

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Process of and Apparatus for Producing Hydrocarbons

We, METALLGESELLSCHAFT AKTIENGESELLSCHAFT, a Corporation organised under the Laws of Germany, of 45, Bockenheimer Anlage, Frankfurt-on-the-Main, 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:—

10 This invention relates to a process of and an apparatus for producing hydrocarbons by the catalytic hydrogenation of carbon monoxide.

It is known to carry out the catalytic hydrogenation of carbon monoxide, for instance by the Fischer-Tropsch-process, in such a manner that in addition to hydrocarbons, greater or less amounts of oxygenated hydrocarbon derivatives, particularly alcohols, fatty acids or the like are simultaneously obtained. For this purpose reactors are used in which the catalyst is disposed between cooling elements which are narrowly spaced apart and are maintained at a constant temperature by water under pressure. These reactors are of a special, relatively difficult construction and cannot be made in any desired size. Moreover they have a lifetime of about only 5 to 10 years, since the boiling water under pressure has a considerable corrosive effect. Such reactors have a small capacity; in continuous operation they can be charged with only about 100 N-litres (i.e. volume of gas at 0° C. and 760 mm. Hg, dry) of synthesis gas per litre of catalyst per hour. Since the heat of reaction must be removed transversely to the gas passage through the catalyst granules towards the cooling surface, greater quantities of gas would cause an increase of the reaction temperature, which might entail carbon deposits and clogging of the catalyst near the entrance of the gas into the catalyst.

Hitherto the capacity was increased by recycling the synthesis gas through the reactor. However more than twice the normal capacity could not be economically reached. Higher reactor capacities are possible with other known processes using

granulated or pulverulent catalysts maintained in suspension by the flowing gas. In these processes however the heat of reaction must be removed at a constant temperature by coolers operating with boiling water under pressure.

Another known method of operation employs very large quantities of circulating gas to effect cooling. If for instance, working at about 20 atmospheres gauge and using fused iron catalysts, the gas temperature rise may be 10 to 30° C., then 50–150 times the quantity of the feed gas has to be recycled. This renders the process uneconomic, so that it was not adopted in practice.

The process of the present invention aims at enabling the synthesis reactor to operate at a very high capacity with respect to both feed gas and output of hydrocarbons formed; and at simplifying the construction of the reactor.

To this end, the present invention provides a process of producing hydrocarbons, and if desired, oxygenated hydrocarbon derivatives by the catalytic hydrogenation of carbon monoxide, in which synthesis gas containing carbon monoxide and hydrogen is passed through a succession of layers of catalyst, which process is characterised by reducing the temperature of the gas leaving one layer of catalyst by cooling, by an amount approximately equal to or only slightly less than the increase in temperature produced in the layer of catalyst, before said gas traverses the next layer of catalyst.

The invention is preferably carried out in apparatus comprising at least five and preferably more, catalyst layers. The employment of a plurality of catalyst layers eliminates the fundamental drawback of the known process i.e. the necessity of circulating large quantities of gas.

The temperature control according to the invention may be effected, for instance, by leading the gas along cooling surfaces after it has left each individual layer of catalyst. Liquid condensation products, dropping from the catalyst layer or forming on the cooling surfaces, may be removed by conventional

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methods before the gas enters the next catalyst layer.

Preferably only a small part of the hot reaction gas leaving the last catalyst layer 5 is withdrawn from the reactor and worked up in known manner. The bulk of the gas, if necessary after removal of any liquid products such as paraffins, is boosted by a blower or a similar device, and reintroduced 10 into the first catalyst layer. Before this circulating gas enters the first catalyst layer, the temperature of the gas is adjusted to the starting temperature of the reaction e.g. it is reduced by about 10 to 15° C. on its 15 way from the last to the first catalyst layer, for example due to normal heat losses. In the first catalyst layer the circulating gas may react again.

The quantity of gas passing through the 20 catalyst and the volume of the catalyst layers are adjusted in such a manner that within the first catalyst layer the temperature rises about 5° C. to 15° C. Before the gas enters the next catalyst layer it is cooled by 25 coolers as hereinbefore described, or also by addition of suitable amounts of cold gas, e.g. cold feed gas, to such an extent that the temperature is about the same as that the gas had on entering the preceding catalyst 30 layer. In the following catalyst layers the operation is analogous.

In carrying out the invention the conversion of  $\text{CO} + \text{H}_2$  entering each catalyst layer is advantageously kept below 2% and 35 preferably at 0.3 — 1% of the total amount of gas entering each layer. Consequently the change of composition of the gas in the catalyst layer is small and the reaction is stopped before detrimental rises of temperature can occur.

The gas may be cooled between the layers by cooling elements which are cooled preferably by boiling water or oil. In such case, in the first stage of synthesis, hot feed gas 45 may be added to the hot circulating gases before entering the catalyst. A further advantage can be obtained by introducing cold feed gas, uniformly distributed, into the various catalyst layers of the reactor. By 50 the admixture of cold or warm feed gas—which is, however, not heated up to the reaction temperature—the temperature of these gases is likewise reduced between leaving one catalyst layer and entering the 55 next. By virtue of this reduction of temperature, the heat of reaction evolved can be rendered innocuous.

The hereindescribed process can be improved by introducing, instead of cold feed 60 gas or together with the latter, cold circulating gas between the various stages. Cold gas may be obtained by branching off a portion of the gas leaving the reactor and cooling it, for instance, to 20° C. to 30° C.

By this cooling, paraffins, oils and reaction 65 water are separated so that the cold gas subsequently introduced into the reactor is almost free from the reaction products of the synthesis. In this embodiment of the invention the partial pressure of water and 70 reaction products within the reactor is therefore considerably reduced. Thus the catalytic capacity is increased and the formation of methane is reduced. Moreover the octane number of the products of reaction is in- 75 creased since most of the additional hydrogenation of the olefines formed by the synthesis, which are introduced into the furnace in substantial amounts if hot gas only is recycled, is avoided. 80

If a ratio of fresh feed gas to cold circulating gas of 1 : 3 up to about 1 : 5 (according to the reaction temperature) is applied, all of the heat of reaction can be absorbed by these cold gases, and a sufficient reduction 85 of temperature of the gases between each pair of catalyst layers can be attained, so that further means for cooling the gases between the layers can be dispensed with. If the volume of circulating cold gas is 90 sufficiently large (its upper limit is the aforementioned ratio, since otherwise the gas would have to be heated say to 50° C. to 100° C.) the volume of hot circulating gas may be reduced, if desired. This is par- 95 ticularly feasible if an extremely high olefine content of the products and thus a maximum octane number is desired, or if preferably products are to be made having an especially high content of oxygen. 100

The hot gas circulation may be dispensed with completely if a sufficiently large number of catalyst layers, for instance 15 to 30 layers or more, are used. The number of catalyst layers, the ratio of hot gas and cold gas 105 circulated to feed gas, and the temperature increase within one catalyst layer are related to each other. The higher the number of catalyst layers, the smaller the amount of circulating gas may be kept, and the smaller 110 can be the temperature increase within each catalyst layer.

Cheap plants and high yields of synthesis products are thus made possible, as the investment costs are greatly influenced by 115 the nature of the equipment for transporting and cooling the gas. Moreover the formation of methane is reduced and thus the yield increased if the process is carried out with a small difference of temperature within the 120 catalyst layer. Moreover, this temperature difference may be the greater, the higher the drop of concentration in  $\text{CO} + \text{H}_2$  of the gas within the catalyst layer. The process of the present invention is therefore particularly 125 advantageous in case of intensive conversion of  $\text{CO} + \text{H}_2$ , i.e. if about 90 to 98% of the  $\text{CO} + \text{H}_2$  present in the fresh feed gas are.

transformed on their passage through all catalyst layers. By virtue of this the content of inert substances of the circulating gases becomes so high that the gas entering each individual catalyst layer contains but a few per cent of  $\text{CO} + \text{H}_2$ . Thus a considerable decrease of concentration within the catalyst layer results which would cause a reduction of reaction temperature within the catalyst layer. This reduction is compensated by the temperature rising within the catalyst layers in the direction of the gas flow in accordance with the invention. The hereindescribed process thus renders it possible to adapt the temperature of the individual catalyst particle to the  $\text{CO} + \text{H}_2$  concentration prevailing in the vicinity thereof in each particular case, and thus to obtain a uniform capacity of the catalyst within the layer, which was not possible in the reactors hitherto employed.

If, for instance, a synthesis gas of 88% purity (carbon monoxide + hydrogen) is used and the degree of conversion of carbon monoxide and hydrogen contained in the gas amounts to 98%, the heat of reaction corresponds to a temperature increase of the synthesis gas of  $1400^\circ\text{C}$ . Provided the temperature increase between the gas entering and leaving each contact layer is to be, for instance, only  $14^\circ\text{C}$ ., the known process would require for the absorption of the heat of reaction an amount of circulating gas of 100 times the quantity of fresh gas used.

For modern synthesis plants consuming up to about 200,000 cubic metres ( $0^\circ\text{C}$ ., 760 mm. Hg, dry) of feed gas per hour, 20,000,000 cubic metres of circulating gas per hour would be necessary, which is scarcely possible in practice, not even by application of the most modern means. According to the hereindescribed process only about 1,060,000 cubic metres of cold gas per hour are required for removal of the reaction heat if 200,000 cubic metres of synthesis gas are introduced per hour. In the various catalyst layers this cold gas is preheated, for instance from  $30^\circ\text{C}$ . to  $280^\circ\text{C}$ ., by mixing it with the gas leaving a preceding layer, and the gas leaving the preceding catalyst layer is simultaneously cooled from, for instance,  $295^\circ\text{C}$ . to  $280^\circ\text{C}$ . In this example 40 catalyst layers are provided. By the use of additional measures, for instance indirect cooling, between the layers, the amount of cold gas may be even further reduced. The number of layers may be reduced for instance to 12 by passing a hot gas recycle through all layers. The number of layers and the quantities of hot and cold gases recycled may in each particular case be easily chosen by a comparison of the cost for gas compression on the one hand and for the reactor capacity on the other hand.

The hereindescribed process also entails

the advantage that the working conditions, for instance the load of the catalyst reactors in terms of cubic metres of  $\text{CO} + \text{H}_2$  transformed per kilogramme of catalyst per day, and the quantity of hot gases recycled can be varied within rather wide limits. The composition of the reaction products may thus be influenced. By operating in accordance with the invention, for instance, at high reaction temperatures and with relatively large quantities of hot gas and particularly of cold circulated gas (and maintaining the increase of temperature constant within each catalyst layer) products are obtained which are rich in olefines and have a high octane number. The catalyst remains dry so that it guarantees a high reaction velocity. The operation may be carried out under normal or elevated pressure, for instance at 20 atmospheres and more.

The synthesis may also be directed to a high yield of paraffins. In the latter case the temperature is kept so low, for instance at  $180^\circ\text{C}$ . to  $250^\circ\text{C}$ ., that the residual gas leaving the reactor and branched off from the hot or cold circulating gas still has a  $\text{CO} + \text{H}_2$  content of about 20 to 60%, so that the total amount of  $\text{CO} + \text{H}_2$  reacted upon is below 80%, preferably 50 to 70%. In the latter case it is advantageous to connect two or more reactors in series so that the gas which has partly been converted in one reactor is worked up in the following reactor or reactors.

Moreover, in carrying out the hereindescribed process, the circulation of gas, for instance of hot gas, may be adjusted in such a manner that, even if a high percentage synthesis gas is used, the gas transformed at the catalyst has a high content of, for instance 80 to 90% of inert gases (carbon dioxide, nitrogen and methane). This involves the advantage, that the gas leaving the reactor is practically completely utilized so that a single-stage synthesis is sufficient. This simplifies and cheapens the whole plant the separation of the reaction products. Moreover, hot spots in the catalyst itself even in case of very high load can thus be effectively avoided.

The catalyst may have the usual grain size of, for instance, 2 to 10 mm. In some cases, for instance with large throughput of gas per unit period, the grain size may even be coarser, which has for instance the advantage that the pressure drop in the catalyst layers becomes smaller. It is also possible to use a pulverulent catalyst material, for instance by keeping the catalyst in suspension by the gas passing through from the bottom to the top of the reactor. Even in the case of a suspended catalyst, coarser catalyst granules of, for instance, 2 to 10 mm. may be used. In such case however, the gas

velocity must be very high in order to keep the catalyst material in suspension, but this does not offer any difficulties with a suitable number of stages and volumes of gas in circulation.

The number of catalyst layers to be provided in the reactor may vary with the quantity of hot gas recycled. The use of smaller quantities of hot gas is suitably combined with an increased number of catalyst layers, but the quantity of cold gas used need not be changed for the same load of fresh synthesis gas.

The quantity of cold gas is distributed among the various catalyst layers advantageously in such a manner that the increase of the temperature of the gas within each catalyst layer is the same. Thus cold gas is introduced into each catalyst layer in equal quantities. It is also possible to vary the quantities of cold gas during operation, or to pass through the catalyst layers alternatively cold gas and fresh synthesis gas or, if desired, various mixtures of feed gas and cold gas, or to introduce into the various catalyst layers different amounts of feed gas or cold gas or a mixture of both.

It is also possible to vary the amounts of cold gas recycled. By passing, for instance, the gas leaving a catalyst layer over surfaces cooled by boiling water before it enters the next catalyst layer, the elimination of heat of reaction by cooling and conversion of this heat into steam may be performed more or less completely by a corresponding alteration of the size of the cooling surfaces used and of the cold gas stream. The indirect cooling may even be carried out to such an extent that the cold gas stream becomes unnecessary and only hot circulating gas and fresh synthesis gas are introduced into the catalyst layers.

The catalyst may be used in various layers in succession. The layers, for instance, which the hot gas enters first may be charged with old catalyst and the following layers with a progressively fresher catalyst. The catalyst is, for instance, filled into boxes which may be comparatively easily removed from one catalyst layer and placed into another or in and out of the reactor, preferably with the aid of a protective gas such as carbon dioxide, in order to avoid any ingress of air. This arrangement is advantageously used even if the catalyst remains in the same layer throughout the whole of its life.

In carrying out the invention, horizontal or inclined cylindrical containers may be advantageously used in which the individual catalyst layers are vertically or obliquely disposed between screens, slotted or perforated plates or similar partitions permeable to gases. In view of the danger of the catalyst mass sliding together in the

course of a working period, as a result of which gas short circuits may occur, the individual catalyst layers may be closed at their top by a body which is easily movable and impermeable to gases and bears with its own weight on the catalyst material. It may be useful, for instance, to employ piston-like, freely movable bodies in the filling openings for the catalyst material with which the casings for the catalyst layers are provided. When the catalyst material slides together, these piston-like bodies also sink down and thus prevent the formation of gas short circuits. The opening of the filling tube should not be filled with catalyst material since in this part of the catalyst material the gas current will be slower and the gas will stay longer than in the remaining parts of the catalyst material. This longer time of stay of the gas in the tube may give rise to hot spots which may spread throughout the catalyst material and render the synthesis impossible.

Laminated or pipe coolers may be disposed between the individual, vertically or obliquely arranged catalyst layers for cooling the gas before it enters the following layer. The cooling agent employed in these coolers is preferably boiling water or boiling oil. If cold gas is added between the layers, it is advantageously mixed carefully with the remaining gas to avoid local differences of concentration in the mixture which would cause hot spots in the catalyst material.

When conducting the synthesis so as to obtain high-boiling hydrocarbons such as paraffins or the like which condense at the reaction temperature and drop downwards from the catalyst layers, the horizontal reactor, as compared with the vertical reactor, offers the advantage of an extremely simple removal of the paraffins. It is merely necessary to connect the lowest point of the reactor or of the individual catalyst sections with a pipe for eliminating the condensation products. Additional measures are unnecessary. Thus it is impossible that, as occurs in vertical reactors, paraffin or similar liquid products obtained by the synthesis drop from one layer into the following layer, since the layers in the horizontal reactor are arranged vertically. This also guarantees a uniform reaction velocity in all layers.

Moreover, the process of the present invention can employ all the additional measures which are used in known processes for the catalytic hydrogenation of carbon monoxide. Iron, cobalt or nickel catalysts manufactured in known manner may, for instance, be used. In the hereindescribed process the heat of reaction of the synthesis may be contained to a great extent in the gases leaving the reactor. Contrary to the

older reactors of the Fischer-Tropsch synthesis, this fact enables the utilization of this heat for other operations, for instance, for separating rich washing oils, such as are obtained during the production of gasoline from the residual gas of the synthesis.

In order to enable the invention to be more readily understood, reference is made to the accompanying drawings which illustrate diagrammatically and by way of example three different reactors according to this invention, and in which:

Fig. 1 is a vertical section of a vertical reactor;

Fig. 2 shows the arrangement of cooling surfaces in another vertical reactor;

Fig. 3 is a vertical section of a horizontal reactor; and

Fig. 4 is a transverse section.

In the embodiment shown in Fig. 1, two gas cycles are employed, namely one hot gas stream 1 and one cold gas stream 2. Feed gas is introduced into the plant at 3. The residual gas leaves the plant through the conduit 4. 5 is the blower for hot gas, 6 is the blower for cold gas. The steam generator 7 and the condensation plant 8 serve for cooling the gas arriving through the piping 9 and for separating products from the gas. From the cold gas stream 2, partial streams branch off through the conduits 10 into the various sections 11 of the reactor which are formed by perforated trays 12 carrying the catalyst layers. Devices 14 for thoroughly mixing the gas flowing through the reactor with the partial streams of the cold gas, are provided in the sections. At 13, the synthesis gas charged with reaction products leaves the reactor. Hot gas is introduced at 15. 16 is a furnace which serves for heating the gas when the operation of the plant is started. The division of the gas leaving the reactor into hot gas, cold gas and residual gas, the supply of fresh synthesis gas and the temperature adjustment of cold gas and hot gas are effected in such a manner that in each section, the mixture of cold gas and gases leaving the preceding section through the perforated tray has the prescribed temperature which is either the same in all sections or may increase from layer to layer uniformly or in accordance with certain rules, the latter for instance if catalysts of different age are used for the process. The increase of temperature in each catalyst layer may be kept small. Generally the temperature differences between the gas entering and leaving the individual catalyst layers are controlled to between 10° C. and 30° C.

The process of the present invention permits a gas throughput which is about 5 to 15 times that which may be used in the known Fischer-Tropsch synthesis. The gas

may, if desired, be transformed practically completely in a single reactor so that a multi-effect synthesis is not necessary. Moreover, the reactor illustrated is much cheaper and simpler than the known types, and it is no longer necessary to have it manufactured by specialist factories.

Fig. 2 shows a reactor provided with indirect cooling. The gas flows through catalyst layers 11. After leaving the catalyst, the gas passes along cooling surfaces 20 and 21, flowing for instance first from top to bottom and then from bottom to top. The gas then reaches the next layer through which it flows after it has been mixed with fresh synthesis gas and, if required, cold gas.

In the horizontal reactor shown in Figs. 3 and 4 catalyst layers 23 are disposed side by side in a pressure vessel 24. The catalyst layers lie between gas-permeable partitions 25 and 26. Between the catalyst layers are cooling pipes 27 which are connected by pipes 29 with the steam collector 30. 31 are fresh gas inlets; 32 and 33 are devices for a hot gas cycle. The residual gas flows off through conduit 34 for further treatment in known condensation plants.

The invention will be illustrated by the following Example:

#### EXAMPLE

The conversion is carried out in a vertical reactor of the kind illustrated in Fig. 1, having a height of about 30 metres and a diameter of about 8 metres. Said reactor contains twelve perforated trays carrying a known granular catalyst. The catalyst may be piled on the topmost perforated tray to a height of, for instance, 1.2 metres. Following the direction of the gas stream, said height may increase regularly or in accordance with other considerations, for instance up to 2.4 metres on the lowest tray.

The total amount of catalyst material in the reactor is 50 cubic metres. It is distributed among the various layers in such a manner that the uppermost layer contains about half the volume of catalyst contained in the lowermost layer. The layers between are graduated uniformly with respect to the volume of catalyst. This reactor allows 10,000 cubic metres (0° C., 760 mm. Hg, dry) of synthesis gas per hour and more to be worked up. A plant which required hitherto 100 old-type reactors, therefore, requires only about 6 to 8 reactors according to the present invention.

60,000 cubic metres per hour of the gas leaving the reactor are recycled to the gas inlet 15 by blower 5 (Fig. 1). The temperature decrease between gas outlet and gas inlet amounts to about 15° C. due to unavoidable heat losses. A quantity of 46,600 cubic metres circulates in the cold gas cycle. After

the hot gas is branched off, the gas passes through the steam generator and the condenser to the blower 6. Before the blower a quantity of residual gas of about 3,600 N. 5 cubic metres (as hereinbefore defined) per hour is branched off which may be worked up in known manner. After the blower the aforesaid quantity of fresh gas is introduced. By the introduction of fresh gas the amount 10 of gas in the cycle is increased to 53,000 N. cubic metres. It is distributed to the lower eleven catalyst layers, and by addition of cold gas the temperature increase of the gas of about 15° C., admissible per layer of 15 catalyst, is balanced. The cold gas may be distributed among the various layers, for instance, in the manner illustrated in Fig. 1.

Having now particularly described and ascertained the nature of our said invention 20 and in what manner the same is to be performed, we declare that what we claim is:—

1. A process of producing hydrocarbons, and if desired, oxygenated hydrocarbon 25 derivatives by the catalytic hydrogenation of carbon monoxide, in which synthesis gas containing carbon monoxide and hydrogen is passed through a succession of layers of catalyst, which process is characterised by 30 reducing the temperature of the gas leaving one layer of catalyst by cooling, by an amount approximately equal to or only slightly less than the increase in temperature produced in the layer of catalyst, before said 35 gas traverses the next layer of catalyst.

2. Process as claimed in Claim 1, wherein the temperature of the gas is reduced between two catalyst layers by indirect cooling and/or admixture of colder gas.

40 3. Process as claimed in either of the preceding Claims, wherein the thickness of the following catalyst layers is greater than that of the preceding ones.

4. Process as claimed in any of the preceding 45 Claims, wherein, in the case of catalyst layers disposed one above the other, the gas is

led through the catalyst layers from top to bottom.

5. Process as claimed in any of the preceding Claims, wherein the gas throughput 50 is kept much greater than in the hydrocarbon synthesis according to Fischer-Tropsch, the increase being for instance five-to-fifteen-fold.

6. Process as claimed in any of the preceding Claims, wherein part of the gas 55 leaving the last catalyst layer is cooled and led back between the layers.

7. Process as claimed in any of the preceding Claims, wherein  $\text{CO} + \text{H}_2$  is added to the gas between the catalyst layers. 60

8. Process as claimed in any of Claims 1 to 4, in which two gas cycles are maintained, the gas of the one cycle being led back without substantial cooling after it has left the catalyst layers and, if desired, after separation 65 of liquid reaction products such as paraffins, and the gas of the second cycle, after having left the catalyst layers and having cooled down, for instance, to room temperature, being freed from at least part of the reaction 70 products and being distributed if desired, in admixture with fresh gas for regulating the temperature, among the various catalyst layers before entering the latter.

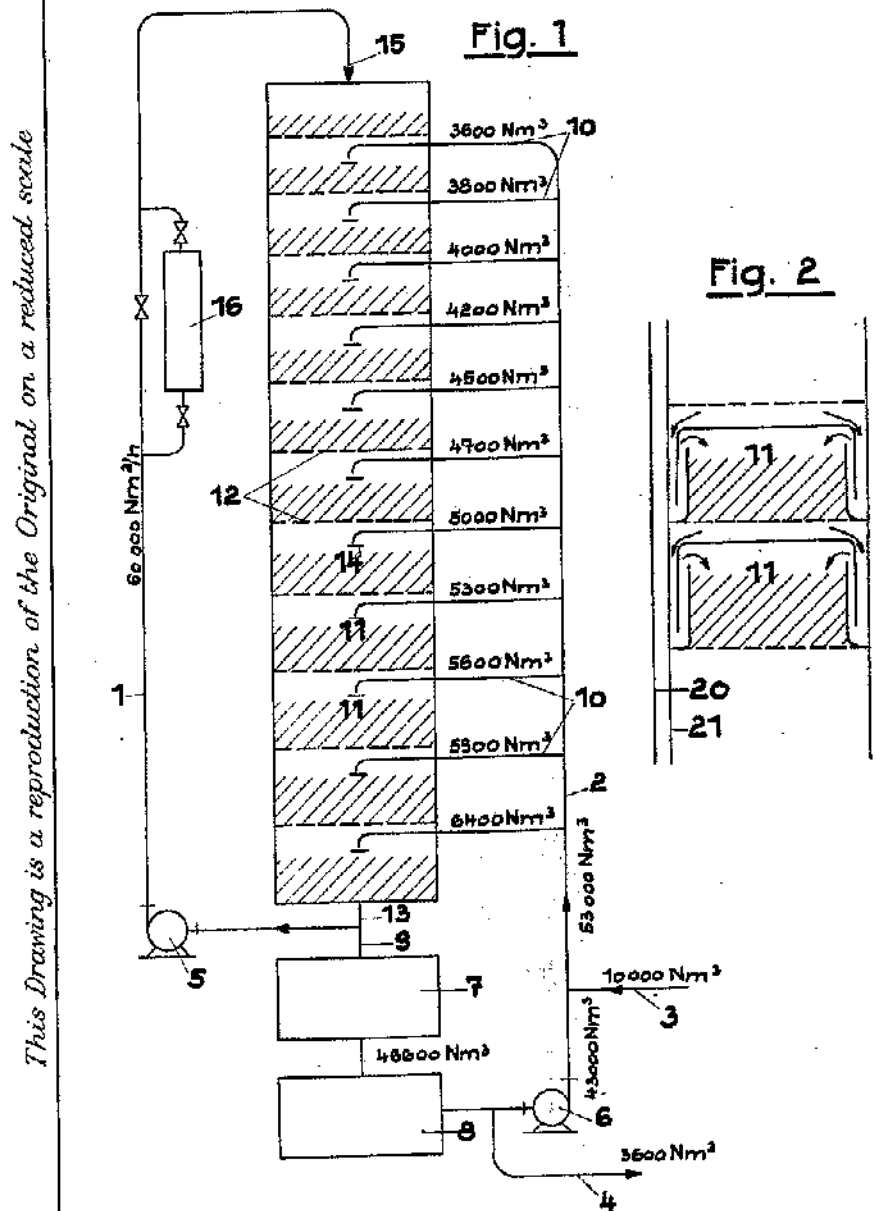
9. Process as claimed in Claim 6, wherein 75 the hot circulating gas is passed in succession through all catalyst layers.

10. Process as claimed in any of the preceding Claims, wherein the temperature with which the gas enters successive catalyst 80 layers is slightly higher than the temperature with which it enters the preceding catalyst layer.

11. A process of producing hydrocarbons by the catalytic hydrogenation of carbon 85 monoxide, substantially as hereinbefore described.

Dated this 14th day of June, 1949.

W. H. A. THIEMANN,  
14 to 18, Holborn, London, E.C.1,  
Agent for the Applicants.



**Fig. 1**

**Fig. 2**

*This Drawing is a reproduction of the Original on a reduced scale*

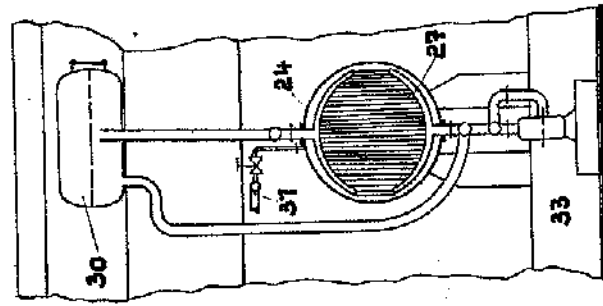


Fig. 4

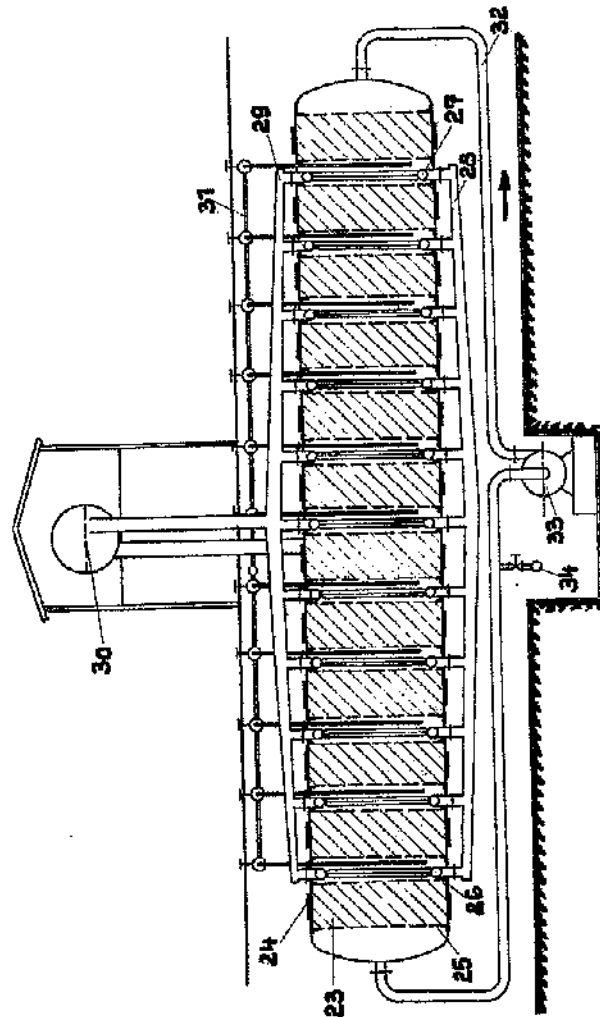


Fig. 3