PATENT SPECIFICATION

728,543

Date of Application and filing Complete Specification: March 3, 1953.
No. 5933/53.

Application made in Germany on March 5, 1952.
Application made in Germany on Feb. 19, 1953.
Complete Specification Published: April 20, 1955.

Index at acceptance:—Class 2(3), B1G.

COMPLETE SPECIFICATION

Process for the Synthesis of Hydrocarbons

We, HEINRICH KOPPERS GESELLSCHAFT MIT BESCHRANKTER HAFTUNG, a German Company, of Moltkestrasse 29, Essen, Germany, 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 present invention relates generally to the production of hydrocarbons by the reaction of carbon monoxide and hydrogen (synthesis gas), or gas mixtures containing these substances, in the presence of catalysts. The invention concerns more particularly a process in which the catalyst is disposed in fixed fashion within a hydrocarbon oil (contact oil) or is suspended in finely divided form in the contact oil.

The synthesis gas is passed through the hydrocarbon oil in finely divided form, there being formed by an exothermic reaction with the assistance of the fixed or suspended catalysts, hydrocarbons which partially dissolve in the hydrocarbon oil and partially form a mixture of gas and vapours with the residual gas. When the reaction has ended, the hydrocarbons formed are separated from the hydrocarbon oil.

The hydrocarbon oil may form a liquid column in the reaction chamber, through which the synthesis gas is then passed so as to come into contact with the contact substance situated in suspension or in fixed fashion in the oil. A so-called internal return then takes place, that is to say, the oil moves upwards in the centre of the reaction chamber and down again along the walls. It has also been proposed to guide the contact oil from the bottom upwards through a reaction chamber in a continuous stream, in which case an external circuit is formed, in which the means for effecting the circulation and any additional devices for cooling and purifying the contact oil are situated.

It has now been found that the actual synthesising operation can be improved and in particular the nature of the hydrocarbons produced may be more effectively influenced by providing within the reaction chamber a fixed cooling arrangement with which the circulating contact oil and the synthesis gas can be brought into contact during their passage through the reaction chamber.

In accordance with the invention, therefore, the mechanically moved stream of contact oil circulating after the separation of the gas, and the synthesis gas are introduced into the reaction chamber below a cooling arrangement disposed therein.

Further experiments have shown that the arrangement of the cooling means within the reaction chamber affords, in addition to the aforesaid advantages, further advantages residing in a more even distribution of the gas in the contact oil. It is known that a certain volume of contact oil must be available for the reaction of the synthesis gas. In the existing reaction chambers provided for these purposes, the contact oil has been situated in wide but relatively low reaction vessels. It has now been found that a substantially more uniform distribution of the gas in the contact oil can be obtained by employing, with the same ratio of volume of contact oil to synthesis gas, a tower-like reaction vessel of small diameter and correspondingly great height and effecting the cooling of the contact oil or mixture of contact oil and gas in the reaction chamber in a number of stages in such manner that the mixture of synthesis gas and contact oil successively flows through cooling stages at increasing temperature. The increased speed of flow of the synthesis gas within the reaction chamber resulting from the tower-like construction of the reaction chamber produces, as already stated, a more uniform distribution of the gas in the contact oil and a correspondingly higher reaction rate.

A further advantage of the subdivision of the cooling means provided within the reaction chambers into a number of separate cooling stages resides in that the reaction of the synthesis gas is uniformly distributed over

the entire height of the reaction tower or the entire quantity of contact oil. Moreover, owing to the fact that the individual cooling stages have a temperature increasing from the bottom upwards, the reaction can be retarded in the places where the concentration of carbon monoxide and hydrogen is highest, namely in the lower part of the reaction tower, by the application of low temperatures. In accordance with the reduction of the concentration of the reaction substances, the temperature is then increased in the higher zones of the reaction tower, so that the complete reaction between the carbon monoxide and the hydrogen, corresponding substantially to equilibrium, is obtained in the neighbourhood of the top of the reaction tower.

The subdivision of the cooling means provided within the reaction chamber into a number of cooling stages independently fed with cooling medium can be effected in various ways. All the cooling stages may be arranged one above the other within the same tower. Alternatively, the reaction tower may be subdivided into two or more units in such manner that a circulation of contact oil takes place in each unit, the synthesis gas flowing successively through the individual reaction chambers. At least one internal cooling means is then provided in association with each of these reaction chambers. If the process is carried out in such an arrangement, not only is it possible to maintain different temperatures in the individual reaction chamber units, but the concentration of catalyst therein may also be varied. It is thus possible to vary the chemical nature of the hydrocarbons produced within relatively wide limits by variation of the temperature and the concentration of the catalyst, so that hydrocarbons may be obtained which it has hitherto been impossible to produce by the processes and arrangements hitherto normally employed for the synthesis of hydrocarbons, or which could not hitherto be produced in sufficient quantities by such processes and arrangements.

While a uniform distribution of the gas within the volume of contact oil can be obtained to a certain extent by the subdivision of the internal cooling means into a number of cooling stages and by the tower-like construction of the reaction chamber in accordance with the invention, this distribution can be further improved by providing for feeding the synthesis gas to the reaction chamber at the lower end of the tower-like reaction chamber, one or a series of nozzles associated with liquid nozzles for the supply of the contact oil, the latter being introduced in such manner that the speed of flow of the contact oil in the region of the gas inlet points is different from the speed of flow of the synthesis gas passing into the liquid, and is more especially greater than the speed of the synthesis gas.

Hitherto, the synthesis gas has been introduced through ceramic filter plates or the like from below into the unbroken column of contact oil, and the contact oil escaping at the top has been fed back at the bottom independently thereof. If the contact oil and the synthesis gas are introduced into the reaction chamber in the manner proposed in accordance with the invention, the current of gas leaving the nozzle apertures will be broken up or divided, immediately after leaving the nozzles, into fine bubbles which are uniformly distributed through the liquid column, it having been found that such bubbles do not tend to recombine to form larger gas bubbles or gas pockets.

It is expedient at the same time so to arrange the pump by which the contact oil is circulated that it produces the pressure necessary for the required inlet speed of the oil. If the catalyst is suspended in the contact oil, impeller pumps are particularly suitable for this purpose because they have not the property of centrifuging the specifically heavier finely divided catalyst from the contact oil.

In accordance with a further proposal of the invention a branch stream of the synthesis gas or, if desired, other gases containing carbon monoxide and hydrogen may be introduced in finely divided form into the return pipe for the contact oil, preferably in the direction of flow beyond the circulating pump, for example the impeller pump, in order thus to counteract any excessive reduction of the quantity of dissolved carbon monoxide and hydrogen in the contact oil. In this case, regard must be had to the fact that the reaction taking place at the catalyst also takes place in the return pipe or condenser, although at lower speed than in the reaction vessel itself, so that the quantity of carbon monoxide and hydrogen in the contact oil may in some cases fall to a value at which the action of the catalyst is not ensured, or is not maintained at the required level.

It is furthermore advantageous to provide in the reaction chamber, means for preventing at the upper end of the reaction chamber, that is at the point at which the synthesis gas and the contact oil are separated, deposition of contact oil and especially catalyst on the walls. These means may reside, for example, in introducing at the upper end of the reaction chamber an additional quantity of contact oil which uniformly washes the walls of the reaction chamber and continuously carries away any deposits of catalyst.

In order to facilitate the separation of the contact oil and the gases dissolved therein at the upper end of the reaction chamber, it is proposed in accordance with the invention to reduce the speed of flow of the gas-

oil mixture at the upper end of the reaction tower in order thus to effect a general steadying of the flow of liquid. This object may be achieved by increasing that cross-sectional area of the reaction chamber which is available for the flow of liquid at the upper end, for example by increasing the diameter of the tower in this region, or, with a contant diameter, by leaving the upper part of the reaction tower free from inserted elements, for example free from cooling tubes.

As has already been mentioned at the beginning, a comparatively large ratio of height to diameter is advantageous for the dimensions of the tower-like reaction chamber, because if this ratio is high, that is to say, if the tower is relatively slender, a particularly favourable distribution of the synthesis gas in the volume of contact oil is obtained. It has been found that the ratio of height to diameter is preferably chosen as about 10:1, but higher and lower values may quite well be chosen for the ratio of height to diameter.

The temperatures at which the process according to the invention is carried out depend upon the catalyst employed and also upon the product which it is desired to obtain by the synthesis. Moreover, the temperature to be chosen depends upon the pressure in the reaction chamber. It has been found that favourable results have been obtained at temperatures below 280° C. if a reaction pressure of about 14—20 atm. is chosen, but economically useful results can be obtained by varying these values in accordance with the particular operating conditions.

The process is illustrated in the accompanying drawings.

Figure 1 is a vertical longitudinal section through a reaction chamber constructed in the manner of a tower having a total of four cooling stages,

Figure 2 shows a nozzle for the simultaneous introduction of synthesis gas and contact oil into the reaction chamber shown in Figure 1,

Figure 3 is a horizontal section through the nozzle base of the reaction tower illustrated in Figure 1, and

Figure 4 is a vertical section corresponding to Figure 3.

The reaction tower consists, in accordance with Figure 1, of an elongated cylindrical vessel 1 of substantially circular cross-section. Situated at the base of the tower are a number of nozzles 2, to which synthesis gas is fed through the pipe 3 and to which contact oil circulated by a pump 5 is fed through the pipe 4. Provided within the reaction chamber 1 are four cooling devices 6, 7, 8 and 9, which preferably consist of vertical tubes through which a suitable cooling medium, for example water is passed. The cooling medium is supplied through the pipe 10 and then flows through the cooling tubes in the same direction as the mixture of contact oil and synthesis gas introduced at the bottom. The cooling medium absorbs heat from the exothermic reaction of the synthesis gas to form hydrocarbons, the said heat then being discharged with the current of cooling medium through the pipe 11. Part of the cooling medium is directly returned into the circuit through the pipe 12, while another part of the heated cooling medium is fed through the pipe 13 to an external cooling device and thereafter re-introduced into the cooling medium circuit. The mixture of contact oil and synthesis gas is varied in its composition as it travels upwards through the contact tower 1, the hydrogen and carbon monoxide disappearing and hydrocarbons being produced in their place. Provided at the upper end of the contact tower is a widened portion 14 in which a relatively steady flow of liquid is maintained. The vapours produced and the unreacted gases leave the reaction tower by way of the pipe 15, while the contact oil is withdrawn through the pipe 16 and is returned into the bottom of the reaction tower by means of the circulation pump 5.

Figure 2 is a vertical longitudinal section through a nozzle provided at the base of the contact tower. The synthesis gas flows from the gas pipe 3 into the inner nozzle tube 18, which terminates in a narrowed portion 17 serving to increase the speed of the current of gas. The inner nozzle tube 18 is surrounded by an outer nozzle tube 20, the cross-section of which is considerably reduced in the region of the mouth of the inner nozzle tube 18 and is then widened again in the manner of a Laval nozzle at 21. The contact oil flows through the annular gap 22 between the inner nozzle tube 18 and the Laval nozzle 21 at great speed and thus breaks up the gas flowing through the inner nozzle tube 18 into extremely fine bubbles, which are then uniformly distributed throughout the volume of contact oil. The contact oil is supplied through the pipe 4, which is controlled by a valve 24.

In Figures 3 and 4, the synthesis gas flows through the pipe 3 into the inner nozzle tubes 18, a valve 19 being provided to ensure that synthesis gas is supplied as equally as possible to all the nozzles. If desired, the said nozzles may also be employed to vary in the required manner the distribution of the synthesis gas over the entire cross-section of the reaction chamber. The contact oil passes from the pipe 16 into the circulation pump 5, which is preferably constructed as an impeller pump. The said circulation pump may also receive fresh contact oil through the pipe 25. The contact oil passes from the circulation pump 5 by way of the pipe 4 and the valves 26 into the annular gap between the

inner nozzle tube 18 and the outer nozzle tube 20, the required difference being produced between the speeds of the synthesis gas and the circulating oil by suitably dimensioning the cross-section of this annular gap.

A cooling device not shown here may be provided in the return pipe 16 in association with the cooling system or systems situated in the reaction chamber.

The application of the invention permits, for example, of working up in a reaction vessel having a diameter of 1 m. and a height of 18 m. more than 4,000 cm. of synthesis gas per hour at a reaction pressure of 50 atm.

If it is desirable or expedient to make the reaction tower 1 shorter, it may, for example, be divided at the centre (substantially in the region of the chain line) and the two halves of the tower may be disposed side-by-side, in which case each half must naturally be provided with a so-called nozzle base. The synthesis gas is then introduced into the second reaction unit after having passed through the first unit and does not leave the installation until it has also flowed completely through the second unit. The contact oil itself may also be maintained in circulation in the two halves of the reaction chamber. However, it is expedient to provide in association with each reaction chamber unit a separate contact oil circuit with the corresponding devices, because it is possible in this manner to maintain the circulation of contact oil separately for each unit and to vary the concentration of the catalyst independently in each of the reaction chamber units.

In this case, it may also be expedient to condense the hydrocarbon vapours formed in each unit of the installation and to separate off the condensed products before the synthesis gas is introduced into the next unit of the installation.

What we claim is:—

1. Process for the production of hydrocarbons by the reaction of carbon monoxide and hydrogen (synthesis gas) in the presence of hydrocarbon synthesis catalysts arranged in fixed fashion or in suspension in a hydrocarbon oil (contact oil), wherein the synthesis gas is introduced at the bottom into a liquid column formed by the contact oil moving in the same direction as the gas, characterised in that the mechanically moved stream of contact oil circulating after the separation of the gases and vapours comprising hydrocarbon products and residual gas, and the synthesis gas are introduced into the reaction chamber below cooling means arranged therein.

2. Process according to claim 1, characterised in that the cooling of the contact oil is effected in a number of stages by the cooling means provided within the reaction chamber, in such manner that the mixture of synthesis gas and contact oil flows successively through cooling stages at increasing temperature.

3. Process according to claim 2, characterised in that the oil-gas mixture is passed through cooling stages which are arranged consecutively with regard to the direction of flow of the synthesis gas but are arranged structurally side-by-side, separate streams of contact oil, if necessary having different concentrations of catalyst, being maintained in circulation in the individual reaction chamber units corresponding to the cooling stages, and the hydrocarbon vapours formed in each reaction chamber unit being condensed and separated off, if desired, before the synthesis gas is introduced into the next unit.

4. Process according to claims 1 to 3, characterised in that the contact oil is introduced at the lower end of the liquid column through one or more substantially ejector-like devices at a higher speed than the synthesis gas entering at the bottom, and is withdrawn from the top of the reaction chamber.

5. Process according to claims 1 to 4, characterised in that the contact oil is circulated by means of a pump which produces the pressure necessary for the required speed of introduction.

6. Process according to claims 1 to 5, characterised in that an impeller-pump is employed.

7. Process according to claims 1 to 6, characterised in that a branch stream of synthesis gas or the like is introduced in finely divided form into the return pipe for the contact oil.

8. Process according to claims 1 to 7, characterised in that the speed of flow of the mixture of gas, vapours and oil is reduced at the upper end of the reaction tower.

9. Apparatus for use in the production of hydrocarbons by the reaction of carbon monoxide and hydrogen (synthesis gas) in the presence of hydrocarbon synthesis catalysts and comprising a reaction chamber through which a hydrocarbon oil (contact oil) is circulated in the form of an upwardly moving stream or column, characterised by the provision of cooling means disposed within the reaction chamber and of means for introducing the synthesis gas and the contact oil, after separation of the formed hydrocarbons and residual gas, into the reaction chamber below said cooling means.

10. Apparatus as claimed in Claim 9, wherein means are also provided for directing an additional stream of contact oil onto the walls of the reaction chamber above the liquid column for the purpose of washing said walls to remove any deposits of contact oil and/or catalyst.

11. Apparatus as claimed in Claim 9 or 10, wherein the reaction chamber is of vertical, tower-like and preferably cylindrical form having a relatively high ratio of height to

diameter (about 10:1) and within which at least two cooling systems are arranged, one above another, through which the contact oil flows successively for cooling in stages.

12. Apparatus as claimed in any of Claims 9—11, wherein at least two reaction chambers structurally and functionally independent are arranged side by side, the synthesis gas being caused to flow successively through said chambers.

HERON ROGERS & CO.,
Agents for Applicants,
Bridge House, 181 Queen Victoria Street,
London, E.C.4.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1955.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

Fig. 1

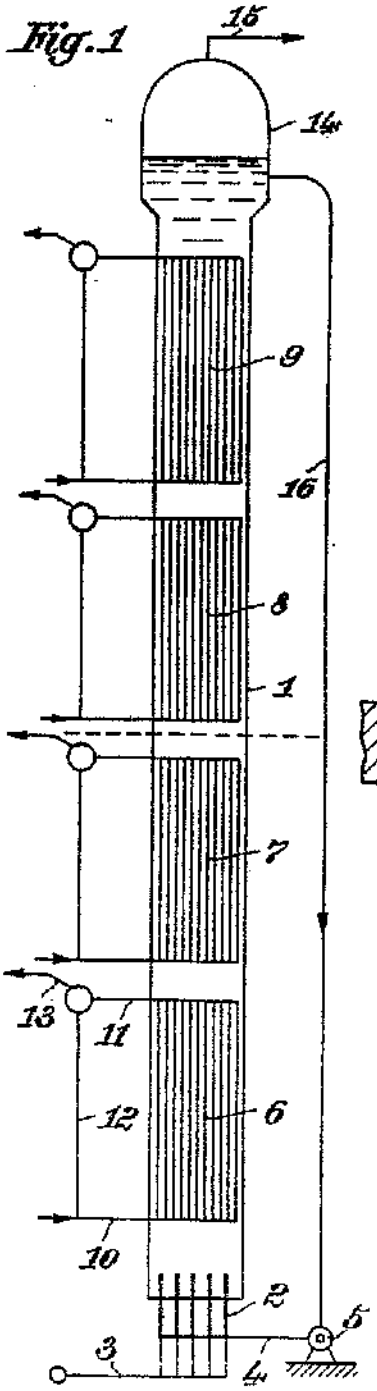
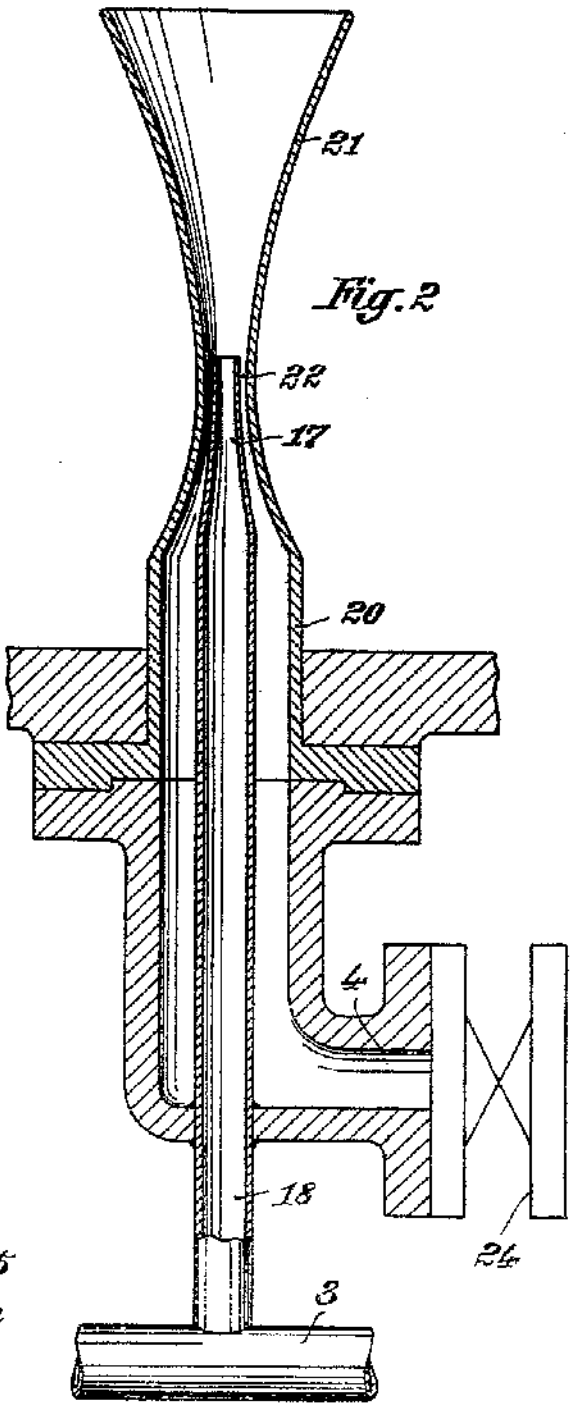


Fig. 2



728,543 COMPLETE SPECIFICATION

2 SHEETS

This drawing is a reproduction of the Original on a reduced scale.
SHEETS 1 & 2

Fig. 4

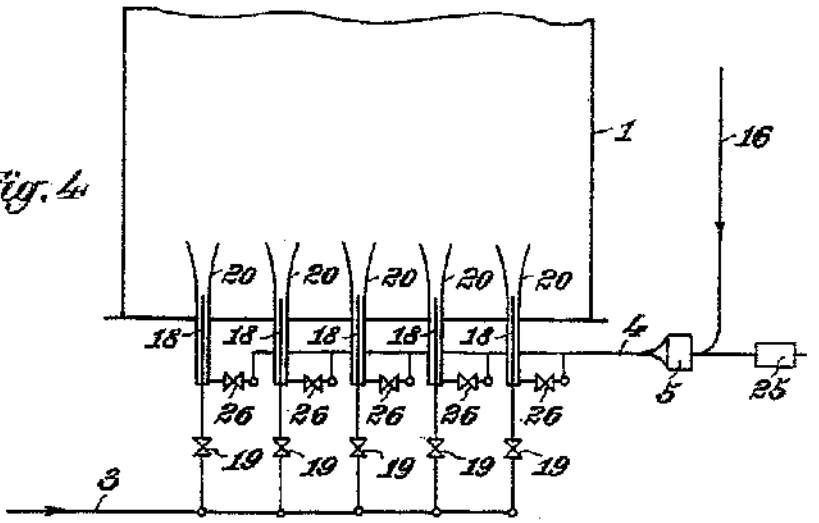
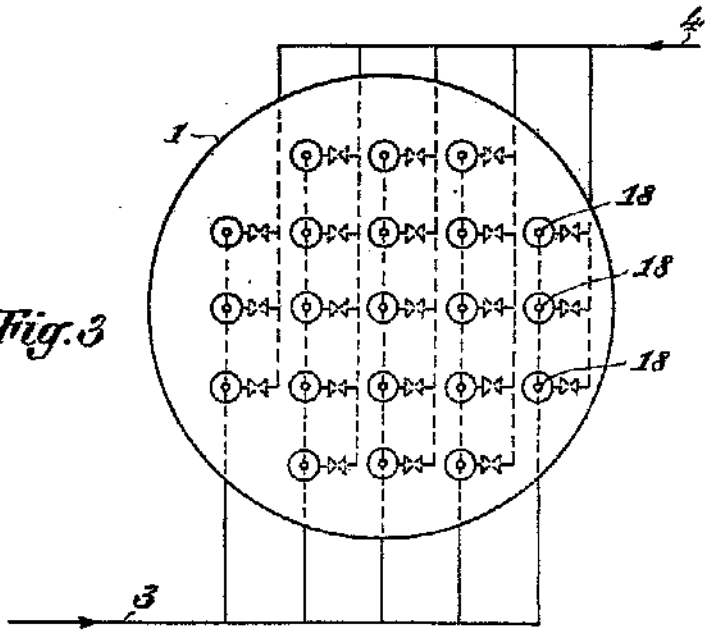


Fig. 3



728,543 COMPLETE SPECIFICATION

2 SHEETS

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

SHEETS 1 & 2

Fig. 1

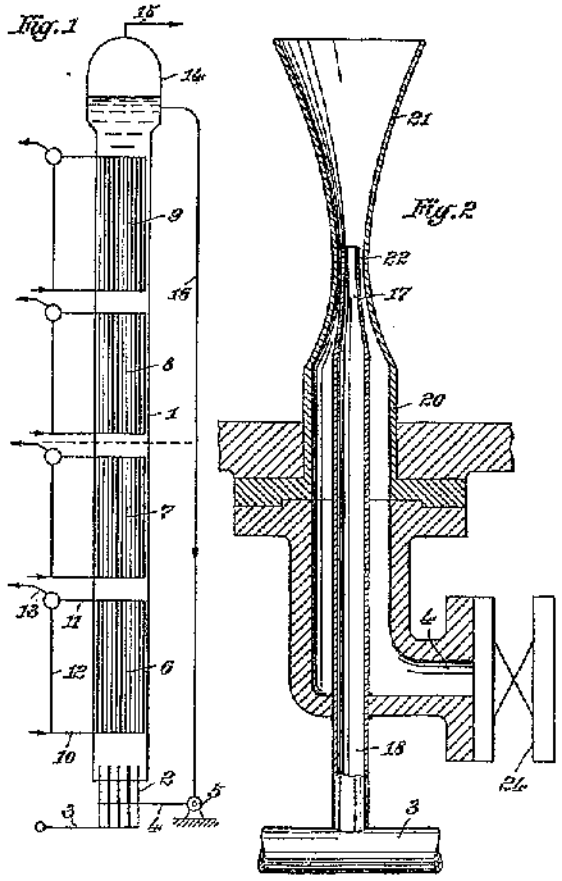


Fig. 2

Fig. 4

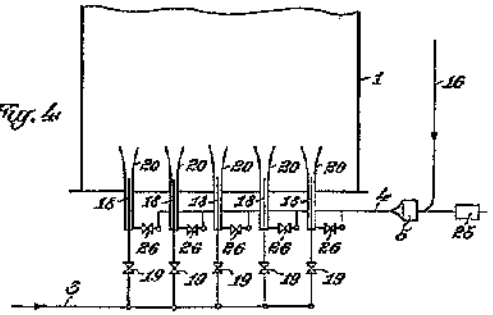
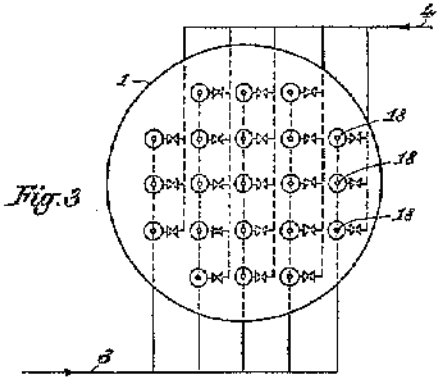


Fig. 3



PATENT SPECIFICATION

728,543

Date of Application and filing Complete Specification: March 3, 1953.

No. 5933/53.

Application made in Germany on March 5, 1952.

Application made in Germany on Feb. 19, 1953.

Complete Specification Published: April 20, 1955.

Ind

ERRATUM

SPECIFICATION No. 728,543

Page 4, line 14, *for* "50" *read* "20"

THE PATENT OFFICE,
16*th June*, 1955.

fashion within a hydrocarbon oil (contact oil) or is suspended in finely divided form in the contact oil.

The synthesis gas is passed through the hydrocarbon oil in finely divided form, there being formed by an exothermic reaction with the assistance of the fixed or suspended catalysts, hydrocarbons which partially dissolve in the hydrocarbon oil and partially form a mixture of gas and vapours with the residual gas. When the reaction has ended, the hydrocarbons formed are separated from the hydrocarbon oil.

The hydrocarbon oil may form a liquid column in the reaction chamber, through which the synthesis gas is then passed so as to come into contact with the contact substance situated in suspension or in fixed fashion in the oil. A so-called internal return then takes place, that is to say, the oil moves upwards in the centre of the reaction chamber and down again along the walls. It has also been proposed to guide the contact oil from the bottom upwards through a reaction chamber in a continuous stream, in which case an external circuit is formed, in which the means for effecting the circulation and any additional devices for cooling and purifying the contact oil are situated.

It has now been found that the actual synthesising operation can be improved and reaction chamber arises, in addition to the aforesaid advantages, further advantages residing in a more even distribution of the gas in the contact oil. It is known that a certain volume of contact oil must be available for the reaction of the synthesis gas. In the existing reaction chambers provided for these purposes, the contact oil has been situated in wide but relatively low reaction vessels. It has now been found that a substantially more uniform distribution of the gas in the contact oil can be obtained by employing, with the same ratio of volume of contact oil to synthesis gas, a tower-like reaction vessel of small diameter and correspondingly great height and effecting the cooling of the contact oil or mixture of contact oil and gas in the reaction chamber in a number of stages in such manner that the mixture of synthesis gas and contact oil successively flows through cooling stages at increasing temperature. The increased speed of flow of the synthesis gas within the reaction chamber resulting from the tower-like construction of the reaction chamber produces, as already stated, a more uniform distribution of the gas in the contact oil and a correspondingly higher reaction rate.

A further advantage of the subdivision of the cooling means provided within the reaction chambers into a number of separate cooling stages resides in that the reaction of the synthesis gas is uniformly distributed over