaction may be raised to above 500 degrees Centigrade, but in general they need not exceed 300 degrees Centigrade, and in

many cases considerably lower temperatures are sufficient which are in favour of the formation of pure methanol. The pressure may be raised to any degree. Less active contact masses require very high pressures and rather high temperatures in order to give ample yields.

In all cases it is important that iron, nickel and cobalt are not present or only in comparatively small amounts and only together with one or more of the aforesaid hydrogenating elements as otherwise methane, or other hydrocarbons may be formed.

The following examples will serve to further illustrate how the invention may be carried into effect but it is to be understood that the invention is in no way restricted to these examples. The parts are by weight where no other statement is made.

EXAMPLE 1.

Prepare a catalyst by introducing 50 parts of asbestos wool into a solution of 86 parts of copper nitrate and from 8 to 10 parts of chromium acetate, heat to boiling, precipitate with sodium carbonate, filter, wash well and dry. Then loosen the asbestos wool and reduce it at between a temperature of 190 degrees to 200 degrees Centigrade by means of hydrogen at ordinary or increased pressure. Over the contact mass thus prepared a gas mixture containing 20 parts, by volume, of hydrogen, for each one part of carbon monoxide is passed at a temperature of from 220 degrees to 250 degrees Centigrade and at a pressure of about 100 atmospheres. The speed of the gas mixture may be between 2 and 10 cubic metres (calculated on ordinary conditions as to temperature and pressure) per hour for each kilogram of contact mass. Between about 20 and 5 per cent. of the carbon monoxide (depending on the speed of passing over) are converted into methanol and small amounts of oily matter, insoluble in water, and a little methane, may sometimes be formed.

Mixtures of carbon dioxide and hydrogen may also be employed which may contain carbon monoxide, hydrocarbons and nitrogen or other inert gases.

EXAMPLE 2.

Introduce 50 parts of asbestos into a dilute solution of 55 parts of potassium dichromate, then add 70 parts of copper nitrate whereby copper chromate is precipitated on the asbestos fibre. Then wash, dry, loosen the asbestos and reduce in an atmosphere of hydrogen at a temperature of about 200 degrees Centigrade.

Over the contact mass thus prepared a gas mixture containing 8 to 10 parts by volume of hydrogen for each part of carbon monoxide is passed at a temperature of about 230 degrees Centigrade and at a pressure of about 150 atmospheres and at the rate of between about 3 and 100 cubic metres (calculated on ordinary conditions) per hour for each kilogram of contact mass. About from a half to a quarter of carbon monoxide in the gas mixture is converted into methanol. Very good yields are also obtained with the chromates or silver, or of silver and copper, or with the molybdates or tungstates of silver, or copper, or any other of the aforesaid hydrogenating metals, or with salts or mixtures of salts of such metals derived from any other of the aforesaid associated elements including salts or mixtures containing more than one hydrogenating element or additional element.

EXAMPLE 3.

Dissolve in water 25 parts of neutral copper acetate and 21.3 parts of silver nitrate, then add 50 parts of asbestos wool, heat to boiling, add 25 parts of chromic acid, evaporate while mixing at intervals, dry loosen the mass and reduce in a current of hydrogen at a temperature of about 400 degrees Centigrade and at a pressure of 25 atmospheres. When a mixture of carbon monoxide and hydrogen (with about 1 volume of the former to each 6 volumes of the latter) is passed over this contact mass at about 230 degrees Centigrade and 120 atmospheres, and with a speed corresponding to between 2 and 200 cubic metres (calculated on atmospheric pressure) per hour and kilogram of contact mass, 10 per cent. and less of the carbon monoxide, depending on the speed of the current, are reduced to methanol.

A contact mass prepared by decomposing potassium chromate with copper acetate and lead nitrate in the presence of asbestos wool can be employed in a similar manner.

EXAMPLE 4.

84 parts of copper nitrate and 10 parts of uranium nitrate are dissolved in water and 50 parts of asbestos wool are introduced. The mixture is then heated to boiling, precipitated with caustic potash lye, filtered thoroughly, washed, dried and loosened. When a mixture of carbon monoxide and hydrogen in the proportion of about 1 to 8 is passed over this catalyst at a temperature of 220 degrees Centigrade and a pressure of 80 atmospheres methanol is produced with very good yield and at great speed. The

gas mixture is passed over at the rate of from 1 to 150 cubic metres (calculated on atmospheric pressure) per hour for each kilogram of contact mass, and 30 per cent. or less of the carbon monoxide will be converted into methanol.

EXAMPLE 5.

A mixture of carbon monoxide and hydrogen, in the proportions of about 1 to 10, is passed at a temperature of about 260 degrees Centigrade and a pressure of 100 atmospheres over a contact mass containing 63.6 parts of copper, 11.4 parts of uranium and 3.9 parts of manganese deposited as hydroxides or carbonates on a carrier. Between 0.5 and 50 cubic metres of gas (calculated on ordinary pressure) may be employed per hour and kilogram of contact mass and 30 per cent. or less of the carbon monoxide are converted into methanol. On cooling the reaction gases methanol condenses with an excellent yield. The percentage of either uranium or manganese or both may also be higher. With such contact masses or with higher pressure, the yield may rise to 50 per cent. or more.

EXAMPLE 6.

Pass a mixture of 10 parts, by volume, of carbon monoxide and 90 parts, by volume, of hydrogen, at a temperature of about 220 degrees Centigrade and a pressure of 100 atmospheres over a catalyst consisting of asbestos with an intimate mixture of 50 parts of manganese dioxide, 30 parts of copper oxide, 15 parts of cobalt oxide, and 5 parts of silver oxide precipitated thereon which has been reduced beforehand at a temperature of about 200 degrees Centigrade in a current of hydrogen at ordinary or increased pressure. The reaction gas leaving the catalyst will deposit, on cooling, a liquid chiefly consisting of methanol. Very good results are also obtained when employing salts of the acid high oxides of the associated elements together with hydrogenating elements. For example the reduction products of copper or silver vanadate, copper or silver manganate, or the like may be used. When a speed of gas current corresponding to between 5 and 250 cubic metres (calculated on ordinary conditions) per hour and kilogram of contact mass is employed, 5 per cent. or less of the carbon monoxide will enter reaction.

EXAMPLE 7.

Dissolve so much of copper nitrate, as corresponds to 21.8 parts of copper, and 10 parts of thorium nitrate in water, add 50 parts of asbestos, heat to boiling, pre-

cipitate with an excess of caustic potash lye, filter off, wash thoroughly, dry, loosen the asbestos and reduce in a current of hydrogen at ordinary or increased pressure at a temperature of about 200 degrees Centigrade.

When a dry mixture of carbon monoxide and hydrogen in the proportions of about 1 to 7 is passed over this mass at a temperature of about 220 degrees Centigrade and a pressure of 100 atmospheres, methanol is produced with good yield. The speed of the gases may amount to from 3 to 50 cubic metres (calculated on ordinary conditions) per hour and kilogram of contact mass, the yield reaching 10 per cent. or less of the carbon monoxide.

EXAMPLE 8.

Dissolve so much of copper nitrate as corresponds to 21.8 parts of copper, 10 parts of uranyl nitrate and 5 parts of thorium nitrate in water, add 50 parts of asbestos wool, heat to boiling, precipitate with an excess of caustic potash lye, filter off, wash thoroughly, dry, loosen and reduce at a temperature of about 200 degrees Centigrade in a current of hydrogen at ordinary or increased pressure. When a dried mixture of carbon monoxide and hydrogen in the proportions of about 1 to 5 is passed over this catalyst at a temperature of about 220 degrees Centigrade reaction takes place at about 35 atmospheres and a liquid is obtained with good yields chiefly consisting of methanol. About 5 per cent. of the carbon monoxide are converted into methanol when 3 cubic metres of gas mixture (calculated on atmospheric pressure) per hour are employed for each kilogram of contact mass. The higher the pressure the higher the yield. With 90 atmospheres gas pressure, about 20 per cent. of the carbon monoxide enter reaction. By increasing the speed of the gas the percentage of carbon monoxide undergoing hydrogenation is reduced. Other organic compounds especially oily substances are either not at all obtained or only in very small amounts.

If instead of a mixture of hydrogen and carbon monoxide a mixture of hydrogen and carbon dioxide, for example in the proportions of 5 to 1, is passed over the said catalyst at a temperature of about 220 degrees Centigrade and a pressure of about 100 atmospheres, the reaction gases, on cooling, give a liquid which is composed of water and chiefly methanol, and in quantity corresponds to about 10 per cent. or less of the carbon dioxide passed over, when the speed of the gas current was between 1 and 100

cubic metres (calculated on atmospheric pressure) per hour and kilogram of contact mass.

EXAMPLE 9.

5 A contact mass is prepared from 21.8 parts of copper in form of the nitrate, 10 parts of uranyl nitrate, 5 parts of cerium nitrate and 50 parts of asbestos wool, substantially as described in the foregoing example, and a mixture of one volume of carbon monoxide and 10 parts of hydrogen is passed over this mass at a pressure of about 50 to 150 atmospheres and at a temperature of about 220 degrees Centigrade. Methanol is recovered from the reaction gases by cooling.

The pressure and proportions of carbon monoxide or dioxide to hydrogen may be varied within a wide range, but the hydrogen should preferably be present in an exceeding quantity in all cases. The greater the pressure, the greater the yield and the quantity of gases undergoing reaction, the yield corresponding to about 30 per cent. or less of the carbon monoxide passed over the catalyst, depending on the variety of the gas current which may vary between say 1 and 250 cubic metres (calculated on ordinary conditions) per hour for each kilogram of contact mass.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. The process of synthetically manufacturing methanol or products substantially consisting of methanol by cataly-

tically reducing carbon monoxide or di- 40
oxide at elevated temperature and pressure which is characterised by the use of contact masses containing besides one or more of the following elements, copper, silver, gold, zinc, cadmium and lead, 45
also titanium, vanadium, chromium, manganese and other cognate elements related to them namely, zirconium, cerium, thorium, niobium, tantalum, molybdenum, tungsten, uranium, or boron, or more than one of these elements, or compounds thereof and preferably also using such gas mixtures as contain more hydrogen, by volume, than carbon oxides, which gas mixtures should be used in any case when mixtures of zinc, with oxides of chromium, manganese, molybdenum, titanium, or cerium are used as catalysts. 55

2. In the process of manufacturing methanol, according to Claim 1, the use of catalysts of the kind described which are free from alkali compounds and from iron and nickel. 60

3. The process of manufacturing methanol, substantially as described in the foregoing examples. 65

4. As an article of manufacture methanol, either pure or mixed with oily substances when prepared according to the foregoing clauses. 70

Dated this 23rd day of August, 1923.

JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London, W.C.2,
Agents. 75

Reference has been directed in pursuance of Section 7, Sub-section 4, of the Patents and Designs Acts, 1907 and 1919, to Specification No. 20,488 of 1913.