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COMPLETE SPECIFICATION.

Process and Apparatus for the Hydrogenation of Carbon-Monoxide.

We, HEINRICH KOPPERS GESELLSCHAFT MIT BESCHRANKTER HAFTUNG, of Moltkestrasse 29, Essen, Germany, and RHEINPREUSSEN AKTIENGESELLSCHAFT FUR BERGBAU UND CHEMIE, of Homberg, Germany, both Joint Stock Companies organised under the laws of the German Federal Republic, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for the hydrogenation of carbon monoxide and also to apparatus for carrying out this method.

Carbon monoxide hydrogenation is effected by bringing a gas mixture (synthesis gas) containing carbon monoxide and hydrogen into contact with a finely divided catalyst suspended in a suitable liquid, for example a hydrocarbon oil, at elevated temperatures of between approximately 200 and 300° and at high pressure of between approximately 5 and 50 atmospheres, for the purpose of forming mainly hydrocarbons. This method is known by the name "liquid phase synthesis" in scientific literature.

In practice the synthesis gas is forced from below into the column of liquid containing the suspended catalyst. The gas then rises through the liquid in the form of bubbles of a greater or lesser degree of fineness, the desired reactions occurring in these circumstances. Since these reactions are exothermic, it must be ensured that the heat is eliminated to an extent such that there is no disturbing increase in temperature.

As long as the cross-sectional loading in the column of liquid does not exceed a certain value in this liquid phase synthesis, the typical advantages of this method manifest themselves fully. If, however, the load exceeds approximately 25 working litres of gas per square centimeter of reaction area cross-section, a deterioration of the reaction occurs, as has been observed. Experiment has shown that with considerable gas loads there is a downward movement of the liquid, during which certain components of the residual gas, especially carbon dioxide, which are dissolved in the contact oil, pass into the region of the supply of the synthesis gas. There they effect a reduction of the partial pressure of the reaction gases, namely carbon monoxide and hydrogen, and this reduction of the partial pressure reduces the extent of the reaction. This downward movement of the liquid occurs because the bubbles of gas, for example, in the middle of the column, entrain liquid in the upward direction, which liquid then flows down again in the edge regions.

This movement of the liquid from top to bottom is difficult to control. It has already been proposed to avoid such movement by withdrawing the contact oil at the head of the reaction chamber and returning it to the cycle at the bottom, so that there is a co-directional flow of contact oil and synthesis gas inside the reaction chamber. Although it is possible in this way to make the movement of the liquid well-defined, it is not possible to avoid the disadvantage of returning of, for example, carbon monoxide to the inlet of the reaction chamber, unless the gases dissolved in the recycled contact oil are removed by expansion or by other additional measures.

It is an object of the present invention to provide a method for the hydrogenation of carbon dioxide which avoids the above mentioned disadvantage. It is a further object of the present invention to provide apparatus for carrying out such a method.

According to one aspect of the present invention there is provided a method for the hydrogenation of carbon monoxide in which a gaseous mixture of carbon monoxide and hydrogen is passed successively through at least two volumes of a suspension of hydrogenation catalyst in a liquid conventionally used for catalyst suspension in carbon monoxide hydrogenation processes, each volume being such as only to be capable of partially hydrogenating the carbon dioxide in the mixture, and the residual gas mixture and product of hydrogenation occurring in the first of said two volumes are cooled, prior to passing them through said second volume, to a temperature which is most favourable to the optimum further partial hydrogenation occurring in said second volume of the suspension.

According to another aspect of the present invention there is provided apparatus for carrying out the process claimed and comprising a reaction vessel, at least one partition for dividing off the vessel into two compartments which can be filled with liquid contents of the vessel to constitute two volumes each with a free gas space above them, means for passing a gas through one volume so that it issues from the liquid volume in one compartment into the free gas space thereabove, means for transferring the issued gas from said free gas space so that it passes through the volume in the other compartment and means for cooling said gas as it is being so transferred.

The invention also provides the aforesaid apparatus when each compartment has therein as liquid volume a suspension of hydrogenation catalyst in a liquid conventionally used for catalyst suspension in carbon monoxide hydrogenation processes in a volume sufficient to leave a free gas space in the compartment and only to hydrogenate partially the carbon monoxide in a gaseous mixture of carbon monoxide and hydrogen passed therethrough.

By the method of the invention the existing methods of liquid phase synthesis can be obviated by dividing up the amount of hydrocarbon oil (contact oil) required for the suspension of the catalyst into a number of partial amounts separated by the partitions in the apparatus of the invention. The synthesis gas, after it has come into contact with the first partial amount of contact oil in the form of small bubbles, is in the first instance collected before being supplied, together with a part of the products formed during the reaction, to a second or third or further partial amoumts of contact oil, and is then finally divided again, while by cooling to eliminate the reaction heat forming in it, each partial amount of contact oil is individually kept at a temperature which is the most favourable for the reaction of the synthesis gas entering this partial amount of contact oil at any time.

It is true that there is still a certain return of residual synthesis gas within the partial amounts of contact oil in the case of large gas loads, but the disturbing influence of these returned residual synthesis gases may be made practically as small as desired if the total amount of contact oil is divided up into a larger number of partial amounts. The concentration difference between the gas entry to such a partial amount and the gas discharge are then so small that returned residual synthesis gases do not produce a disturbing reduction of the partial pressures of carbon monoxide and hydrogen. Very different methods may be employed to cool the individual partial amounts. It is possible to provide cooling devices within the partial amounts themselves, which devices operate, for example, with the production of useful steam. It is also possible to divert the supply of liquid of such a partial amount through an external cycle and provide a cooling device in this external cycle. By adjustment of the speed of circulation it is also possible to ensure that the finely divided catalyst is always satisfactorily held in suspension and that no disturbing deposits form.

The division of the total amount of contact oil into a number of partial amounts also has the advantage that a different catalyst concentration can be maintained within each partial amount, in order in this way to obtain favourable adaptation of operating conditions to the residual concentration of synthesis gas at any given time.

Further features of the method and apparatus of the present invention will readily be apparent from the following description of a number of embodiments of apparatuses for performing the method according to the invention which are illustrated in the accompanying drawings, in which:—

Figure 1 shows an apparatus employing external cooling, the cooling acting on a mixture of contact oil and synthesis gas.

Figure 2 likewise illustrates an apparatus employing external cooling, in which the cooling is active only on the circulating contact oil.

Figure 3 shows an apparatus with internal cooling.

The reaction vessel (Figure 1) in which the reactions of the carbon monoxide with the hydrogen to form hydrocarbons take place is denoted by reference 1. This is advantageously a cylindrical vessel which has a sufficient resistance to pressure. The reaction vessel has two conical intermediate bottoms 2, the apexes of which are directed in the downward direction. The contact oil is divided at the bottom of the reaction vessel and the other on the respective intermediate bottoms 2. A suitable catalyst which accelerates the hydrogenation reactions is suspended in finely divided form in this contact oil. The fresh synthesis gas is taken through the pipeline 4 through the heat exchanger 5, in which its temperature is brought to the temperature most favourable for the reaction, by heat exchange with hot residual gas coming through the pip 6. The synthesis gas then flows through the pipe 7 into a mixer 8, where it is mixed with contact oil which is withdrawn from the reaction vessel 1 through the pipe 9. The mixture of contact oil and synthesis gas in which the hydrogenation reactions already begin then passes into the cooler 10, which is so arranged that it withdraws from the mixture precisely the heat which was newly developed in consequence of the hydrogenation reactions. The cooling device is constructed, for example, as a steam boiler, to which the boiler feed water is fed through the pipe 11 and from which the steam generated is withdrawn by way of the pipe 12. The mixture of contact oil and synthesis gas, the temperature of which has been regulated, then passes through the pipe 13 into the reaction vessel 1 and there it is introduced through a spray tube 14 into the supply of contact oil present there. During the passage through the contact oil, further hydrogenation reactions occur, so that finally a certain percentage of the carbon monoxide and hydrogen originally contained in the synthesis gas is consumed. The temperature of the lowermost partial amount of contact oil is regulated in consequence of the fact that the steam withdrawal from the cooling device 13 is regulated with the aid of the regulating valve 15, the position of which is dependent on the temperature of the temperature sensing means 16.

The synthesis gas which has not been consumed in the lowermost partial amount of contact oil rises into the free space 17 above the same and then passes through the pipe 18 into the mixer 8*a*, in which it is mixed with the contact oil withdrawn through the pipe 9*a* from the next highest partial amount. There further reaction again takes place between the active constituents of the synthesis gas, as already described previously.

In the same way the residual synthesis gas escaping from the second amount of contact oil is in turn brought into contact with the contact oil of the next highest stage, the procedure being exactly the same as already described previously.

The reaction mixture consisting mainly of the resulting hydrocarbons, carbon dioxide and water vapour, and residual amounts of carbon monoxide and hydrogen, escapes through the pipe 20 from the reaction vessel, then passes into a cooler 21, constructed as a steam generator. The feed water is fed to the cooler through the pipe 22. The steam is withdrawn through the pipe 23 and combined with the steam originating from the other coolers. The condensate accumulating in the cooler 21 is collected in a tank 24 and passes through the siphon pipe 25 back into the uppermost partial amount of contact oil. The remaining mixture of gas and vapours passes through the pipe 6 into the heat exchanger 5 and is taken from there through a pipe 26 into another cooling device, which is not shown here and in which the hydrocarbons are separated from the other gaseous constituents of the mixture.

It is important that the liquid levels in the individual partial amounts of contact oil should be kept constant. In the case of the uppermost partial amount of contact oil, this is effected by the fact that the liquid level indicator 27 acts on a regulating valve 28 which regulates the cooling capacity of the cooler 21, namely in such manner that when the liquid level drops there is a more intensive cooling, that is to say a greater formation of condensate.

The liquid levels of the other lower partial amounts are kept constant by the fact that from the higher partial amount contact oil can be drained off into the next lowest partial amount by means of the level indicator 29 by way of valves 30, if there is any drop in the liquid level.

It is necessary from time to time or even continually to introduce fresh contact oil into the system and withdraw a corresponding fraction of consumed oil, in order that the activity of the catalyst suspension may remain unchanged. The supply of fresh catalyst suspension is effected through the pipe 31, the withdrawal through the pipe 32.

In the apparatus shown in Figure 2, the fresh synthesis gas is returned to the heat exchanger 5 by way of the pipe 4, in order to bring its temperature to the most favourable value for the synthesis. The synthesis gas then passes through the pipe 40 to a distributor pipe 41, into which the pipe 42 carrying the contact oil discharges. The retion vessel 1 again has two intermediate bottoms, but they are substantially level. The contact oil is withdrawn from each partial amount through the pipe 43, then taken through the cooler 44 and finally forced by the pump 45 into the pipe 42. In this case, therefore, a mixture of contact oil and synthesis gas enters the lowermost partial amount from below, it being ensured that the pipeline through which the mixture flows is as short as possible, in order that the exothermic hydrogenation reactions should take place as far as possible only within a relatively large liquid volume. With this form of performance as well, regulation of the cooling effect of the cooler 44 is effected by means of the temperature of the partial amount of contact oil, namely in this case by way of a regulating valve 45 in the feed water line 46.

The non-converted synthesis gas is withdrawn from the free space above the liquid through the pipe 47 and introduced into the contact oil stream, which is forced into the next highest partial amount by means of the pump 45*a*. This stream of oil has been withdrawn in exactly the same manner as partial amount of contact oil through the already described, from the next highest pipe 43*a* and regulated in respect of its temperature in a cooler 44*a*. The process already described is repeated in exactly the same manner in the next highest partial amount. The mixture of gas and vapours finally escapes from the rection vessel through the pipe 20, passes into the cooler 21 and hence through the pipe 6 to the heat exchanger 5. The condensate passes through the condensate tank 24 and the siphon tube 25 back into the uppermost partial amount of contact oil. The liquid level of the uppermost partial amount is monitored by means of the level indicator 27. The latter simultaneously regulates the valve 48 in the feed water line leading to the cooler 21. The steam formed in the cooler 21 is again withdrawn through the pipe 23 and combined in manner not shown with the steam produced in the individual cooling devices.

Between the individual partial amounts are connecting lines 49, through which a certain amount of contact oil from one partial amount can pass into the lower partial amount if the level regulator 50 operates a regulating valve 51 accordingly.

Used contact oil is removed from the process through the pipe 52. Fresh contact oil is introduced into the cycle through the pipe 53.

In the embodiment shown in Figure 3, the cooling devices are disposed inside the reaction vessel. The reaction vessel 1 has two intermediate bottoms, which converge conically in the downward direction but which both have an opening 60 at the bottom. Each partial amount of contact oil is at a level such that its surface passes just into the region of the opening 60. The synthesis gas arrives through the pipe 4 by way of the heat exchanger 5 and the pipe 61 and enters the lowermost partial amount of contact oil from below and is distributed there in the form of fine bubbles. Internals 62 ensure that there is the most uniform possible distribution of the gas bubbles over the entire cross-section of the liquid. The hydrogenation reactions taking place in the contact oil generate heat which is eliminated immediately at the point of its development by means of the cooling device 63. The cooling device is constructed as a steam generator in this case too. Its cooling capacity is adapted to the conditions at any given time by regulating the feed water supply by means of the valve 64. The non-reacted synthesis gas collects in the space 65 between the surface of the contact oil and the intermediate bottom and is then forced through the opening 60 into the next highest partial amount, intimate mixture of the synthesis gas with the contact oil taking place. The distribution of the gas and the cooling of the oil is in these circumstances effected in the same way as already described. This process may be repeated once more or, if desired, a number of times.

The cooling of the mixture of gas and vapours emerging from the reaction vessel is effected in the same way as described in connection with Figure 2.

In the above-described exemplified embodiments, division of the contact oil into three partial amounts has been shown. This type of division is in on way necessary however. In some cases it will be sufficient to divide the contact oil into two partial amounts only, while in other cases division into four or more partial amounts will be preferable.

A characteristic feature of the method according to the invention is that the synthesis gas which has already passed through contact oil is collected in a number of intermediate stages without separation of the hydrocarbons which have formed in the meantime. In this way, cooling and reheating of the synthesis gas, which would influence the economy of the complete process, is avoided.

WHAT WE CLAIM IS:—

1. A method for the hydrogenation of carbon monoxide in which a gaseous mixture of carbon monoxide and hydrogen is passed successively through at least two volumes of a suspension of hydrogenation catalyst in a liquid conventionally used for catalyst suspension in carbon monoxide hydrogenation processes, each volume being such as only to be capable of partially hydrogenating the carbon monoxide in the mixture and the residual gas mixture and product of hydrogenation occurring in the first of said two volumes are cooled, prior to passing them through said second volume, to a temperature which is most favourable to the optimum further partial hydrogenation occurring in said second volume of the suspension.

2. A method as claimed in Claim 1 in which said cooling occurs to such an extent as to extract from said residual gas mixture and hydrogenation products substantially all

the heat of reaction developed during the partial hydrogenation occurring in the first of said two volumes.

3. A method as claimed in Claim 1 or 2 in which prior to passage through the first of said hydrogenation catalyst suspension volumes the gaseous mixture is brought to an initial temperature which is most favourable to optimum initial partial hydrogenation occurring in the said first volume.

4. A method as claimed in Claim 3 in which the gaseous mixture is brought to said initial temperature by heating it with the gas which issues from the final volume of the hydrogenation catalyst suspension.

5. A method as claimed in any of the preceding claims in which the gaseous mixture is passed successively through three or more volumes of hydrogenation catalyst suspension and of the residual gas mixture and hydrogenation product issuing from each intermediate partial hydrogenation stage is cooled to a temperature most favourable to optimum partial hydrogenation in the next partial hydrogenation stage.

6. A method as claimed in any of the preceding claims in which different concentrations of catalyst are maintained in the different volumes of the suspension.

7. A method as claimed in any of the preceding claims in which a stream of suspension is continuously withdrawn from and injected back into a volume of suspension and the gaseous mixture to be hydrogenated by the said volume is injected into and suspension stream, cooling being performed on said withdrawn stream.

8. A method as claimed in Claim 7 in which said stream is withdrawn from the bottom of said volume and injected back into said volume near the said bottom.

9. A method as claimed in Claim 8 in which cooling of said volume is carried out after injecting the gaseous mixture into the withdrawn stream.

10. A method as claimed in Claim 7 in which said stream is withdrawn from the top of said volume and injected back into said volume at the bottom thereof.

11. A method as claimed in Claim 10 in which cooling of said volume is carried out before injecting the gaseous mixture into the withdrawn stream.

12. A method as claimed in any of Claims 7 to 11 in which the volumes of suspension are non-contiguous and a gas space exists above each volume and the gaseous mixture and product of hydrogenation to be passed to the next volume is withdrawn from this gas space.

13. A method as claimed in Claim 12 in which the volumes of suspension are maintained substantially equal by transferring of suspension from one volume to another in response to variations in the interface between the suspension and gas space above it.

14. A method as claimed in any one of Claims 7 to 14 in which loss of a catalyst suspension volume during processing is made good by addition of fresh suspension into the withdrawn stream.

15. A method as claimed in any one of Claims 1 to 6 in which cooling is performed within each volume of catalyst suspension.

16. A method as claimed in Claim 15 in which a part of each volume of catalyst suspension is contiguous with a part of another volume with a free gas space existing between non-contiguous parts of consecutive volumes, the gaseous mixture and product of hydrogenation issuing from one volume into said free gas space forcing itself from one volume to the next through the contiguous parts of said volumes.

17. A method for the hydrogenation of carbon monoxide as claimed in Claim 1 and substantially as herein described.

18. The hydrogenation products of carbon monoxide when obtained by the method claimed in any of the preceding claims.

19. Apparatus for carrying out the process claimed in Claim 1 and comprising a reaction vessel, at least one partition for dividing off the vessel into two compartments which can be filled with liquid contents of the vessel to constitute two volumes each with a free gas space above them, means for passing a gas through one volume so that it issues from the liquid volume in one compartment into the free gas space thereabove, means for transferring the issued gas from said free gas space so that it passes through the volume in the other compartment and means for cooling said gas as it is being so transferred.

20. Apparatus as claimed in Claim 19, each compartment having therein as liquid volume a suspension of hydrogenation catalyst in a liquid conventionally used for catalyst suspension in carbon monoxide hydrogenation processes in a volume sufficient to leave a free gas space in the compartment and only to hydrogenate partially the carbon monoxide in a gaseous mixture of carbon monoxide and hydrogen passed therethrough.

21. Apparatus as claimed in Claim 19 or 20 in which the reaction vessel is fitted with a conduit through which liquid from a liquid volume is arranged to be drawn and passed back into said volume, a pump for so passing said liquid from said volume through said conduit and means for injecting the gas into said conduit.

22. Apparatus as claimed in Claim 21 in which said conduit is also fitted with a cooler constituting the means for cooling the gas injected into the conduit.

23. Apparatus as claimed in Claim 21 or 22 in which a partition and also the bot-

tom of the reaction vessel is conically dished and the conduit is positioned so that liquid is withdrawn from the volume at the apex of the cone and injected back into the volume just above the apex of the cone.

24. Apparatus as claimed in Claim 21 or 22 in which a partition and also the bottom of the reaction vessel is undished and the conduit is positioned so that liquid is withdrawn from the volume near the surface thereof and injected back into the volume at the bottom thereof.

25. Apparatus as claimed in Claim 19 or 20 in which a partition is so formed as to allow consecutive volumes to be contiguous and the vessel has coolers so located therein that each volume of liquid is cooled by a cooler.

26. Apparatus as claimed in Claim 25 in which a partition is conically dished but has an aperture at the apex of the cone, which aperture is so positioned as to be coincident with the interface between a liquid volume and its free air space which encircles the cone.

27. Apparatus as claimed in Claim 19 and 20 and substantially as herein described with reference to the accompanying drawings.

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930,656 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale.

Fig. 1

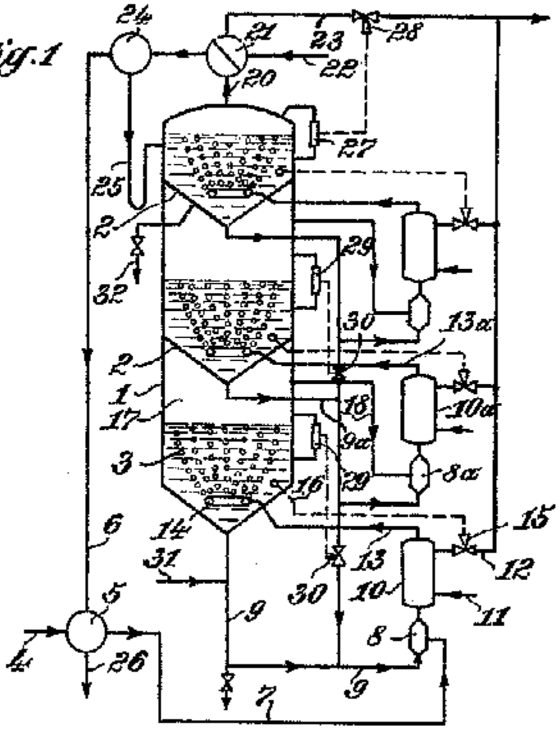

Fig. 2

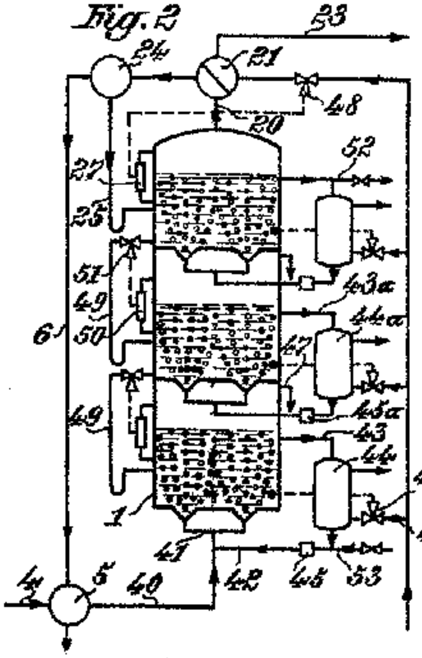

Fig. 3