[Second Edition.]

PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Process for Preparing Catalytically, Alcohols and other Oxygenated Organic Compounds.

I, LUIGI CASALE, Doctor of Chemistry, of 9, Via del Parlamento, Rome (7), 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:—

Hydrogen or hydrogen and gaseous hydrocarbons can as is known react with carbon monoxide and carbon dioxide giving a series of different reactions whose nature is in relation with the conditions in which such reactions are obtained.

The reactions obtainable from a compressed mixture of the aforesaid gases by means of catalytic agents are industrially very important, the simplest are those producing methyl and ethyl alcohol, i.e.:

$$CO + 2H_2 = CH_3OH$$
$$CO_2 + 3H_2 = CH_3OH + H_2O$$
$$CO + H_2 + CH_4 = C_2H_5OH$$
$$CO_2 + 2H_2 + CH_4 = C_2H_5OH + H_2O$$

but together with these reactions other more complex reactions can be brought about, resulting in the formation of higher alcohols and also of aldehydes, ketones and organic acids. Amines also can be obtained if some nitrogen is contained in the reacting mixture.

Not only reactions causing the formation of a single compound or of a mixture of easily separable compounds are industrially important: By suitable variations in working conditions, i.e. reaction pressure and temperature, composition of the catalytic agent, percentage composition of the reacting mixture; many mixtures of organic compounds (principally alcohols, aldehydes, ketones and organic acids) can be obtained as final products. Such mixtures may be difficult to separate, but they can be used, as they are obtained or after passing them through simple and very inexpensive treatments, principally as denaturants for ethyl alcohol, or solvents, or fuels for heating or for lighting purposes.

Since the aforesaid reactions take place with diminution of volume, they are caused to take place under high pressure: The temperatures can vary according to the desired reaction within wide range and although in some cases it is necessary to keep the temperature around 250° C., in other cases it may be necessary to work above 450° C. In each case only part of the mixture passed over the catalyst reacts and consequently it is advantageous to pass the same mixture again over the catalyst, after previous separation of already formed compounds.

For preparing methyl alcohol, ethyl alcohol and higher alcohols either alone or together with other oxygenated compounds, in accordance with the process of this invention, a mixture of hydrogen and carbon monoxide or hydrogen and carbon dioxide or hydrogen, carbon monoxide and carbon dioxide, or a mixture of the aforesaid kind in which the hydrogen is wholly or partially replaced by a gaseous hydrocarbon before being passed over the catalyst—which is situated in an annular space—first receives heat from the gases of reaction proceeding from the catalyst and then receives heat from an electric heating device which is centrally disposed in said annular space but separated by a wall from direct contact with the catalyst or from the said wall heated by the catalytic reaction or from both of these sources and having thereby attained the reaction tem-

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perature is passed over the catalyst, afterwards giving up all or the greater part of its heat to the fresh entering mixture, all of said operations taking place in a single apparatus.

The catalysis apparatus which is known from my prior Specification No. 193,789 and does not form part of the present invention, is constituted by a series of at least four concentrically placed tubes, so disposed that while the interior space of the innermost tube constitutes the space in which the electric heat appliance is placed, the annular space comprised between this tube and the next one constitutes the space in which the catalyst is placed and the other annular spaces constituting a heat exchanger. In some cases I use also a space for circulating cold gases along the interior wall of the outside tube, destined to withstand the pressure of the gases.

Such apparatus can be constructed so as to permit the changing of the catalyst by simply removing plugs closing small apertures placed in the closing plates.

To explain the operation of the process of this invention apparatus is illustrated in the annexed drawing, in which 1 is the outside pressure resisting tube (consequently its walls are very thick) 2, 3, 4 are a series of tubes dividing the internal space of tube 1 into four annular spaces shown respectively by the numerals 6, 7, 8 and 9. The electric heating appliance is placed in space 6, the catalyst in 7 while the gases circulate in spaces 8 and 9 as follows: They enter the apparatus through tube 11 and pass through passage 12 into the space 9. They then flow from the lower end to the upper part of space 9 and in their passage are heated by absorbing the heat given out through tube 4 by the gases flowing through space 8. After arriving at the upper part of space 9 they flow through the passage 13 into the space 6. In this space the gases complete their absorption of heat from the electric heating appliance or from heat yielded by the catalysis space 7 through wall 2 (in the latter case the electric heating appliance will be used only for heating the gases at the start) or from both the said sources of heat. Having now attained the reaction temperature, the gases enter space 7, through which they flow from the lower end to the upper part and come into contact with the catalyst. Finally they flow from the upper to the lower part through space 8, where, as mentioned above, they yield their heat to the gases entering and are afterwards discharged through passage 14 into the cooler, by means of tube 15.

The annexed drawing illustrates in the dotted lines, two modifications which can be introduced in the gas circuit. As shown it is possible to have another tube, besides the above said tubes, i.e. tube 5 and consequently space 10. In this case the gases can either enter tube 11 as above, and flow through spaces 9 and 10 as two streams which are united by passing through holes placed in the upper end of tube 5, or they can enter the apparatus through tube 16 at the upper end of the apparatus and flow first through space 10 from the upper to the lower part and then from the lower to the upper part through space 9. In both the cases the successive flow is the same as previously indicated.

To facilitate heat exchange between the gases flowing through the spaces 8 and 9 and through the spaces 6 and 7, the surfaces of the tubes 2 and 4 can be increased by means of ribs, grooves or similar appliances. On the contrary the tube 3 or a part of the same will be constructed, if necessary, of material having low thermic conductivity.

As shown in the drawing, the discharge of the catalyst is accomplished by opening the plug 19, and charging is effected by simply removing one or more plugs similar to 17 and introducing the catalyst through the passages 18.

In addition to facility in changing the catalyst, the most important advantages of the apparatus above described are: the rational utilisation of internal space of the catalysis apparatus, uniformity of temperature in the space containing the catalyst, facility of adjusting this temperature within required limits and large recovery of heat. Moreover the temperature of the pressure resisting tube is very low; consequently its mechanical resistance is excellent.

In using the apparatus described it is desirable to cause the reactions to take place in a closed circuit of apparatus: This circuit should consequently comprise also a condenser for cooling the gases which have reacted, one or more apparatus for separating the already formed compound or compounds from the uncombined gases and an apparatus for circulating the gases. If necessary other apparatus, such as oil separators, gas purifiers etc. can be inserted into this circuit.

Fresh gas mixture is continuously admitted into the circuit in a quantity corresponding to the separated compounds, so that all of the operations accomplished in the apparatus take place continuously.

I wish it to be understood that I do not claim as broadly novel the utilisation of the heat of the reaction now in question

for heating the fresh gaseous reaction mixture, 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 process for preparing methyl alcohol, ethyl alcohol and higher alcohols either alone or together with other oxygenated organic compounds, by means of catalytic reactions between compressed and heated carbon monoxide and hydrogen, characterised by the fact that the mixture before being passed over the catalyst, which is situated in an annular space, first receives heat from the gases of reaction proceeding from the catalyst and then receives heat from an electric heating device which is centrally disposed in said annular space but separated by a wall from direct contact with the catalyst or from the said wall heated by the catalytic reaction or from both of these sources and, having thereby attained the reaction temperature, is passed over the catalyst, afterwards giving up all or the greater part of its heat to the fresh entering mixture, all the aforesaid operations taking place in a single apparatus.

2. A process as claimed in Claim 1, characterised by the fact that carbon dioxide or a mixture of carbon monoxide and carbon dioxide is used instead of carbon monoxide.

3. A process as claimed in Claim 1 or 2, characterised by the fact that a gaseous hydrocarbon or a mixture of gaseous hydrocarbon and hydrogen are used instead of hydrogen.

4. A process as claimed in the preceding claims, characterised by the fact that the apparatus in which the catalysis is caused to take place is constituted by a series of at least four concentrically placed cylindrical tubes, of which the innermost contains the space in which the electric heating appliance is placed, the annular space comprised between this tube and the successive one contains the catalyst and the other annular spaces constitute a heat exchanger and in certain cases also one or more spaces through which cold gases flow, thus maintaining the interior walls of the pressure resisting tube at a low temperature; all these tubes of the said apparatus being so disposed that the gases before entering the catalysis space are partially heated by the heat contained in the gases issued from the catalysis space, this heating being completed either by heat from the catalysis space or from an electric heating appliance or by both, and having thus attained the reaction temperature the gases are passed over the catalyst, yielding afterwards the largest part of their heat to the gases entering the catalysis tube.

5. A process as claimed in the preceding claims, characterised by the fact that the apparatus referred to in Claim 4 forms part of a closed circuit of apparatus permitting the removal of the products already formed and to pass again over the catalyst the gas mixture which has not reacted, after previous addition of fresh mixture corresponding in quantity to the separated compounds, all of these operations taking place continuously in the apparatus of the closed circuit.

6. The process for the production of methyl alcohol, ethyl alcohol and higher alcohols either alone or together with other oxygenated organic compounds, substantially as described.

Dated this 21st day of May, 1926.

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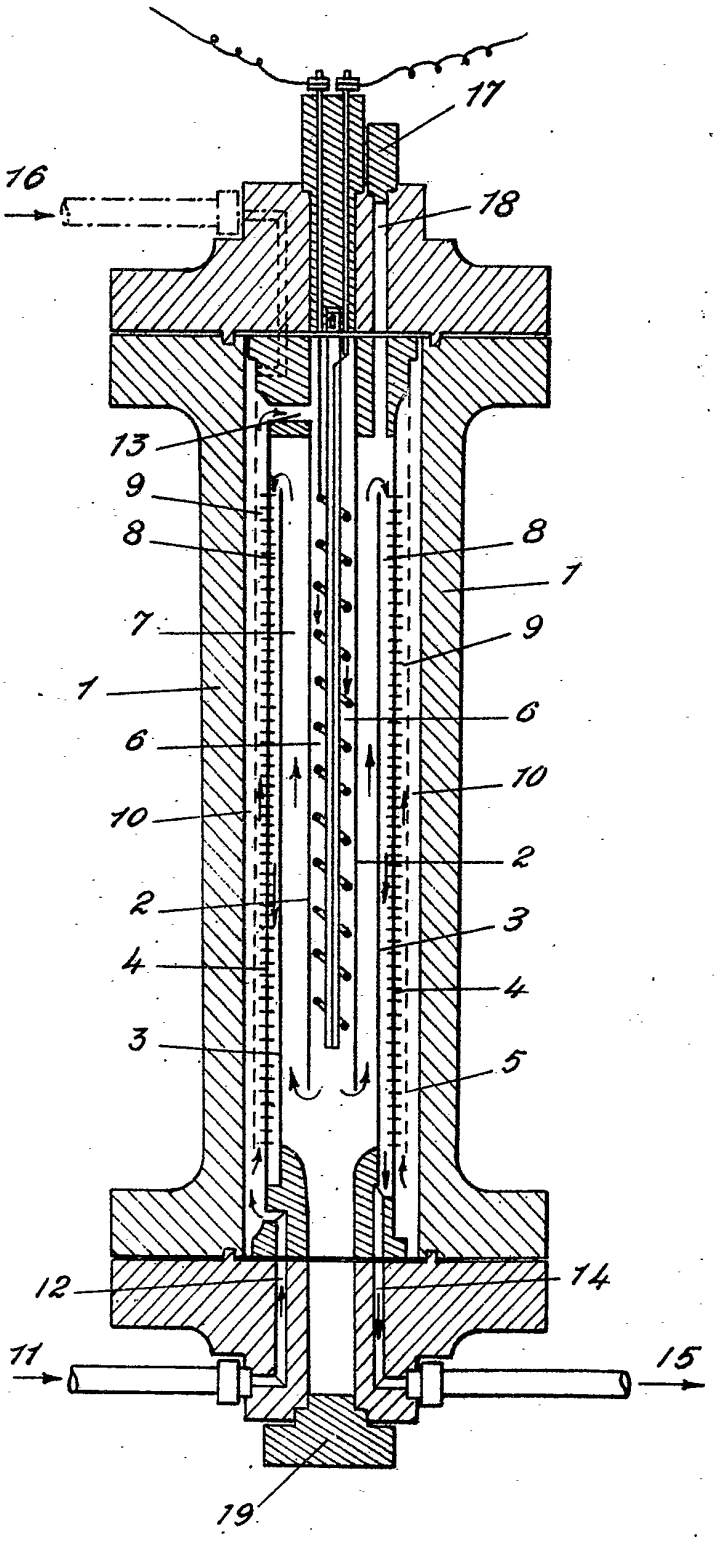

[This Drawing is a reproduction of the Original on a reduced scale.]

Charles & Read Ltd. Photo Litho.