PATENT SPECIFICATION

680,821

Date of Application and filing Complete Specification Nov. 8, 1949.
No. 28671/49.
Complete Specification Published Oct. 15, 1952.

(Under this application which was originally made under Section 91 of the Patents and Designs Acts, 1907 to 1946 a Specification was laid open to public inspection on June 8, 1950.)

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

COMPLETE SPECIFICATION

Process and Apparatus for the Catalytic Hydrogenation of Carbon Monoxide

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

In carrying out the catalytic hydrogenation of carbon monoxide for the manufacture of hydrocarbons and/or oxygen-containing derivatives thereof, large quantities of heat are evolved which have to be removed as quickly and completely as possible, as otherwise the synthesis temperature increases to such an extent that there is an extensive production of methane and other hydrocarbons of low molecular weight. In practice, for carrying out the carbon monoxide hydrogenation, synthesis reactors are used which are provided with an effective heat exchange device, for example, in the form of a system of tubes. The built-in cooling tubes have flowing through them water or other cooling liquids, for example, hydrocarbons, which take up the heat evolved in the synthesis.

For technical reasons, water cooling is generally preferred. Boiling water, because of its high heat of vaporisation, offers, as cooling agent, one of the surest means for the removal of the considerable amount of heat evolved during the reaction, effective removal of such heat being of decisive importance in the synthesis. Furthermore, boiling water enables the heat of reaction so removed, to be converted into useful steam in a simple and ready manner. Each synthesis reactor, or each group of synthesis reactors, is provided for this purpose with a steam drum connected to the system of cooling tubes in the synthesis reactor. Convection currents and local formation of steam result in the necessary water circulation inside the cooling-tube system. The steam generated is continuously drawn off from the steam drum mounted above the synthesis reactor, so that the cooling temperature may be regulated, in known manner, by regulating the pressure at which the steam is withdrawn.

Modern synthesis reactors for the hydrogenation of carbon monoxide generally operate with the catalyst provided in thin, vertical layers or pockets or in narrow vertical tubes. The synthesis gas is passed downwardly through the pockets or tubes. The entrant synthesis gases are so extensively converted in the upper part of each vertical layer or column of catalyst that approximately the whole of the gas conversion hitherto obtained in the reactor has been effected in the upper half of the vertical layer or column of catalyst, whilst the lower half, for all practical purposes, has not participated in the conversion, and has hitherto been considered as a catalyst reserve. In some circumstances this lower half of the catalyst filling can even produce undesired effects, for example, the hydrogenation of olefinic hydrocarbons already formed to paraffin hydrocarbons or the formation of carbon dioxide by the following reaction: $CO + H_2O = CO_2 + H_2$.

In the lower part of the catalyst filling no further appreciable conversion can take place, since the temperature which is maintained constant throughout the whole layer or column of catalyst, is no longer sufficient, in the lower part, to effect conversion of the residual synthesis gases. To obviate this disadvantage, the layers or columns of catalyst have, in the hydrogenation of carbon monoxide, already been operated with a temperature rising in the direction of the gas flow. In this way the upper part of each layer or column of catalyst has been maintained at the optimum temperature for the conversion of the freshly entering gas, whilst the temperature in the lower part of the layer or column of catalyst has been raised to such an extent, that the residual and unconverted part of the synthesis gases has also been converted to a large extent.

To carry out this method of operation, the tubes or pockets containing the catalyst were cooled by flowing steam or by hydrocarbon fractions the individual components of which boil over a broader temperature range.

This method of operation represents a further development of the so-called progressive or multi-stage synthesis. This, as is known, is operated with 2 to 3 synthesis reactors connected in series all filled with the same catalyst mass, but operated at progressively rising temperature. There is a basic difference only in so far that in this known multi-stage synthesis, before passing into the next reactor, the synthesis products formed in the previous reactor are removed wholly or in part from the gas stream by condensation. When the temperature of the layers or columns of catalyst in the direction of the gas flow is raised in a single reactor this possibility does not exist. The synthesis products formed in the cooler catalyst zone must be carried over in their entirety into the hotter catalyst zones.

The accurate maintenance of a catalyst temperature increasing in the direction of the gas flow presents appreciable difficulties, in particular as in all tubes or pockets, as uniform a temperature gradient as possible is desired. It has now been found that a more regular rise in synthesis temperature throughout the whole catalyst filling of a reactor can be achieved if the reactor is provided with a number of zones each of which can be cooled independently of the others. This method can be used for synthesis reactors operating at pressures below and above atmospheric pressure.

According to the invention therefore, a process for the production of hydrocarbons and/or oxygen-containing derivatives thereof by the catalytic hydrogenation of carbon monoxide, includes the step of indirectly cooling the catalyst in sections by the evaporation of a liquid or liquids, each section being cooled independently of the other sections in the same reactor and the cooling of the sections being controlled to maintain a catalyst temperature which increases in the direction of flow of the synthesis gases.

It is of particular advantage that existing synthesis plants can be readily converted for operation in accordance with the invention. Each synthesis reactor must then have, in addition to the one steam drum hitherto provided, a further n^{-1} steam drums, when the synthesis operation is to be carried out with n cooling zones. The only further alteration required is the installation of a few pipes for the cooling medium.

No additional steam drums are required if several reactors are connected together in a number equal to the number of cooling zones provided in each reactor. The cooling medium circuits of all reactors are similarly disposed in relation one to another in respect of their zone temperature, and are combined into appropriate cooling systems, each system being connected to one of the steam drums already provided above the synthesis reactors.

The process according to the invention may be carried out particularly advantageously with synthesis reactors in which the catalyst is contained in vertical rectangular pockets, which are bounded by metal plates or sheets and traversed, perpendicularly to the surface of the plates or sheets, by numerous cooling tubes which are connected to one another outside the furnace by elbows or headers to inlet and outlet pipes. Synthesis reactors of this type are known and are identified in the following description and in the appended claims, as "multi-plate reactors".

In the accompanying drawings, there is diagrammatically shown by way of example, a number of synthesis reactors provided with means for cooling the catalysts in zones according to the invention.

Figure 1 shows, in vertical section, a multi-plate reactor provided with several, separate steam drums;

Figure 2 shows the method of connecting together several multi-plate reactors each provided with a separate steam drum;

Figures 3 and 4 show vertical sections through multi-tubular reactors.

In Figure 1 a synthesis reactor 1 is shown, which is provided with vertical parallel metal plates or sheets 2 between which the catalyst is disposed in known manner. The synthesis gases enter the reactor at 3 and the synthesis products and unconverted gases are withdrawn at 4.

The multi-plate reactor shown by way of example, is provided with three separate cooling systems 5, 6 and 7. Each cooling system comprises a number of cooling tubes which, in a multi-plate reactor, pass through the metal sheets or plates 2 in a direction perpendicular to the surfaces of the sheets or plates, the tubes comprising one cooling system being connected by pipes to the corresponding steam drum. The tubes of the uppermost cooling system 5 are connected by an inlet pipe and by an outlet pipe to the steam drum 8; the tubes of the cooling systems 6 and 7 are connected in similar manner to the steam drums 9 and 10 respectively. Each of the steam drums is connected through a separate reducing valve 11 to a common pipe through which the steam is withdrawn.

In this manner, the pressure on the water in each of the cooling systems may be independently controlled so that the temperature in each of the zones of the reactor traversed by the cooling systems, may be maintained at the desired level. Thus by maintaining the pressure of the highest level in cooling system 7, at the lowest level in cooling system 5 and at an intermediate level in cooling system 6, the temperature of the catalyst is controlled so that it increases in the direction of flow of the synthesis gases.

If the synthesis reactors in which different zones are to be maintained at different temperatures, are operated with only one steam drum each and several reactors are to be grouped together in a multi-stage synthesis, then the nests of cooling tubes and the steam drums are connected in the manner shown in Figure 2.

The synthesis reactors 12, 13 ,14 are each formed, in a similar manner to the reactor shown in Figure 1, with three cooling systems 15, 16 and 17 lying one above the other to provide three cooling zones with each reactor. Steam drums 18, 19 and 20 are provided above the reactors 12, 13 and 14 respectively. As may be seen from the lines of flow in Figure 2, the lowermost cooling zone of each of the three synthesis reactors is connected to the steam drum 18, the middle cooling zone of each reactor being connected to the steam drum 19 while the uppermost cooling zone of each reactor is connected to the steam drum 20. By means of the reducing valves 21 the individual steam drums may be connected to a common withdrawal pipe 22.

Though the method according to the invention may be carried out most simply with synthesis reactors operated at normal atmospheric pressure, it is no way limited to the use of such reactorss. Synthesis reactors which are operated at superatmospheric pressures may also be cooled in zones in accordance with the invention. Such reactors may be of the multi-plate type hereinbefore described or they may be of the multi-tubular type. By the term " multi-tubular reactor " is to be understood a reactor in which the catalyst is contained in narrow tubes which are beaded or otherwise held in fluid-tight manner at both ends in tube plates and are surrounded by the shell of the reactor, through which the cooling agent is passed. If multi-tubular reactors of this type are, during operation, to be cooled in zones or sections according to the method of the invention, further intermediate plates or floors have to be built into the reactor. The zones or sections formed by the intermediate plates or floors are each provided with an outlet and inlet for the cooling agent. It is in this case advantageous to use individual reactor sections 23, 24 and 25 (Figure 3) mounted with their respective end plates or floors directly adjacent. The synthesis gases are passed into the reactor through a pipe 26, and the synthesis products, including the unconverted gases are withdrawn at the bottom of the reactor through an outlet 27. The uppermost reactor section 23 is provided with a circuit 28 for the cooling medium, by means of which the steam generated in this circuit passes out of the steam drum 29 through a reducing valve 30 into the main steam pipe 31. In a similar manner, the two reactor sections 24 and 25 are cooled by the cooling medium in circuits 32 and 33 respectively, which are connected through reducing valves 34 and 35 to the main steam pipe 31. By appropriate regulation of the reducing valves 30, 34 and 35, the temperature at which the cooling agent in each of the circuits 28, 32 and 33 boils, may be varied, and the temperature of the catalyst in the reactor sections 23, 24 and 25 may be controlled so as to increase in the direction of the gas flow.

It is also possible to provide the individual reactors sections in separate housings or shells, as is shown schematically in Figure 4. The reactor sections 36, 37 and 38 are provided with separate circuits for the cooling agent and the circuits are connected through reducing valves 39, 40 and 41 to a steam outlet pipe 42. By regulating the reducing valves, the pressure in each of the circuits may be varied so as to maintain the temperature in each of the three reactor sections at the desired level. The synthesis gases are passed to the first reactor section 36 through the pipe 43 to stream successively through the sections 36, 37 and 38, after which the synthesis products and residual gases are withdrawn through a pipe 44. The reducing valves 39, 40 and 41 are brought into operation in such a way that the lowest temperature of the cooling agent is in reactor section 36 and the highest in reactor section 38. In this way the synthesis operation can be carried out with a catalyst the temperature of which rises in the direction of gas flow.

In order to simplify the illustration, only three reactor sections are shown in the drawings. It will be understood, however, that it is possible to vary this number and to operate the synthesis with a greater number of cooling zones or sections if so desired.

The temperatures maintained in the individual cooling zones in the reactor are dependent upon the conditions of operation of the synthesis, mainly upon the type and age of the catalyst. If cobalt catalysts are used, then for a synthesis reactor operating with three cooling zones, the temperature of the cooling agent, which is preferably water under pressure, in the first or uppermost zone is generally held within the range 170° C. to 185° C. The middle reactor zone is generally operated at a temperature between 180° C., and 195° C., whilst in the lowest zone temperatures within the range 190° C. to 210° C. are generally used. The temperatures are so chosen within the given ranges that between the cooling agent temperatures of the three zones there exist differences of approximately 10° C.

With iron catalysts, higher temperatures for the cooling zones are used. The temperatures are governed by the type of catalyst and by the synthesis pressure.

It is an advantage of the process of zone cooling according to the invention that, with the use of a limited number of cooling zones, a practically uniform rise of catalyst temperature in the direction of flow of the synthesis gas can be obtained. At the positions where the individual cooling zones meet, by virtue of the use of material of good heat conductivity in the construction of the tubes, a levelling out of the difference in temperature of the cooling agent in adjacent zones is effected. In carrying out the invention on a large scale, each reactor will generally be provided with more than three cooling zones. The difference in the temperature of the cooling agent in adjacent zones may then be only 2° C. to 3° C., which differences are decreased in the layers or columns of catalyst to give a substantially uniform increase in temperature in the catalyst mass in the direction of gas flow. The use of water under pressure as the cooling agent is effective to provide a particularly intensive cooling. If, on the other hand a boiling mixture of hydrocarbons is used to produce a catalyst temperature increasing in the direction of the gas flow, then a similarly intensive removal of heat at high temperature levels is not possible.

A carbon monoxide hydrogenation reactor which is cooled by the method according to the invention, provides numerous advantages in synthesis technique.

By activation of catalyst layers which have not previously been used, or which are not completely spent, the same or a higher gas conversion can be obtained with gas loads appreciably higher than those hitherto employed, so that the output of the reactor may be considerably increased. The synthesis temperature, reckoned as an average over the whole catalyst layer, is in this case lower than the temperature of a catlyst bed operated at a uniform temperature. The formation of higher boiling hydrocarbons may therefore be appreciably increased; or it is possible to obtain, in a single stage, a gas utilization previously possible only in multi-stage operation. In this way the formation of methane and other normally gaseous hydrocarbons may, to a large extent, be suppressed.

The conversion of the synthesis gas is, in the process according to the invention, spread substantially uniformly over the whole catalyst layer. In this way not only is better use made of the catalyst, but its life is also lengthened. In addition, there is a corresponding increase in the synthesis yield.

The rise in synthesis temperature necessitated by decrease in the activity of the catalyst, may be carried out in an advantageous manner by the process according to the invention and it may be adapted to the particular properties of individual catalysts.

Finally, in the method of cooling the catalyst according to the invention, synthesis gases may be used, the composition of which, that is to say, the carbon monoxide-hydrogen ratio of which, corresponds to the true utilization ratio. For example it is possible to use synthesis gases having such carbon monoxide-hydrogen ratios that hitherto they could only be processed in a synthesis operation provided with means for recycling the gases, for example, synthesis gases which contain one volume of carbon monoxide per two volumes, or even more than two volumes, of hydrogen. In this manner, a further lowering of the synthesis temperature is possible and the formation of hydrocarbons of greater molecular weight is increased.

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

1. A process for the production of hydrocarbons and/or oxygen-containing derivatives thereof by the catalytic hydrogenation of carbon monoxide, which includes the step of indirectly cooling the

catalyst in sections, by the evaporation of a liquid or liquids, each section being cooled independently of the other sections in the same reactor, and the cooling of the sections being controlled to maintain a catalyst temperature which increases in the direction of flow of the synthesis gases.

2. A process according to claim 1, in which the liquid used for cooling is water under pressure.

3. Apparatus for carrying out the process according to claim 1 or claim 2, which includes a multi-plate reactor, as hereinbefore defined, provided with two or more independent nests of tubes through which the cooling liquid may circulate, each nest of tubes being connected by an inlet pipe and an outlet pipe to a separate steam or vapour drum provided with a pressure reducing valve and the nests of tubes being positioned one above the other in the direction of gas flow through the reactor.

4. Apparatus according to claim 3, in which a number of similar multi-plate reactors, each provided with a steam or vapour drum, are connected in parallel, the number of reactors being equal to the number of nests of tubes provided in each reactor, and the inlet and outlet pipes from corresponding nests of tubes in the reactors being connected to the same steam or vapour drum.

5. Apparatus for carrying out the process according to claim 1 or claim 2, which includes a vertical, multi-tubular reactor as hereinbefore defined, divided into two or more superposed sections, a steam or vapour drum provided with a pressure reducing valve for each section, and inlet and outlet pipes connecting one section with one drum.

6. A process for the production of hydrocarbons and oxygen-containing derivatives thereof by the hydrogenation of carbon monoxide, in which the reactor or reactors is or are cooled in the manner hereinbefore described.

7. Apparatus for carrying out the process of claim 1 or claim 2, substantially as hereinbefore described with reference to Figure 1.

8. Apparatus for carrying out the process of claim 1 or claim 2, substantially as hereinbefore described with reference to Figure 2.

9. Apparatus for carrying out the process of claim 1 or claim 2, substantially as hereinbefore described with reference to Figure 3.

10. Apparatus for carrying out the process of claim 1 or claim 2, substantially as hereinbefore described with reference to Figure 4.

Dated the 7th day of November, 1949.
EDWARD EVANS & CO.,
14—18, High Holborn, London, W.C.1.

**Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1952.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.**

Fig.1

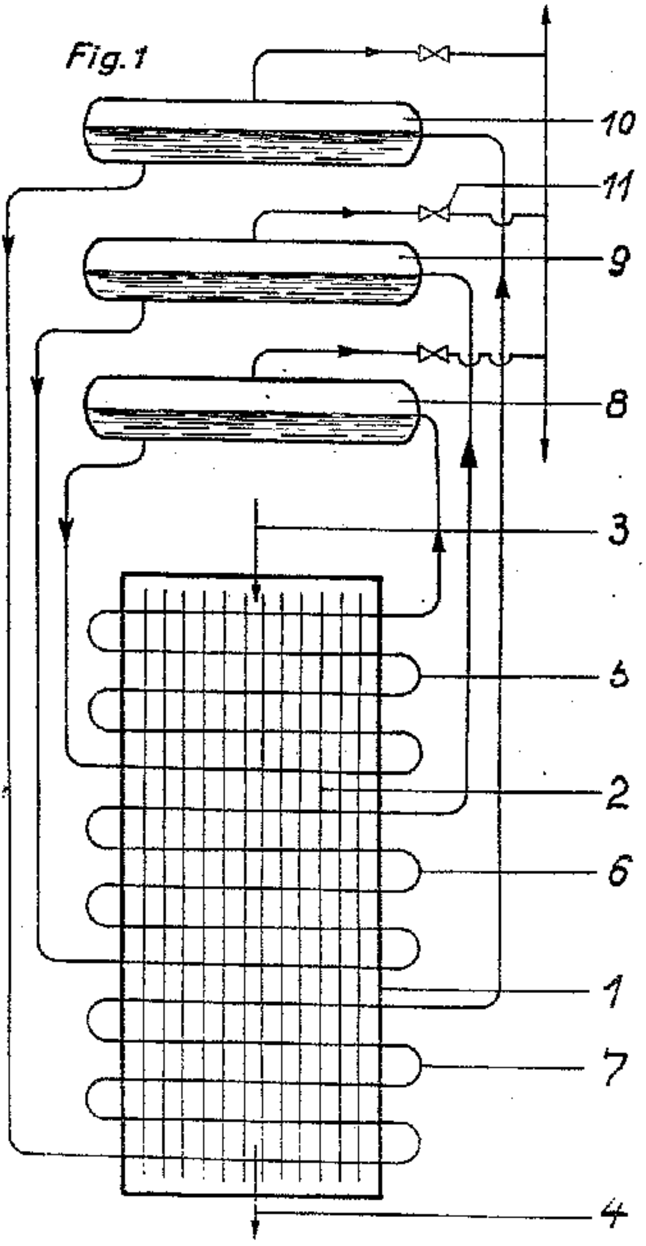
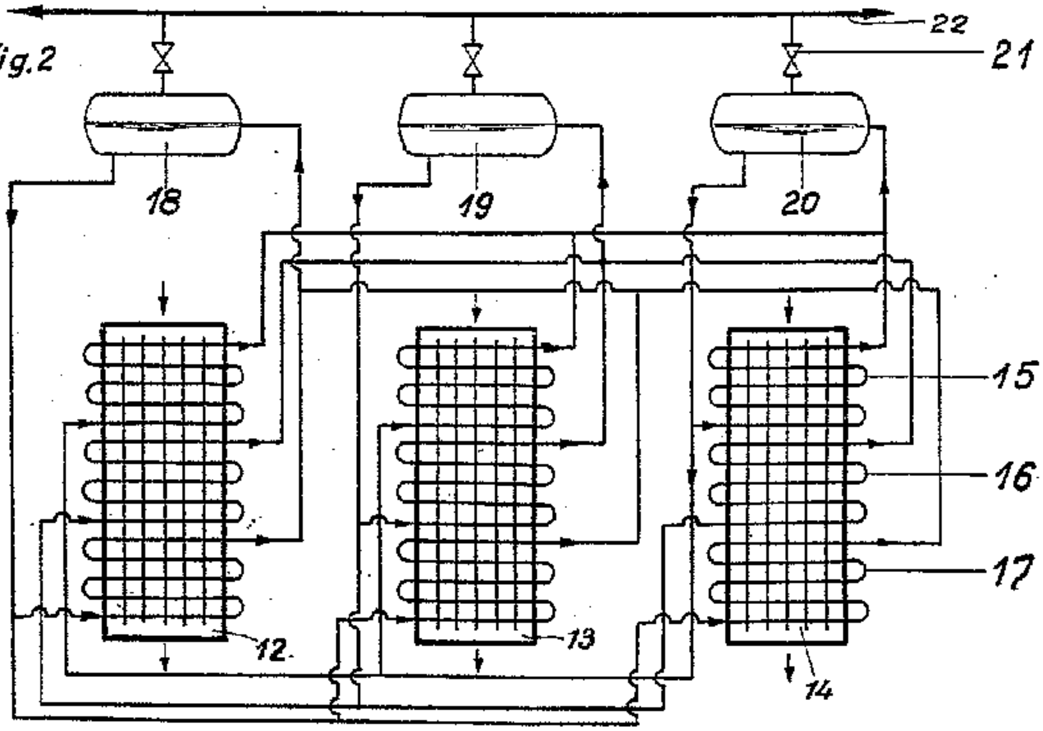


Fig.2

680,821 COMPLETE SPECIFICATION
4 SHEETS *This drawing is a reproduction of the Original on a reduced scale.*
SHEETS 1 & 2

Fig. 2



680,821 COMPLETE SPECIFICATION
4 SHEETS *This drawing is a reproduction of the Original on a reduced scale.*
SHEETS 1 & 2

Fig.1

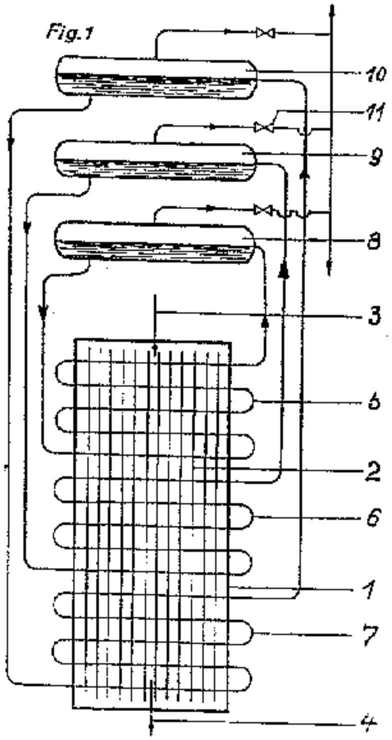
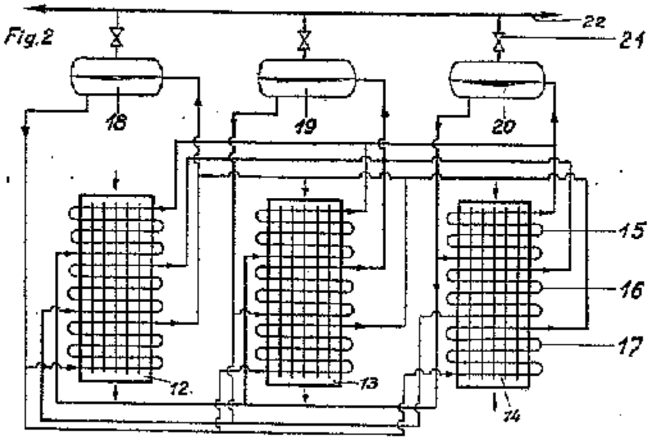


Fig.2



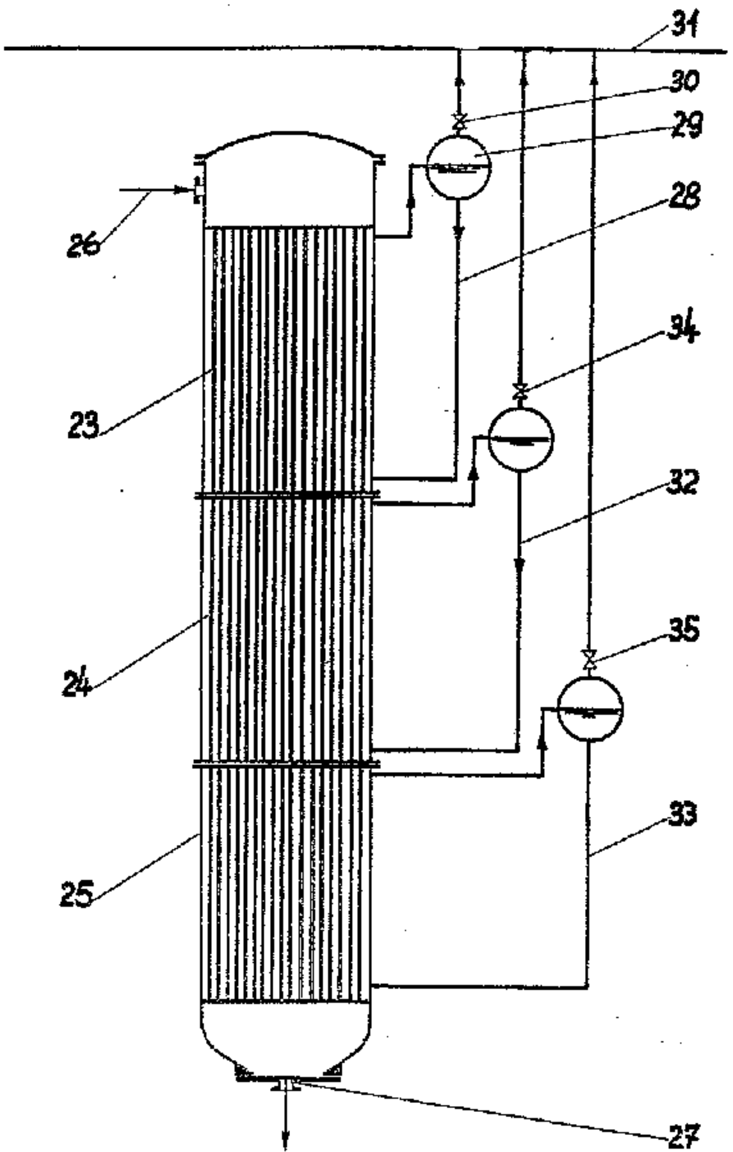


Fig. 3

680,821 COMPLETE SPECIFICATION
4 SHEETS *This drawing is a reproduction of the Original on a reduced scale.*
SHEETS 3 & 4

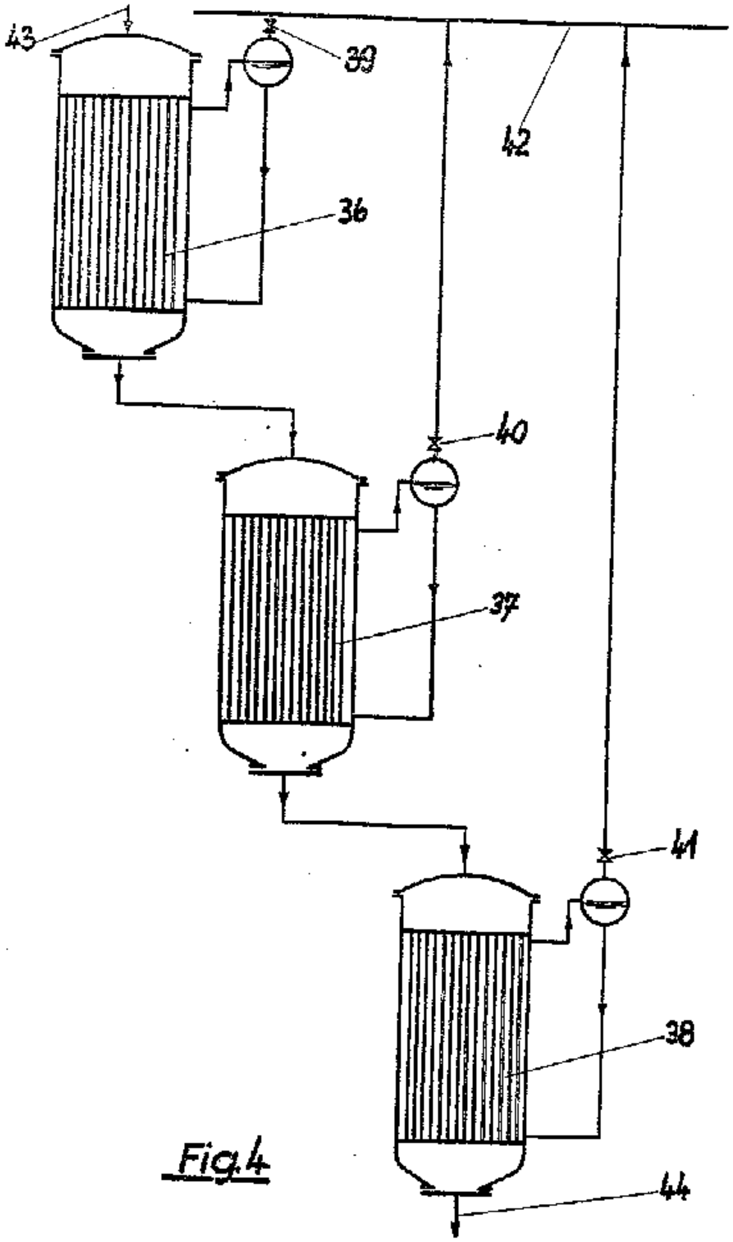


Fig.4

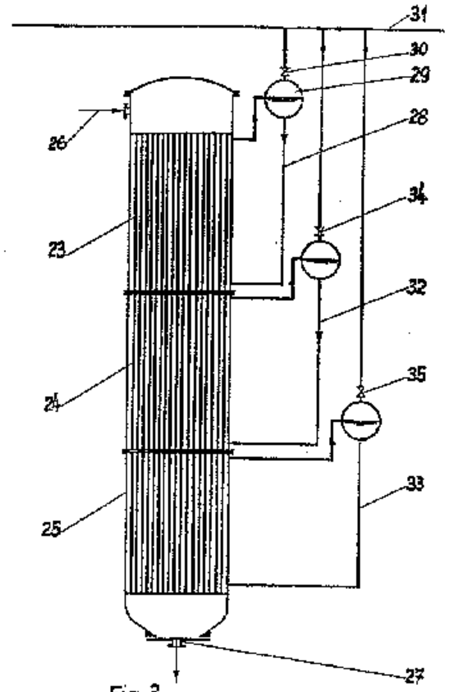


Fig.3

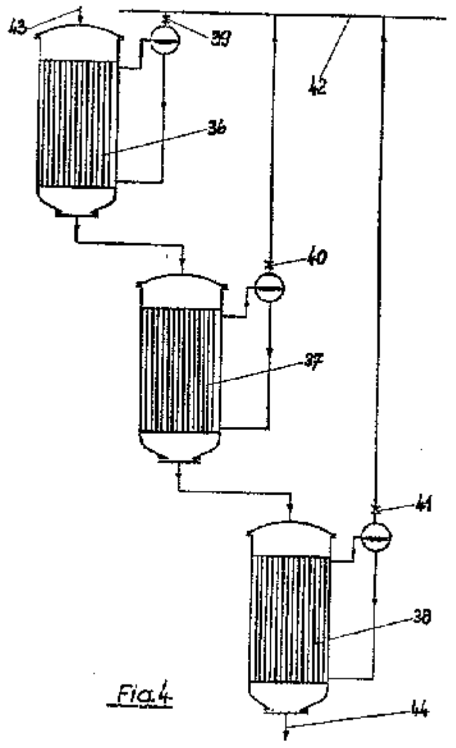


Fig.4