[Second Edition.]

PATENT SPECIFICATION.

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COMPLETE SPECIFICATION.

Process for Catalytically Preparing Methanol or Higher Alcohols or other Oxygenated Organic Compounds or Mixtures of the same.

I, Dr. LUIGI CASALE, Chemist, of 9, Via del Parlamento, Rome, Italy, an Italian subject, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a method for producing methanol or higher alcohols or other oxygenated compounds or mixtures of alcohols and oxygenated compounds by means of catalytic reactions between selected mixtures consisting of carbon monoxide and/or carbon dioxide, hydrogen or/and a gaseous hydrocarbon, such reactions taking place continuously in a closed circuit of apparatus.

By passing mixtures consisting, for instance, of carbon monoxide and hydrogen or carbon dioxide and hydrogen or carbon monoxide, carbon dioxide and hydrogen, or carbon monoxide, hydrogen and methane or carbon monoxide and methane or carbon dioxide and methane or carbon monoxide, carbon dioxide and methane, over catalysts, it is possible to obtain different compounds, the nature of which varies according to the temperatures and pressures at which reaction is caused, with the catalysts employed and with the composition of the mixtures.

The following equations will serve to illustrate reactions which can take place:

(1) $CO + H_2 = HCHO$

(2) $HCHO + H_2 = CH_3OH$

(3) $CO + 2H_2 = CH_3OH$

(4) $2CO + 2H_2 = CH_3COOH$

(5) $CH_4 + CO = CH_3CHO$

(6) $CH_4 + CO_2 = CH_3COOH$

(7) $CO + CH_4 + H_2 = C_2H_5OH$

For information concerning the reactions expressed by equations 3, 4, 5 and 7, see French Patent No. 540,543.

These equations show that methyl alcohol, ethyl alcohol, formaldehyde, acetaldehyde and acetic acid can be obtained, but mixtures of alcohols and other oxygenated compounds (chiefly higher alcohols, aldehydes, ketones and organic acids) can also be produced and can be profitably used for many purposes.

Since a certain quantity only of the gaseous mixture which is passed over the catalyst reacts to form one or more reaction products, it is usual to pass, over the catalyst again, the mixture remaining after the reaction products have been separated from the whole with a further quantity of mixture corresponding to that separated in the form of reaction product or products in order to keep the conditions of the reacting system unaltered.

The plant for producing the reaction products comprises in addition to the catalytic apparatus, heat exchanging apparatus, condensing apparatus, receiving apparatus, a circulating pump which may be a piston pump or a centrifugal or a rotary pump and in some cases other kinds of apparatus such as gas purifiers.

The use of pumps, however, has a drawback in that the gases are liable to carry along some of the oil which is used for lubrication of the pistons and stuffing boxes, and this oil must be separated with great care or it will poison the catalyst. The usual oil separators are not sufficient for such separation and purifiers for removing the very last traces of oil must be introduced into the circuit. The circulation pump, oil separator and the purifier form as a whole an expensive plant of considerable weight and the expense of operating such plant including power, lubricants, labour, repair etc. increases materially the cost of manufac-

ture. In addition the losses by leakage of gas mixture when passing through the plant and those occasioned by the periodical purging of the oil separator must be taken into account.

The method according to the present invention has been studied with the object of avoiding said drawbacks. For this purpose in place of the circulating pump an apparatus is used which, although containing no moving part whatever, brings about the circulation of the gases in the circuit; the only condition for its operation being that the mixture admitted to the circuit should be under a pressure of a certain number of atmospheres higher than the pressure existing within the circuit itself. It is obvious that, under such conditions, the mixture entering the circuit will undergo a diminution of pressure, so that a part of its potential energy is transformed into kinetic energy. It is this kinetic power which I utilise for obtaining the circulation of the gases.

An embodiment of a circulating apparatus which can be used for carrying the invention into effect is shown in cross section in Fig. 1 of the accompanying drawings, Fig. 2 representing diagrammatically a closed circuit which includes such circulating apparatus.

Referring to Fig. 1 of the drawings, *a* designates the body of the apparatus formed with very thick walls of suitable metallic material, *b* is a diffuser cone, *c* a nozzle, *d* a regulating needle for the nozzle *c*, *e* a stuffing box and *f* a filter to retain impurities liable to obstruct the nozzle.

The fresh mixture is admitted at A through the filter *f*, the mixture being previously compressed to a higher pressure than that of the mixture to be circulated. The fresh mixture flows out of the nozzle *c* at high speed, carrying with it the mixture to be circulated which enters the apparatus at B. The excess of pressure of the mixture flowing in at A above the pressure existing in the circuit is determined by the quantity of gas mixture to be circulated by the resistance of the apparatus forming the circuit, by the speed to be imparted to the gaseous mixture, and by the working pressure.

Such circulating apparatus may be inserted at any point on the circuit where it is deemed convenient to admit the mixture. The absence of movable parts eliminates the drawbacks connected with the use of circulation pumps, while the use of the oil separator and purifier is unnecessary. Moreover the apparatus has the advantage of being inexpensive to manufacture, is exceedingly easy to operate, and occupies a very small space. The cost of power consumed in order to admit the mixture under a pressure higher than that of the circuit is always very much lower than that incidental to operating a circulation pump.

A plant for obtaining the above mentioned compounds in accordance with the invention is illustrated diagrammatically in Fig. 2 in which 1 shows a one, or more, stage compressor; 2 the piping through which the compressed gases flow; 3 the circulating apparatus illustrated in Fig. 1; 4 a synthesis apparatus; 5 a heat exchanger; 6 a condenser and 7 a receiver for collecting the products condensed in the condenser 6. A pipe 8 connects the circuit through which the gases flow, with the suction pipe 9 of the compressor, while 10 is a cock, the opening of which may be regulated at will, and 11 is a pipe connecting the different apparatus of the circuit. The arrows indicate the passage of the gases.

By using the circulating apparatus described above it is also possible to obtain the circulation of the gases when no reaction is taking place between them, this corresponding in practice to the period when the plant is being started or stopped. It will readily be understood the fresh mixture of gases cannot be introduced into the circuit when no reaction is taking place without increasing the pressure, because there is no removal of reaction product and therefore no diminution of volume in the circulating mixture. On the other hand the introduction of fresh mixture of gases is necessary to cause the operation of the circulating apparatus. A volume reduction in the gaseous mixture is therefore brought about by causing part of the mixture in the circuit, in quantity equal to that which would normally be removed as catalysed reaction product or products, to leave the circuit through the pipe 8, regulated by cock 10, the mixture passing to the suction pipe of the compressor 1. In this way the circulation can be continued even though no reaction is taking place in the circuit.

I make no claim per se to the circulating apparatus shown in Fig. 1 of the accompanying drawings, but:—

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. A method for producing methanol or higher alcohols or other oxygenated compounds or mixtures of alcohols and

other oxygenated compounds by means of catalytic reactions, between carbon monoxide and/or carbon dioxide, hydrogen or/and a gaseous hydrocarbon, taking place in a closed circuit of apparatus, wherein the reacting gases are caused to flow through said closed circuit by means of an apparatus having no moving parts and utilising therein the kinetic energy obtained by transformation of part of the potential energy of the mixture admitted into the circuit under higher pressure than the pressure of the circuit.

2. Carrying out the method claimed in Claim 1 in a plant comprising catalytic apparatus, heat exchanging apparatus, condensing apparatus and receiving apparatus in combination with the circulating apparatus described with reference to Fig. 1 of the accompanying drawings, said apparatus forming together a closed circuit.

3. Carrying out the method claimed in Claim 1 in an apparatus arranged and operating substantially as described with reference to Fig. 2 of the accompanying drawings.

Dated this 27th day of July, 1925.

DICKER & POLLAK,
Chartered Patent Agents,
20 to 23, Holborn, London, E.C. 1,
Agents for the Applicant.

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2nd Edition

FIG. 1.

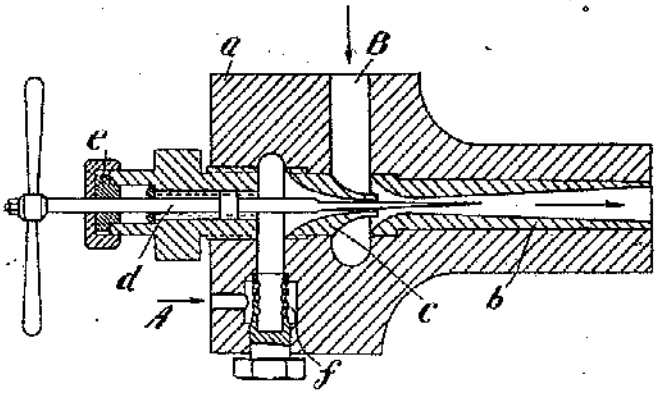
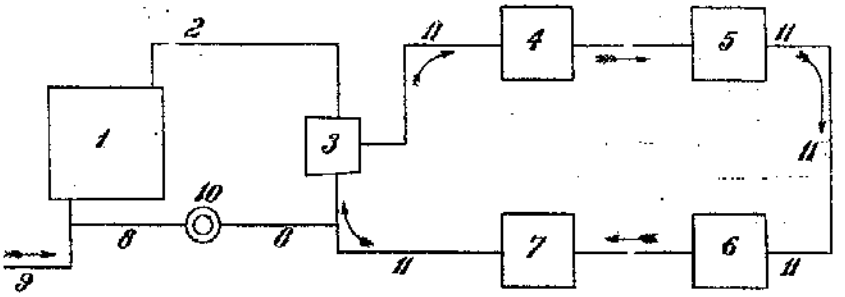


FIG. 2.



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