RESE

PATENT SPECIFICATION

680,241

Date of Application and filing Complete Specification: Feb. 14, 1950.
No. 3756/50.
Application made in Germany on April 29, 1949.
Complete Specification Published: Oct. 1, 1952.

2882

Index at acceptance :—Class 1(i), F3a1x.

COMPLETE SPECIFICATION

Improvements in or relating to the Catalytic Hydrogenation of Carbon Monoxide

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a German joint-stock Company, 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:—

The invention relates to the catalytic hydrogenation of carbon monoxide.

The synthesis of hydrocarbons and oxygen containing organic compounds by the hydrogenation of carbon monoxide in the presence of a catalyst, is an exothermic reaction and uniform utilisation of the whole of the catalyst mass together with a high loading of the synthesis reactor, can only be approached if the temperature of the catalyst mass increases in the direction of flow of the synthesis gases. It is, in general, preferred to pass the synthesis gas downwardly through the catalyst mass in order that high melting paraffins and the liquid products of the synthesis can flow downwardly and be withdrawn without hindering the synthesis process. To obtain a uniform or more uniform utilisation of the catalyst mass, the catalyst temperature must in these circumstances, be at its maximum at the lower end of the reactor.

For the purpose of maintaining the catalyst temperature at the lower end of the reactor at a higher level than the catalyst temperature at the upper end of the reactor, the Applicants have previously proposed the use of a stream of steam as the cooling agent or a heating of a cooling agent which is passed into the reactor at its lower end. For the same purpose the Applicants have proposed, in earlier Patent Applications, the use of cooling agents which do not boil at a uniform temperature throughout their mass, and in particular, a method of cooling the reactor in zones, in which the individual zones comprising cooling tubes or cooling jackets are connected to separate vapour drums. These vapour drums permit the vapor produced by absorption of the reaction heat to be removed at pressures which correspond to the temperatures at which it is desired to maintain the cooling agent in the individual cooling zones, so that the catalyst is cooled to a different degree in the several zones.

In the last described method of cooling reactors, either each reactor has to be provided with a number of vapour drums or as many reactors must be grouped together in parallel as there are cooling zones. Thus a complicated system of pipes must be provided, and in the second case, if one reactor has to be taken off-stream, for example, for the purpose of renewing the catalyst, the other reactors connected with it must also cease operation. The results in a drop in production.

According to the invention, a process for cooling a reactor in the catalytic hydrogenation of carbon monoxide comprises passing a fluid cooling agent through the reactor in indirect heat transfer relation with the catalyst, the cooling agent being passed through two or more cooling zones provided in series, the cooling zones being connected one to the other through throttle means operating to produce a progressive decrease in the direction of flow of the cooling agent.

Of the reactors in use in the catalytic hydrogenation of carbon monoxide, two types are identified in the following description and in the appended claims as the "multi-plate" and the "multi-tubular" types respectively.

The multi-plate type of reactor is provided as a casing within which numerous vertical metal plates or sheets are disposed in substantially parallel relation, the sheets or plates being traversed by horizontal tubes through which the heat transfer or cooling agent is passed. The tubes are connected to a steam drum disposed externally of the reactor casing. The catalyst granules are disposed between the metal plates or sheets and thereby form vertical, substantially rectangular layers through which the tubes carrying the heat transfer medium pass substantially at right angles.

The multi-tubular type of reactor is provided with numerous, vertically-disposed narrow tubes within which the catalyst is contained, the tubes being beaded at their ends into tube plates or being otherwise held in the tube plates in fluid-tight manner. The vertical, catalyst-containing tubes are surrounded by the reactor casing and a heat transfer medium is circulated about the tubes for removal of the heat of reaction. The multi-tubular type of reactor is commonly used when the synthesis is carried out at medium pressures.

In carrying the invention into effect with a reactor of the multi-plate type, two or more cooling zones are provided one above the other in the reactor. Each cooling zone is provided as a bundle of horizontal tubes which tubes pass through the vertical layers of catalyst as hereinbefore described. Each bundle of tubes is provided at each end with a header, the headers of each pair being disposed on opposite sides of the reactor. The headers of adjacent bundles are connected together in series, a throttle or pressure reducing valve being provided in each of the lines between the headers of adjacent zones. Thus the heat transfer medium is passed into the header of one cooling zone and flows in parallel through the bundle of tubes into the other header of the cooling zone. The heat transfer medium then passes from the latter header through a pressure reducing or throttle valve into a header of the next, overlying cooler zone.

According to a modification of the invention in its application to a multi-plate reactor, the pressure reducing or throttle means are provided in each of the horizontal tubes through which the heat transfer medium passes.

In carrying the invention into effect with a reactor of the multi-tubular type, the reactor is divided into a series of superposed cooling zones by one or more plates through which the vertical, catalyst-containing tubes pass, the plate or plates being disposed more or less horizontally within the reactor. The catalyst-containing tubes are expanded or beaded into, or brazed or welded to the horizontal plates or otherwise joined in pressure-tight manner to the plates. The plates are also joined in pressure-tight manner to the surrounding jacket or shell and the superposed cooling zones are connected in series through pressure-reducing valves.

The accompanying diagrammatic drawing illustrates the application of the process of the invention to a reactor of the multi-plate type.

1 is a reactor of the multi-plate type, through which the synthesis gases are passed downwardly, the synthesis products being withdrawn at the lower end of the reactor. The heat of reaction is removed by means of liquid or gaseous heat transfer media under superatmospheric pressure, in particular by means of water under pressure.

The heat transfer or cooling medium flows through parallel bundles of tubes *2–6* which traverse the reactor horizontally. The catalyst is provided in a series of vertical beds or layers within a series of vertically disposed, parallel metal sheets or plates *34*. The individual cooling tubes are mounted at their headers *7–16* which are disposed to the right and to the left of the reactor. Above the synthesis reactor there is provided a vapour drum *17* into which the vapour produced by heating of the cooling medium in the tube bundles *2–6*, passes. The drum *17* is provided with an outlet pipe *18* for removal of the vapour. The cooling medium so removed from the system, is replaced by feeding an equal amount of the cooling medium into the system through the line *19*. Thus, where the cooling or heat transfer medium is water, an amount of water, say condensate water, equivalent to that removed through the line *18* in the form of steam, is fed into the system through the line *19*.

A pump *20* draws the heat transfer or cooling medium from the vapour drum *17* and forces it into the header *7* of the lowermost cooling zone. From the header *7* the heat transfer medium flows in parallel through the tube bundle *2* into the header *8* on the opposite side of the reactor. The heat transfer medium then passes from the header *8* into a vapour separator *21*. The liquid space in the separator *21* is connected through a pressure-reducing or throttle valve *22* to the header *9* of the next cooling zone, whilst the vapour space of the separator *21* is connected through a pressure-reducing or throttle valve *23* with the vapour drum *17*. The vapour evolved due to absorption of heat by the cooling medium in its passage through the tubes *2* of the first cooling zone, is thus separated from the cooling medium before the medium passes through the valve *22* into the header *9* and from there into the cooling tube bundle *3* of the second cooling zone. Such vapour does not therefore interfere with the transference of heat and cannot form vapour pockets within the headers and tubes of the tube bundle *3*.

The cooling medium passes through the bundle of tubes *3* into the header *10* and then into the vapour separator *24*, which allows the liquid cooling medium to flow on through a pressure-reducing or throttle valve *25* into a header *11* of the third cooling zone, whilst that portion of the cooling medium which has been converted into vapour passes through a pressure-reducing or throttle valve *26* directly to the vapour drum *17*. From the header *11* the cooling medium next flows, in similar manner, successively through tube bundle *4*, header *12*, steam separator *27*, pressure-reducing or throttle valve *28*, header *13*, tube bundle *5*, header *14*, steam separator *30*, pressure-reducing or throttle valve *31*, header *15*, tube bundle *6*, and into the header *16* of the last or uppermost cooling zone. From the header *16* of the last cooling zone, the cooling medium passes through a line *33* to the vapour drum *17*. The vapour formed in the cooling zones *4* and *5* passes through the pressure-reducing or throttle valve *29* and *32* into the drum *17*.

The cooling agent in the tube systems *2*, *3*, *4*, *5* and *6* which form five cooling zones placed one above the other, can be kept at a pressure which decreases successively in each of the cooling zones by means of the throttle valves *22*, *25*, *28* and *31*, if the pump *20* passes the cooling agent at a sufficiently high initial pressure into the header *7* of the first cooling zone. In the tube bundle *2*, that is to say, in the first cooling zone, the cooling agent is under the initial pressure imparted by the pump *20*. The pressure on the cooling agent is reduced by passage through the pressure-reducing or throttle valve *22* and the tube system *3* of the second cooling zone operates at this reduced pressure. The valves *25*, *28* and *31* effect further reductions in pressure to the final pressure which is common to the tube bundle *6* and the vapour drum *17*. Thus the pressure in the several heat transfer or cooling zones decreases in the direction of flow of the heat transfer or cooling medium. In consequence, the boiling point of the cooling medium in the several zones decreases zone by zone, in the direction of flow of the medium, with the result that the catalyst is cooled and maintained at a temperature which decreases in the same direction. Thus the temperature of the catalyst increases in the direction of flow of the synthesis gases.

Five cooling sections or zones have been diagrammatically illustrated by way of example in the drawing. The process according to the invention may, however, be carried out with a greater number of cooling zones. Between the several cooling zones, the temperature of the catalyst gradually evens out so that it is possible to realise a temperature which rises uniformly from top to bottom of the catalyst beds or columns.

The throttle or pressure-reducing means according to the invention can also be provided inside the individual cooling tubes, in each case before the tubes enter the second of their two headers in the direction of flow of the cooling medium, that is to say, before the tubes of tube bundles *2*, *3*, *4*, *5* and *6* enter the headers *8*, *10*, *12*, *14* and *16* respectively. This manner of carrying the invention into effect only lends itself to such cases where the fall in pressure and difference in temperature between the individual cooling tube zones may remain the same throughout the synthesis run. If, by reason of decrease in the activity of the catalyst, it is desired gradually to raise the synthesis temperature, then, between the individual headers *8/9*, *10/11*, *12/13* and *14/15* in the construction diagrammatically illustrated by way of example in the drawing, adjustable pressure-reducing or throttle valves must be provided, by means of which the degree of catalyst cooling, and thus the temperature throughout the mass of catalyst, may be altered and adjusted to meet the changed synthesis conditions.

For hydrogenation of carbon monoxide in the presence of a cobalt catalyst, the temperature of cooling agent in the uppermost cooling zone, that is in the tube bundle *6*, is set, according to the length of time the catalyst has been on-stream, for example at 180° C.–190° C. If water is used as the heat transfer or cooling agent, this corresponds to a pressure of 10.4 to 12.9 kg. per sq. cm. With the same type of catalyst, the temperature of the cooling agent in the lowermost cooling zone, that is to say, in the tube bundle *2*, is normally within the range 190° C.–205° C. which range corresponds to a water pressure of 12.8–17.8 kg. per sq. cm. The intermediate cooling zones, namely the zones cooled by the tube bundles *3*, *4* and *5* in the reactor illustrated in the drawings, are operated at water pressures lying between these values.

A particular advantage of the process according to the invention is that one is not confined to a linear temperature increase for it is possible, by appropriate adjustment of the throttle or pressure-reducing valves, to produce an optimum temperature gradient within the reactor. The pump *20* in a synthesis reactor operating with a cobalt catalyst has, apart from frictional resistance, to overcome a difference in pressure of 2.4–4.7 kg. per sq. cm.

Other temperatures and water pressures hold where the hydrogenation of carbon monoxide is effected in the presence of an iron catalyst. In such a case, the temperature of the cooling agent in the uppermost cooling zone may, for example, be within the range 220° C.–230° C. with a water pressure of 23.6–28.5 kg. per sq. cm. whilst the temperature in the lowermost cooling zone may be within the range 240° C.–260° C., with a water pressure of 34.1–47.8 kg. per sq. cm.

What we claim is:—

1. A process for cooling a reactor in the catalytic hydrogenation of carbon monoxide by passing a fluid cooling agent through the reactor in indirect heat transfer relation with the catalyst, in which the cooling agent

passes through two or more cooling zones providing in series, the cooling zones being connected one to the other through throttle means operating to produce a progressive decrease in the pressure from one cooling zone to the next in the direction of flow of the cooling agent.

2. A process according to claim 1, in which the throttle means comprise adjustable pressure-reducing valves.

3. A process according to claim 1, or claim 2, in which the cooling agent is water.

4. Apparatus for carrying out the process according to claim 1, including a reactor of the multiplate type, as hereinbefore defined, provided with two or more cooling zones connected in series, each cooling zone comprising a bundle of tubes through which the cooling agent is passed, and pressure-reducing or throttle means being provided in each of the tubes of each cooling zone.

5. Apparatus for carrying out the process according to any one of claims 1 to 3, including a reactor of the multi-plate type as hereinbefore defined, in which each cooling zone comprises a bundle of tubes through which the cooling agent is passed, a header connected to each end of each bundle of tubes, pipes between the headers to connect the cooling zones in series and an adjustable pressure-reducing or throttle valve in each of said pipes through which the cooling agent flows from one zone to the next.

6. Apparatus according to claim 5, for use with a liquid cooling agent vapourisable under the conditions within the reactor wherein a vapour separator is provided in each of said pipes before the pressure-reducing or throttle valve and a conduit is provided connecting the vapour space of each separator with a vapour drum, each said conduit also being provided with a pressure-reducing valve.

7. Apparatus for carrying out the process according to any one of claims 1 to 3, including a reactor of the multi-tubular type as hereinbefore defined, one or more plates dividing the reactor into two or more cooling zones, which zones are connected in series and a pressure-reducing or throttle valve between adjacent cooling zones through which valve or valves the cooling agent flows from one zone to the next.

8. A process for the catalytic hydrogenation of carbon monoxide, in which the reactor is cooled substantially in the manner hereinbefore described.

9. Apparatus for carrying out the process according to claim 1, substantially as hereinbefore described and illustrated.

EDWARD EVANS & CO.,

14–18, High Holborn, London, W.C.1,
Agents for the Applicants.

Redhill: Printed for Her Majesty's Stationery Office, by Love & Malcomson, Ltd.—1952.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

680,241 COMPLETE SPECIFICATION
1 SHEET

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