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COMPLETE SPECIFICATION

Process for Cracking and Refining Synthetic Hydrocarbons

We, RUHRCHEMIE AKTIENGESELLSCHAFT of Oberhausen-Holten, Germany, and LURGI GESELLSCHAFT FUER WAERMETECHNIK m.b.H. of Frankfurt a.Main, Germany, both of German nationality, 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 a process for cracking and refining the hydrocarbons obtained by the catalytic hydrogenation of carbon monoxide.

Synthesis products which may boil within wide limits are obtained by the catalytic hydrogenation of carbon monoxide; the products obtained depend on the synthesis conditions and the catalyst used. Immediately downstream of the reactor, liquid, hydrocarbon mixtures boiling above about 300°C. are usually separated in the form of the "reactor paraffins." Thereafter, the temperature of the reactor gases is decreased to about 100°C. by means of heat exchangers, thereby recovering a "heat exchanger condensate." Further cooling to approximately normal room temperature results in the separation of the so-called "cold condensate." The residual gases, by being subjected to oil scrubbing or to cooling to a temperature as low as —40°C. or to a suitable treatment with active carbon, give the "low-temperature condensate."

To obtain as large as possible a quantity of motor fuels, the products which, at the different boiling ranges and at normal pressure, are separated in the liquid state, are processed without the reaction water and the products in solution in the reaction water. These products to be processed include a primary gasoline fraction, a diesel oil fraction, and higher boiling hydrocarbons. The higher boiling hydrocarbon mixtures (reactor paraffins) are subjected to thermal or catalytic cracking. Since the products of the catalytic hydrogenation of carbon monoxide consist preponderantly of straight-chain and saturated hydrocarbons, the cracking of these products, in contrast to the cracking of petroleum products, may be effected without the formation of coke or hydrogen-poor fuel oils and without the formation of aromatic hydrocarbons, resins and cracking residues.

The primary gasolines and cracked gasolines obtained are subjected to an after-treatment (hot refining) with bleaching earths or other aluminium silicates at elevated temperature (450°C., for example). This results, on the one hand, in an isomerisation and, on the other hand, in a displacement of carbon-to-carbon double bonds from the terminal to the middle or an intermediate position in the molecule.

It has now been found that by virtue of the fact that synthesis products obtained by the hydrogenation of carbon monoxide may be cracked with practically no residue, it is possible to combine the thermal cracking of the high boiling hydrocarbons, the fractionation of part of or of the whole of the hydrocarbon product and the isomerisation of the hydrocarbons boiling in the gasoline range, in a manner which is surprisingly advantageous from the operational standpoint and with regard to the supply of heat which is required.

According to the invention, a process for treating a hydrocarbon mixture of wide boiling range obtained by the catalytic hydrogenation of carbon monoxide and containing constituents boiling above 300°C, comprises cracking the hydrocarbons boiling above 300°C to yield hydrocarbons boiling in the gasoline range and/or diesel oil range, fractionating products of cracking and at least part of the original hydrocarbon mixture in a common fractionating unit, and withdrawing hydrocarbons boiling in the gasoline range from the common fractionating unit

[*Price 3s. 6d.*]

and subjecting them to isomerisation in the vapour state, the steps of cracking of the hydrocarbons boiling above 300°C, fractionating the part of the original hydrocarbon mixture and the cracked products in the common fractionating unit, and isomerising the hydrocarbons boiling in the gasoline range being carried out in such manner that part at least of the heat of the exit vapours from the cracking stage is employed to heat the feed to the isomerisation stage whilst part at least of the heat of the exit vapours from the isomerisation stage is used to heat an intermediate hydrocarbon fraction having an initial boiling point of about 100°C and obtained by fractional condensation of effluent vapours from the catalytic hydrogenation reactor, the intermediate hydrocarbon fraction being then passed into the common fractionating unit from which the higher boiling constituents of the intermediate hydrocarbon fraction are withdrawn and passed to the cracking stage. The water formed in the hydrocarbon synthesis and the products dissolved in that water do not constitute any part of the feed in the process of the invention.

Preferably, the total primary, hydrocarbon synthesis product which can be liquefied at normal pressure, is fed directly or indirectly to the common fractionating unit. Such synthesis product consists of the hydrocarbons which boil below the intermediate hydrocarbon fraction and which can be liquefied at normal pressure (the cold condensate and the low temperature condensate), the intermediate hydrocarbon fraction and the hydrocarbons boiling above about 300°C. As hereinbefore stated, the hydrocarbons boiling above about 300°C. are subjected to cracking before being fed into the common fractionating unit. The combination of steps forming the preferred method of carrying out the invention is hereinafter referred to as "Thermoforming." The cold condensate and the low temperature condensate are preheated before being passed into the common fractionating unit, the preheating being preferably effected by indirect heat exchange with one or more of the streams drawn from the common fractionating unit.

One method of carrying out the "Thermoforming" process is illustrated in the flow diagram shown in Figure 1 of the accompanying drawings.

Reactor paraffin (the hydrocarbon fraction boiling above about 300°C) is drawn from tank 1 and heated to 450°–500°C. in a tubular furnace 2 while maintaining the pressure at such a level that vaporisation of the reactor paraffin is prevented. After adequate heating, the hydrocarbons, while being released from pressure, are passed into a separator 3 where separation into gaseous and liquid phases occurs. Steam which has been heated in the tubular furnace 2 to about 500°C. is simultaneously passed through line 4 into the separator 3.

Tank 5 contains the heat exchanger condensate, that is, the intermediate hydrocarbon fraction boiling in the approximate range 100°–300°C. The heat exchanger condensate is pre-heated in a heat exchanger 6 and passed into a column 13 (the common fractionating unit) where any low boiling constituents are removed. From the bottom of column 13, the high boiling constituents of the heat exchanger condensate, free from the low boiling constituents removed in the column 13, pass into a separate tubular coil disposed in the tubular furnace 2 where they are heated to 500°–520°C. Then, under a gauge pressure of 3–10 kg./sq. cm., the high boiling constituents pass into the vapour-liquid separator 3.

From the separator 3, the residual liquid is recycled into the tubular furnace 2 in admixture with reactor paraffin from tank 1. The hydrocarbon vapours in the separator 3, together with the injected steam, are passed through a conduit disposed in the cracking zone of the tubular furnace 2 and then through a cooler and heat exchanger 7. The constituents which, after cooling in the cooler 7, are still in the gaseous state are passed to the fractionating column 13. The hydrocarbons which are liquefied in the cooler 7 are recycled to the cracking furnace 2, except for a small portion which is branched off and separated from polymers in a small distilling column 8 operated with steam. The polymers are withdrawn as the bottoms product from the column 8 while the gaseous overhead products are passed to the fractionating column 13.

The cold condensate, that is, the hydrocarbon fraction having an initial boiling point of about room temperature and a final boiling point of about 100°C, is passed from a tank 9 through a heat exchanger 10 and into the fractionating column 13. The low temperature condensate present in a tank 11 of the oil scrubbing unit, low-temperature treating unit or active carbon treating unit is likewise passed, through a heat exchanger 12, to the column 13. Gasoline and cracked gases are withdrawn overhead from the column 13 and are passed through the heat exchanger 12 into a separator 14, the gasoline condensed in the heat exchanger 12 being separated from the gaseous constituents in the separator 14. This gasoline, except for the part returned as reflux to the top of the column 13, passes to the heat exchanger 7 where it is vaporised and heated to the reaction temperature (about 450°C.) of the isomerisation stage.

The gasoline vapours are passed from the heat exchanger 7 through two or more alternately operated reactors or units 15 constituting the isomerisation stage, in which stage the isomerisation of the hydrocarbons is effected on bleaching earths or other suitable catalysts. The sensible heat of the vapours from the isomerisation stage is transferred in the heat exchanger 6 to the heat exchanger condensate (intermediate hydrocarbon fraction) drawn from the storage tank 5. The gasoline hydrocarbons are then passed to a re-run distillation unit to remove higher boiling constituents which may be formed in small quantities in the isomerisation stage.

The cracked gases obtained by distillation in fractionating column 13 and separated in the separator 14, are passed to a storage vessel 16, and, from thence, are drawn by a compressor 17 and compressed for the purpose of recovering C_3–C_4 hydrocarbons.

The hydrocarbons boiling in the diesel oil range are withdrawn from the fractionating column 13 via a stripper 18. The sensible heat of these hydrocarbons is used, in heat exchanger 10, for heating the cold condensate from the tank 9. Thereafter, the diesel oil fraction is passed into a storage vessel 19.

The bottoms product of the column 13 is, as hereinbefore mentioned, passed through the cracking furnace 2.

In cases where the primary synthesis products have a higher content of lower boiling hydrocarbons and the amount of hydrocarbons to be cracked is consequently smaller, the heating in the heat exchanger 7 of the gasoline from the separator 14 may be insufficient. In such a case, the gasoline from the separator 14 is pre-heated in the heat exchanger 6 prior to being passed through the heat exchanger 7, and a part only of the heat exchanger condensate (intermediate hydrocarbon fraction) from the tank 5 is pre-heated in the heat exchanger 6, the remainder of the heat exchanger condensate being pre-heated in any suitable manner. This manner of operation is indicated by the broken lines in Figure 1.

A further method of carrying out the "Thermoforming" process is illustrated in the flow diagram shown in Figure 2 of the accompanying drawings, in which the numerals 1 to 19 indicate the same or similar units as when used in Figure 1.

In contrast to the method of operation illustrated in Figure 1, the gases leaving the cracking furnace 2, prior to passing through the heat exchanger 7, are passed into a chamber 8*a* where they are precooled (chilled) with injected cold oil. For this purpose, use is made of the heat exchanger condensate (intermediate hydrocarbon fraction) from the storage tank 5 which previously flows through heat exchanger 6. In chamber 8*a*, due to the oil injection, liquid and solid constituents separate and are further processed in the steam-operated distilling column 8 as described with relation to the process illustrated in Figure 1. The gases withdrawn from column 8 are combined with the cracking gases from the chamber 8*a*.

A modification of the process of the invention which is independent of the kind of polymer-separation in column 8, relates to the step of isomerisation and is also illustrated in Figure 2.

In the "Thermoforming" process, the heat requirements of the isomerisation stage are met, in known manner, by the sensible heat of the entrant gasoline vapours. During passage through the isomerisation stage, the vapours are cooled. It is advantageous for some products if the gases are not allowed to cool to any great extent during isomerisation, and the isomerisation is effected in two stages in order that the gasoline vapours can be heated between the stages.

The effluent gases from the first stage of the isomerisation unit 15 are heated by hot, cracked gases in a heat exchanger 7*a*. The products from the second stage of the isomerisation unit 15 transfer a part of their heat in heat exchanger 6*a* to the gasoline from the separator 14 before this gasoline is further heated in heat exchanger 7. The residual heat content of the effluent from the isomerisation stage, as in the method illustrated in Figure 1, is transferred to the heat exchanger condensate withdrawn from storage tank 5.

For the regeneration of the bleaching earths used for isomerisation, an additional unit 15*c* is required. The units 15*a*, 15*b* and 15*c* are operated in the conventional manner in a three-unit cycle. The unit 15*c*, depending on the operational circumstances, is either onstream with unit 15*a* or with unit 15*b*.

The process of the invention for processing carbon monoxide hydrogenation products into gasoline and diesel fuels results in a considerable saving in capital and operational costs as compared with the known method of operation. It is now possible simultaneously to meet the heat requirements for the fractionation of the primary products and for carrying out the isomerisation of the hydrocarbons boiling in the gasoline range, with the same amount of heat which alone was hitherto necessary for the thermal cracking of the high boiling constituents. The saving in equipment includes two tubular furnaces and a fractionating unit for the primary products. The cost of operating the plant is likewise reduced to a corresponding extent.

What we claim is:—

1. A process for treating a hydrocarbon mixture of wide boiling range obtained by the catalytic hydrogenation of carbon monoxide and containing constituents boiling above 300°C, which comprises cracking the hydrocarbons boiling above 300°C to yield hydrocarbons boiling in the gasoline range and/or diesel oil range, fractionating products of cracking and at least part of the original

hydrocarbon mixture in a common fractionating unit, and withdrawing hydrocarbons boiling in the gasoline range from the common fractionating unit and subjecting them to isomerisation in the vapour state, the steps of cracking the hydrocarbons boiling above 300°C, fractionating the part of the original hydrocarbon mixture and of the cracked products in the common fractionating unit, and isomerising the hydrocarbons boiling in the gasoline range being carried out in such manner that part at least of the heat of the exit vapours from the cracking stage is employed to heat the feed to the isomerisation stage whilst part at least of the heat of the exit vapours from the isomerisation stage is used to heat an intermediate hydrocarbon fraction having an initial boiling point of about 100°C and obtained by fractional condensation of effluent vapours from the catalytic hydrogenation reactor, the intermediate hydrocarbon fraction being then passed into the common fractionating unit from which the higher boiling constituents of the intermediate hydrocarbon fraction are withdrawn and passed to the cracking stage.

2. A process according to claim 1, in which the hydrocarbons boiling below the intermediate hydrocarbon fraction and obtained by fractional condensation at normal pressure of effluent vapours from the catalytic hydrogenation reactor, are fed into the common fractionating unit after being preheated by effluent streams from the common fractionating unit.

3. A process according to claim 1 or claim 2, in which hydrocarbons boiling in the gasoline range and drawn from the common fractionating unit are heated both by hot, cracked gases and by gases from the isomerisation stage.

4. A process according to any one of the preceding claims, in which effluent gases from the cracking stage are partially precooled by the injection of a part of the intermediate hydrocarbon fraction.

5. A process according to any one of the preceding claims, in which the isomerisation stage comprises two zones.

6. A process according to claim 5, in which the product from the first zone of the isomerisation stage is heated by hot cracked gases prior to being fed into the second zone of the isomerisation stage.

7. A process according to claim 5 or claim 6, in which the product from the second zone of the isomerisation stage is passed in heat exchange relation with the feed to the first stage of the isomerisation stage.

8. A process according to any one of the preceding claims, in which the isomerisation is effected by means of a bleaching earth or other suitable hydrated aluminium silicate.

9. A process for the production of gasoline from hydrocarbons obtained by the catalytic hydrogenation of carbon monoxide, substantially as hereinbefore described.

10. A process of treating hydrocarbon mixtures obtained by the catalytic hydrogenation of carbon monoxide, substantially as hereinbefore described.

11. A process of treating hydrocarbon mixtures obtained by the catalytic hydrogenation of carbon monoxide, substantially as hereinbefore described with reference to Figure 1 or Figure 2.

12. Hydrocarbons boiling within the gasoline range and/or diesel oil range whenever obtained by the process claimed in any preceding claim.

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53–64, Chancery Lane, London, W.C.2.
Agents for the Applicants.

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1 SHEET
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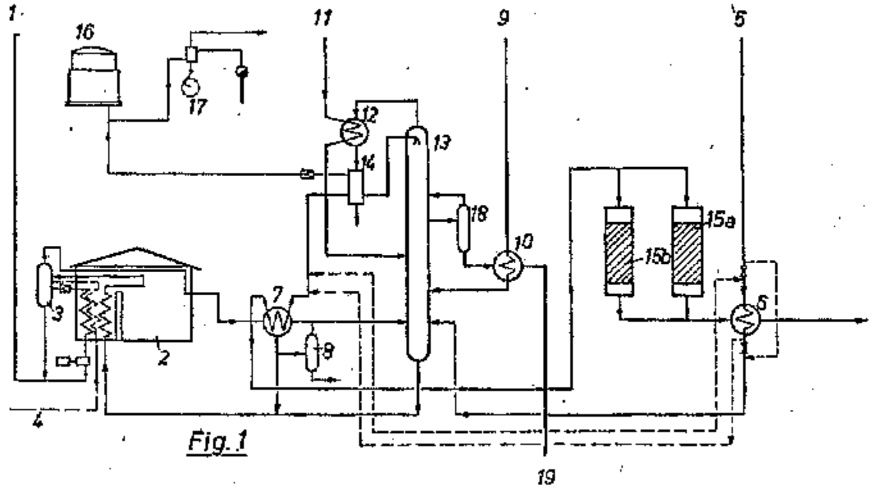

Fig. 1

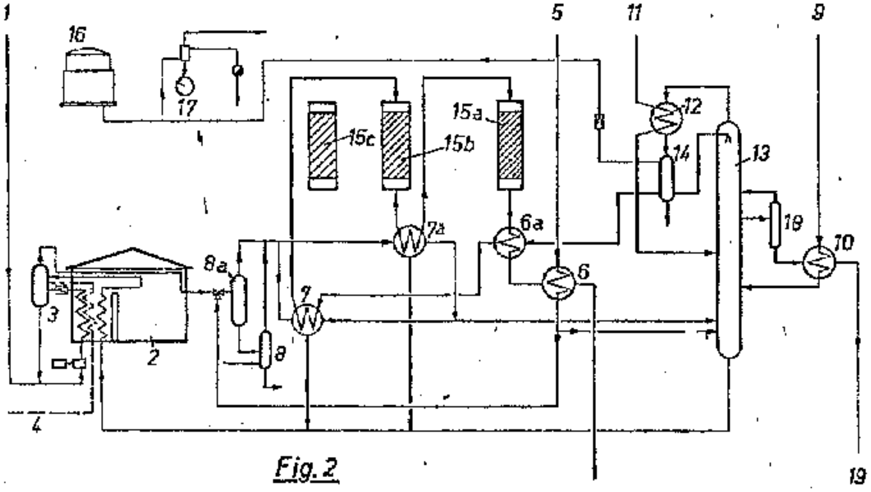

Fig. 2

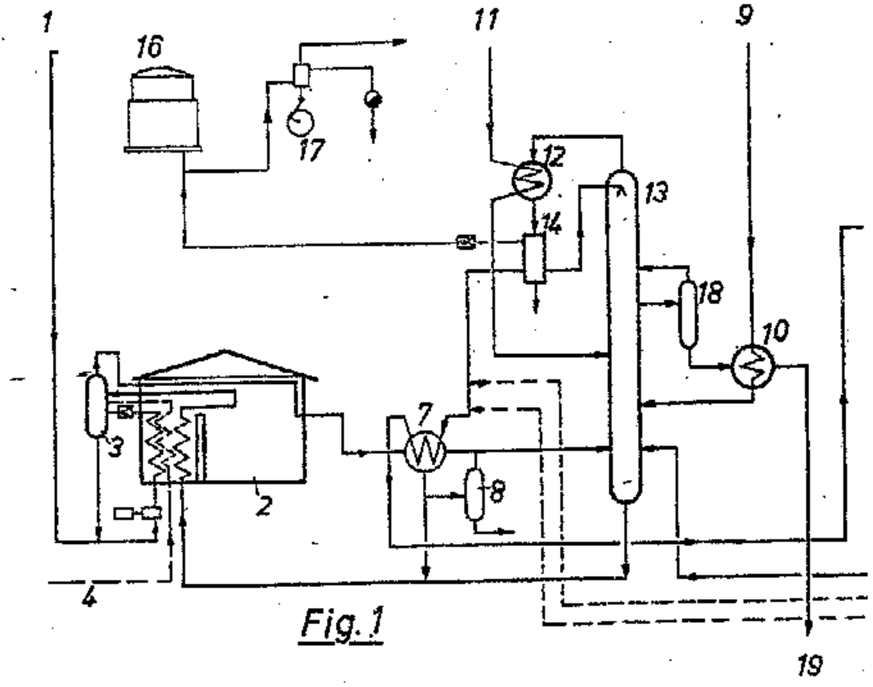
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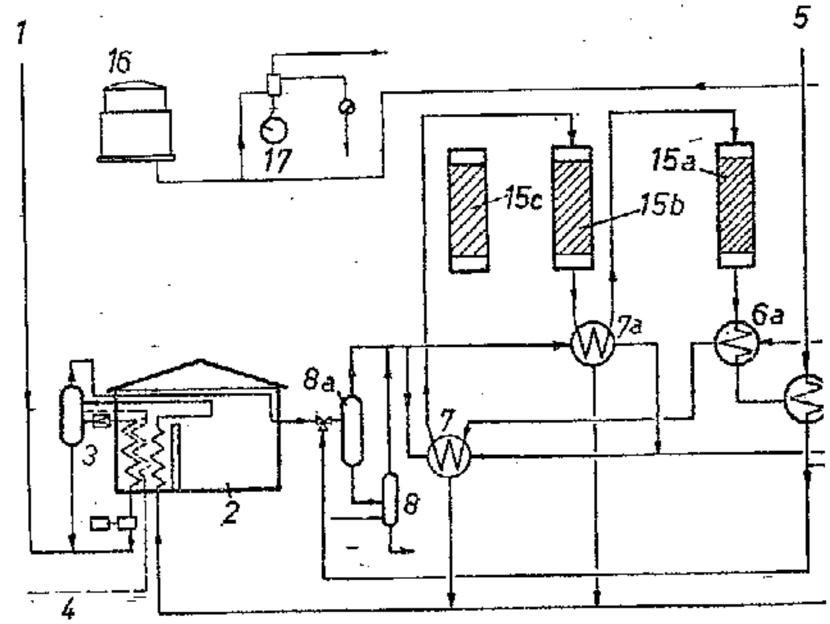
Fig. 1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15b
15a
7a
6a
8a
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Fig. 2

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1 SHEET

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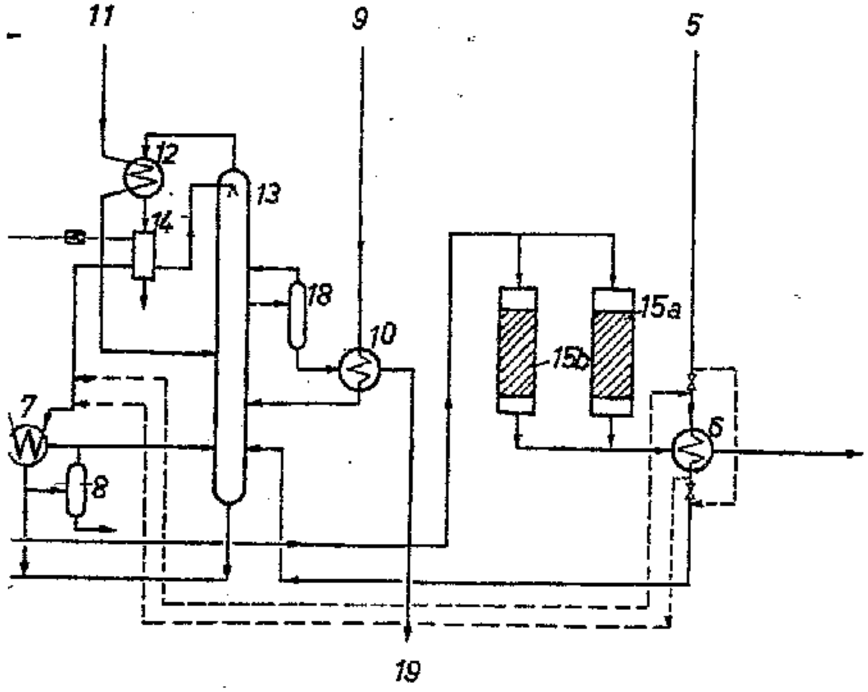

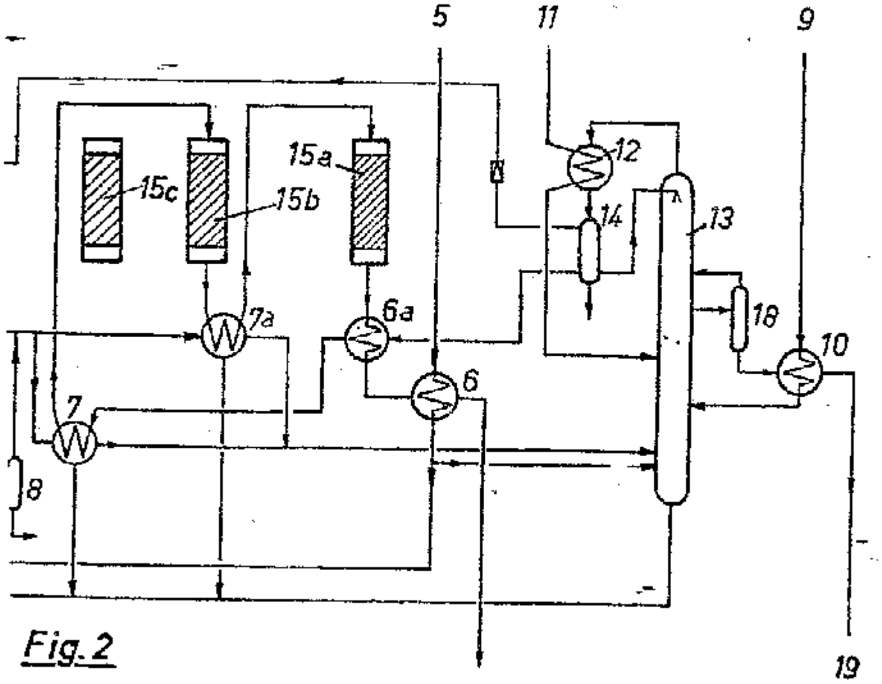

Fig. 2