PATENT SPECIFICATION

596,870

1634

Convention Date (United States of America): Aug. 9, 1944.

Application Date (in United Kingdom): March 1, 1945. *No. 5164/45.*

Complete Specification Accepted: Jan. 13, 1948.

COMPLETE SPECIFICATION

Method of Carrying Out Reactions in the Presence of Solid Contact Material

We, INTERNATIONAL CATALYTIC OIL PROCESSES CORPORATION, a corporation organized and existing under the laws of the State of Delaware, United States of America, of 50 West 50th Street, City and State of New York, United States of America, 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:—

This invention relates to an improved method of carrying out reactions in the vapor and gaseous phase in the presence of catalytic or non-catalytic subdivided solid contact material which needs regeneration after the reaction. There are, accordingly, two steps in the process, the reaction proper and the regeneration of the solid contact material. A method has been proposed in specification No. 558946 wherein the contact material of a particle size of 20 or 30 mesh or smaller is caused to descend through a reaction and superposed regeneration zone, both zones being provided with baffle means, the material being transferred in a fluidized state from the reaction zone to the regeneration zone. In the present invention due to the absence of baffle means, the contact material passes through the reaction and generation zones as a compact bed.

According to the present invention a subdivided contact material as hereinafter defined, is employed and the said material is moved as a descending compact bed through both the regeneration and the reaction zones, and in a fluidized state outside the reaction and regeneration zones while elevating the contact material from a lower to a higher level.

The invention will be described in the following specification when read in conjunction with the accompanying drawings, in which

Figure 1 is a diagrammatic side elevation, partly in section, of an appropriate apparatus for the conversion of hydrocarbons in the presence of a granular contact material in which the regeneration chamber is located above the reaction chamber;

Figure 2 is a side elevation of the principal parts of an apparatus for the conversion of hydrocarbons in which the reaction and regeneration chambers are located at approximately the same level;

Figure 3 is a side elevation of an apparatus with two reaction chambers located one above the other.

The figures and the corresponding process steps will now be conjointly described.

Referring to Figure 1, the hydrocarbon oil such as gas oil from the storage tank 1 is passed by means of pump 2 and line 3 through heat exchange zone 4 to the heating tubes 5. The latter are located in the furnace 6 which may be heated by oil or hydrocarbon gas or coal. The hydrocarbon oil is vaporized during its passage through the heating tubes and heated to an approximate reaction temperature of say 950° F. It will be understood that the reaction temperature may vary within broad limits, say between 800—1150° F. or even within broader limits according to the type of the desired reaction, products, and the nature of the catalyst or of the non-catalytic contact material. The heated hydrocarbon vapors are fed through transfer line 7 to the bottom of the reaction chamber 8 in which they ascent upwardly in countercurrent to the descending bed of catalyst or contact material 9.

The conversion of the hydrocarbon takes place in the reaction chamber in the presence of the contact material which becomes fouled through deposition of carbon thereon. The cracked vapors leave the reaction chamber through overhead line 10 and are passed into the fractionating tower 11. The latter is of conventional design, the above-mentioned heat transfer coils 4 being placed in its upper part for the purposes of refluxing. The cracked hydrocarbons may be fractionated in the fractionating zone into three fractions, namely, a residue which

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is removed through bottom line 12, a heavy naphtha fraction which is collected in pan 13, and removed therefrom through line 14, and vapors comprising light naphtha and hydrocarbon gases which pass over the heat exchange coils 4 through the overhead line 15 into the condenser 16. The condensed light naphtha and the hydrocarbon gases are then discharged into the separator 17, the light naphtha leaving the separator through line 18 and the hydrocarbon gases through overhead line 19. These gases will contain a considerable amount of light but condensible hydrocarbons such as pentanes, pentenes, butanes, butenes, which are removed by conventional methods, such as for example, in an absorption tower.

The bottom part of the reaction chamber ends in a long draw off line 20 of enlarged cross section which serves as a stripping zone. The fouled catalyst or contact material contains a considerable amount of adsorbed hydrocarbons which are preferably removed before regeneration. The stripping is carried out by means of an appropriate inert gas such as steam. The stripping gas is introduced through line 21 and is removed through line 22 for the recovery of hydrocarbons therefrom.

The stripped catalyst is passed from the stripping zone 20 into the line of enlarged cross section 23 through the slide valve or star feeder 24. A sufficient amount of air or of an inert gas such as nitrogen or carbon dioxide is introduced from line 25 to fluidize the granular catalyst passing through the transfer line 23 and to transport the catalyst to the top of the regeneration chamber. In order to keep the catalyst in the fluidized state, air or inert gas may be admitted at several points into 23. In the drawing we have shown introduction of air by means of three valved lines 26, 27 and 28 located at different heights, all three being connected to the air line 25. The catalyst discharged into the regeneration chamber 29 descends therethrough in a downward direction and is regenerated during its passage by means of air or other free oxygen-containing gas admitted into the bottom part of the regenerator through line 30 connected to the air line 25. A distributor (not shown) may be provided to evenly distribute the air through the whole cross section of the regeneration zone. The regeneration gas such as air may also be admitted at other levels into the regeneration chamber such as at 31. The regeneration gases and those used for transporting the catalyst through line 23 are removed through line 32 into a cyclone separator 33 from which the separated catalyst is returned into the regeneration zone 29 through line 34 while the gases leave the separator through line 35. The cyclone separator is a conventional type of apparatus for separating solid particles from gases or vapors by means of centrifugal force. The gases from line 35 may, if desired, be led through another cyclone separator or into some other catalyst recovery system or into a waste heat boiler. The conical bottom section of the regeneration chamber ends in a drawoff line 36 which may serve as a purging zone. Steam or other inert gas such as carbon dioxide, nitrogen, is introduced through line 37 and removed through line 38 for the purpose of purging the regenerated catalyst of the adsorbed regeneration gas. The latter contains free oxygen which should not be introduced into the reaction zone 8 for obvious reasons. The regenerated and purged catalyst or contact material is continuously discharged into the reaction zone 8 by means of the slide valve or star feeder 39. If desired, the contact material may be maintained in the fluidized state during its passage through the enlarged line 36. It will be understood that a catalyst hopper may be interposed between the regeneration and reaction chambers in order to provide an adequate and even supply of the regenerated catalyst to the reaction chamber.

The temperature in the regeneration zone is usually maintained below about 1100°—1200° F. in order to prevent deterioration of the catalyst although higher temperatures may be employed in certain cases. If desired the regeneration chamber may be provided with heat transfer means which will absorb the harmful surplus of the heat engendered by the exothermic reaction of regeneration.

Referring to Figure 2, the heated oil vapors from line 7 mentioned in connection with the description of Figure 1 are discharged into the reaction chamber 40 through which they pass upwardly and countercurrently to the descending bed of catalyst or contact material. The oil vapors undergo the desired conversion during their passage through the reaction zone and are discharged through line 10 into the fractionating tower as described in connection with Figure 1. The conical bottom of the reaction chamber is continued in a transfer line 41 of enlarged cross section which serves as a stripping zone. Steam, nitrogen, carbon dioxide or other inert gas is introduced for this purpose through line 42 and removed through line 43 for recovery of oil therefrom. The fouled catalyst is then discharged through slide valve or star feeder 44 into the transfer line 45 of enlarged cross section. Inert gas, spent regeneration gas, or air from line 46 is admitted into the transfer line at several levels as shown at 47, 48 and 49 in order to keep the catalyst in the fluidized state and elevate the same to the top of the regeneration chamber 50. The fouled catalyst is regenerated during its descent through the regeneration chamber in the form of a compact layer and is then purged in the purging zone 51 by means of steam or other inert gas introduced at 52 and removed at 53. The regenerated and purged catalyst or contact material is discharged through slide valve or star feeder 54 into the transfer line of enlarged cross section 55 in which it is fluidized and kept in a fluidized state by means of air or inert gas introduced at several levels shown at 56, 57 and 58. The transfer line discharges the fluidized catalyst or contact material into the cyclone separator 59 which ends in a stripping zone 60 in which the regenerated catalyst is freed of air by means of steam or other inert gas introduced at 61 and removed at 62. A star feeder or slide valve 63 then discharges the regenerated catalyst or contact material either directly to the top of the reaction chamber or to a hopper (not shown) which in turn feeds the reaction chamber with catalyst.

Air is admitted through lines 68 and 69 preferably through distributors (not shown) in order to effect the burning off of the carbon deposit upon the fouled contact material. A high pressure steam coil (not shown) may be provided within the regenerator for purposes of cooling the contact material. Regeneration gases leave the regeneration chamber 50 through line 70 to be introduced into the cyclone separator 71 from which the separated catalyst is returned to the regeneration zone through leg 72. The regeneration gases leave the cyclone separator through line 73 and may be introduced into another cyclone separator or some other means of recovering catalyst still present in the gases.

Referring to Figure 3, heated crude oil is introduced through line 74 into the fractionating tower 75 in which it is fractionated into gasoline removed through overhead line 76, a residue removed through bottom line 77, a heavy naphtha fraction collected in pan 78 and removed therefrom through line 79 and a gas oil fraction collected in pan 80 and removed therefrom through line 81. The heavy naphtha fraction is passed by means of pump 82 through the heating tubes 83 located in the furnace 84 while the gas oil fraction is passed by means of pump 85 through the heating tubes 86 located in furnace 87. The vaporized and heated heavy naphtha is then discharged into reaction chamber 88 to be passed either concurrently or countercurrently to the bed of catalyst descending in the same. The cracked naphtha is then discharged through line 89 to a fractionating tower (not shown). The catalyst after its passage through the reaction zone 88 is admitted by means of slide valve 90 into a second reaction chamber 91 located below the first one and the heated and vaporized gas oil is also discharged into the reaction chamber 91 into contact with the descending bed of catalyst therein. The cracked gas oil is removed from this reaction chamber by means of line 92 into a fractionating tower (not shown). It will be understood that lines 89 and 92 may discharge their contents into the same or into two separate fractionating towers. The fouled catalyst is then removed from reaction chamber 91 through the stripping zone 93 of enlarged cross section in which it is stripped of adsorbed hydrocarbons by means of steam or other inert gas introduced through line 94 and removed through line 95. The stripped fouled catalyst is then admitted through slide valve 96 into the transfer line 97 of enlarged cross section to be passed in the fluidized condition to the top of the regeneration chamber. Inlet lines 98, 99 and 100 are shown at different levels through which air or inert gas is admitted into the transfer line 97 in sufficient quantity to fluidize and transport the fouled catalyst. The regeneration of the catalyst takes place in the regeneration chamber 101 by means of air admitted through lines 102 and 103. Regeneration gases leave the regeneration chamber through line 104 to be introduced into the cyclone separator 105 from which separated catalyst is returned to the regeneration chamber through line 106. The regeneration gases leaving the cyclone separator through line 107 may, if so desired, be introduced into a further catalyst recovery system.

The catalyst descends through the regeneration chamber 101 in the state of a compact bed or layer and leaves 101 in a regenerated condition passing first through stripping zone 108 then through the transfer line 109. In the stripping zone the catalyst is freed of adsorbed regeneration gases by means of steam or other inert gas introduced through line 110 and removed through line 111. The stripping zone 108 and the transfer line 109 are separated from each other by means of the slide valve 112 to regulate the amount of catalyst passing therethrough. Inert gas is admitted into the transfer line 109 at 113, 114 and 115 in sufficient amount to keep the regenerated catalyst in the fluidized condition and simultaneously effect its upward transfer. The catalyst in the fluidized state is then discharged into the cyclone separator 116, the catalyst passing into the reaction chamber 88 through the leg 117 and the inert gas leaving the cyclone separator through line 118 to be preferably introduced into another cyclone separator or Cottrell precipitator for the complete recovery of the catalyst and the return thereof into the reaction chamber 88.

In most cases it will be advantageous to maintain a higher cracking temperature in the reaction zone 88 for the heavy naphtha than in the reaction zone 91 for the gas oil.

Figure 3, however, only represents a particular exemplification of the method of cracking two oil fractions simultaneously according to the present invention. A first modification may be necessary whenever the deposition of the carbon in reaction zone 88 is not light. In that case part of the partly spent catalyst may be bled off during its passage from reaction zone 88 to 91 and submitted to regeneration while part of the regenerated catalyst may be discharged into the upper part of the reaction zone 91.

Another modification of the same process relates to the relative position of the two reaction chambers 88 and 91. It is not necessary that reaction chamber 88 be placed above reaction chamber 91 but they may be placed on approximately the same level. In this case it will be necessary to transfer the partially spent catalyst from the bottom of the reaction chamber 88 to the top of reaction chamber 91 through a transfer line of enlarged cross section in which the catalyst is maintained in the fluidized state.

The contact material may be of a catalytic or non-catalytic nature. It is sometimes advantageous to carry out thermal cracking in the presence of a non-catalytic contact material upon which deposits the coke formed during the cracking. In other cases the conversion of hydrocarbons is carried out in the presence of a solid subdivided catalyst which has a definite catalytic action upon the conversion reactions. Any of the catalysts employed in the art of catalytic conversion of hydrocarbons may be used in the present process. Activated bentonites, montmorillonites, synthetic impregnated or plural gels may be mentioned as examples. The catalyst may also be deposited upon a carrier. Sometimes it is advantageous to employ a shaped catalyst in the form of pellets or spheres of a few mm. diameter. Such catalysts usually show a lower rate of attrition than catalysts of uneven shape.

The present invention may be advantageously employed in the conversion of hydrocarbons carried out in the presence of a catalytic or non-catalytic contact material such as catalytic cracking, isoforming, reforming, hydroforming, aromatization, polymerization, dehydrogenation, hydrogenation, treatment of hydrocarbons for the removal of sulphur compounds or unsaturates. By the term "hydrocarbon reactions" it is meant to designate not only conversion of hydrocarbons but also the so-called Fischer Tropsch process in which hydrocarbons are formed from a mixture of carbon monoxide and hydrogen in the presence of a catalyst.

The synthesis of hydrocarbons from carbon monoxide and hydrogen is usually carried out at an approximate temperature of say 390° F. in the presence of a catalyst. The latter may be a metal of the iron group such as cobalt deposited on kieselguhr carrier. A small amount of thorium or magnesium activator is in most cases present with the iron group catalyst. In such a process there is usually no deposition of carbon upon the catalyst so that it will not be necessary to burn it off. However, it is desirable to regenerate the catalyst by freeing the same from wax and heavy hydrocarbons deposited thereon by means of gaseous or light hydrocarbons. In the synthesis process carried out according to the present invention the regeneration is effected in the regeneration chamber. The catalyst is present in the form of a descending compact bed in both the reaction and regeneration chambers and the transfer of the catalyst from a lower level to an upper level takes place in the fluidized state. The necessary modifications of the apparatus and process steps from that described in Figure 1, for example, will be obvious to those skilled in the art. Thus, for example, it will be desirable to use a hydrocarbon gas or vaporized light hydrocarbons for the transfer of the catalyst from the bottom of the reaction chamber 9 to the top of the regeneration chamber 29 through the transfer line 23 of enlarged cross section.

The invention may also be used in various organic and inorganic reactions in which the reactants are gases or vapors and the reaction takes place in the presence of a contact material whether or not of the catalytic nature and which contact material of more or less uniform the reaction.

The expressions "subdivided contact material" and "subdivided catalyst" in the specification and claims are meant to designate contact material or a catalyst of a size retained on a screen having a hundred mesh per inch and a screen aperture of 0.149 millimeter but having particles not larger than about 15 mm. in diameter. These are especially advantageous for carrying out the present invention because they can be passed through the reaction and regeneration zones in the state of a compact layer or bed and on the other hand they are comparatively easily fluidized for transfer outside the reaction and regeneration zones. It is advantageous to use a contact material of more or less uniform particle size.

The fluidized condition is a physical state of a mixture of gases or vapors and solid particles in which the solid particles are distributed throughout the gas or vapor and carried by it so that the mixture of gas and solid particles acts in many ways like a fluid. It has, for example, a definite hydrostatic pressure depending on the amount of solid particles per unit volume.

The linear gas or vapor velocities will be among the most important factors contributing to the maintenance of the catalyst or contact material in the form of a moving compact column or in fluidized form, Roughly speaking, the velocity of gases or vapors must increase approximately in direct proportion with the square root of the diameter of the solid particles in order to maintain the same in the fluidized state. The prerequisite for this regularity is that the gases or vapors are present in the turbulent condition of flow in the zone in which the fluidized state is maintained. Thus, for example, if it is found that a 3 mm. diameter catalyst requires a linear vapor velocity of about 6 feet per second for the maintenance of the desired fluidized state in a transfer zone, the linear velocity must be increased to about 12 feet per second with catalyst or contact material of approximately 12 mm. diameter. The necessary velocity is best determined experimentally since it is influenced by other factors such as the shape of the catalyst, the relative density of the solid to the vapors, and the size distribution of the solid particles.

It is evident that lower gas or vapor velocities must be maintained in the reaction and regeneration zones in which the catalyst is present in the form of a descending compact column or layer according to the present invention. In such a zone the gases or vapors themselves are present in the viscous condition of flow.

The following example will illustrate the present process in its application to the cracking of hydrocarbon oils:

A mixed refinery gas oil of gravity 26.7° A.P.I. and aniline point 188° F. was used as feed stock. Its initial boiling point was 260° F. when distilled under 10 mm. absolute pressure with 50% off at 495° F. and 90% off at 628° F. The final boiling point was 694° F. The feed stock was submitted to catalytic cracking in the apparatus illustrated in Figure 1 under the following conditions:

Average temperature in the reaction zone—846° F.

Gauge pressure on the reaction zone—5 lbs. per sq. in.

Space velocity—1.65 v/v/hr.

Nature of the catalyst: Acid treated clay

Average size of the catalyst: 3 mm. in diameter

The following yields were obtained on the gas oil feed:

400° F. end point gasoline of 10 lb. R.V.P.	-	37.2% by volume
Excess butane	-	8.5% by volume
Gas Oil	-	54.8% by volume
Dry gas	-	4.4% by weight
Coke	-	3.5% by weight

Inspection of the gasoline:
Gravity—62.6° A.P.I.
Aniline point—91° F.
Acid heat—47
Bromine number—53
Octane number—80 A.S.T.M.

Distillation: 26% off at 158° F., 50% off at 212° F.

Inspection of the gas oil obtained in the cracking:
Gravity—24.3° A.P.I.
Aniline point—148° F.
Initial boiling point—495° F.
50% off at 637° F.
76% off at 700° F.

Composition of the dry gas:

Hydrogen	- -	30%
Methane	- -	11%
C_2 hydrocarbons	-	17%
C_3 hydrocarbons	-	42%

The expression "compact bed of contact material or catalyst" is meant to designate in the following claims the non-fluidized state of catalyst whether it fills out the whole cross section of the reaction or regeneration zone or is present in the form of a descending compact layer in the zone or in a series of zones.

Many modifications of the invention will be obvious to those skilled in the art. Thus, for example, the reacting hydrocarbon vapors or the regeneration gases may be passed concurrently with the contact material through the reaction and regeneration zones, respectively.

The invention is not to be limited by those specific data which have been given merely for purpose of illustration but only by the following claims.

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. The method of carrying out reactions in the gaseous or vapor phase in a reaction zone in the presence of a subdivided contact material which needs regeneration after the reaction by contact means of gases in a regeneration zone, which comprises employing a subdivided contact material as hereinbefore defined and moving the said material as a descending compact bed through both the regeneration and the reaction zones and in the fluidized state outside the reaction and regeneration zones while elevating the contact material from a lower to a high level.

2. The method according to claim 1 as applied to hydrocarbon reactions in which the contact material is of catalytic nature.

3. The method according to claim 1 or 2 in which hydrocarbon vapors are submitted to conversion at an elevated temperature in contact with a subdivided catalyst as hereinbefore defined.

4. The method according to claim 3 in which, while the catalyst is maintained in the state of a descending compact bed in the regeneration zone, an oxygen-containing regeneration gas is passed over the catalyst.

5. The method according to claims 3 and 4 in which the regenerated catalyst is returned to the upper part of the reaction zone outside both zones in the fluidized state.

6. Method according to claim 3 in which the reaction zone is maintained at a temperature between 800—1150° F.

7. Method according to claim 2 in which hydrocarbon vapors are converted by catalytic cracking, isoforming, polymerization, reforming, hydroforming, dehydrogenation, hydrogenation, aromatization or treated for the removal of sulphur compounds and unsaturates.

8. Method according to claim 2 in which heated naphtha vapors are passed through a first reaction zone and, after separation of the cracked vapors from the catalyst, at least part of the latter is passed in the form of a descending compact bed through a second reaction zone into which heated gas oil vapors are introduced, thereafter separating the cracked gas oil vapors from the catalyst and passing the fluidized catalyst to the top of a regeneration zone from which the regenerated catalyst after separation from the oxygen containing regeneration gas is returned to the first reaction zone.

9. Method according to claim 8 in which the second reaction zone is lower than the first.

10. Method of carrying out gas or vapor reactions in the presence of a subdivided contact material substantially as described and ascertained.

Dated this 1st day of March, 1945.
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Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1948.
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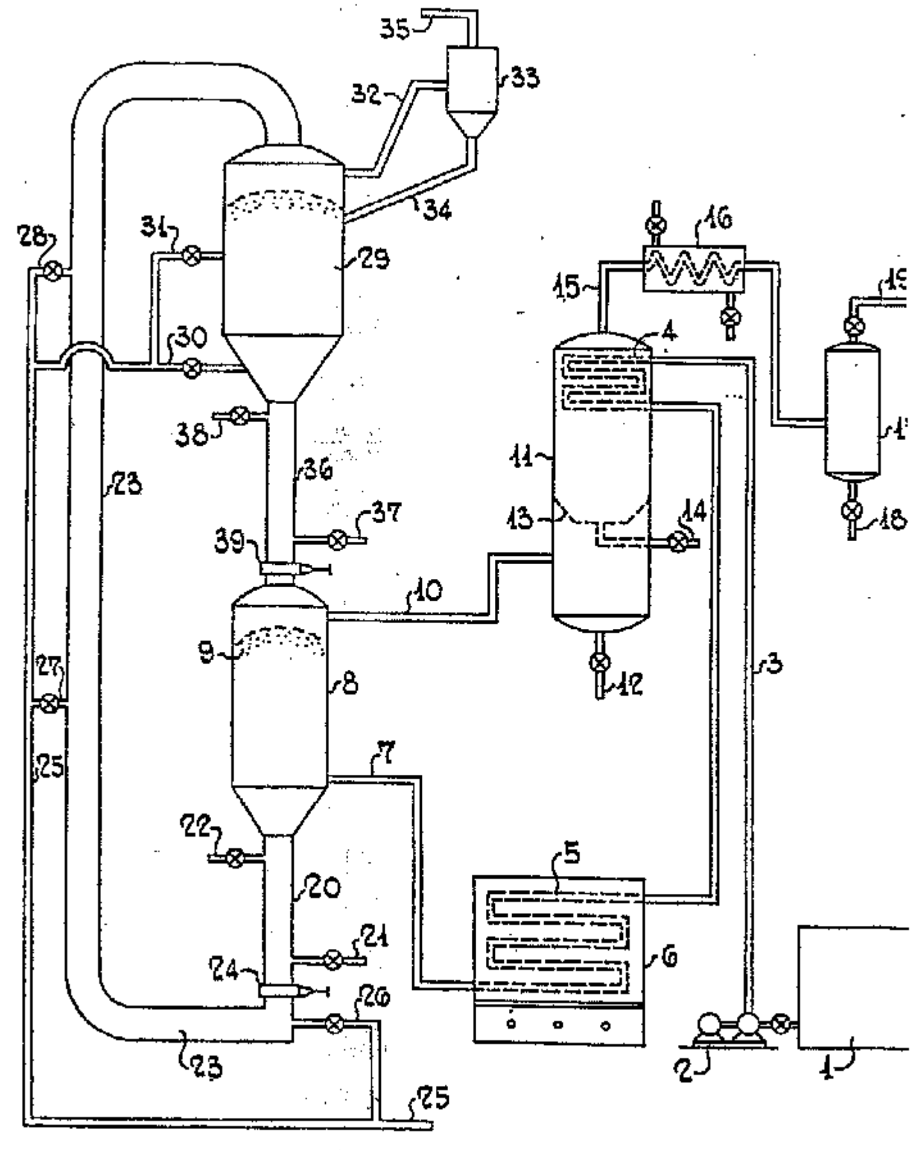
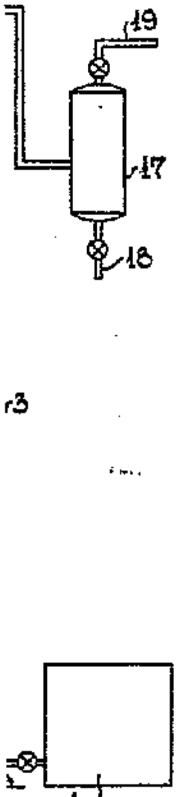


FIG.-1.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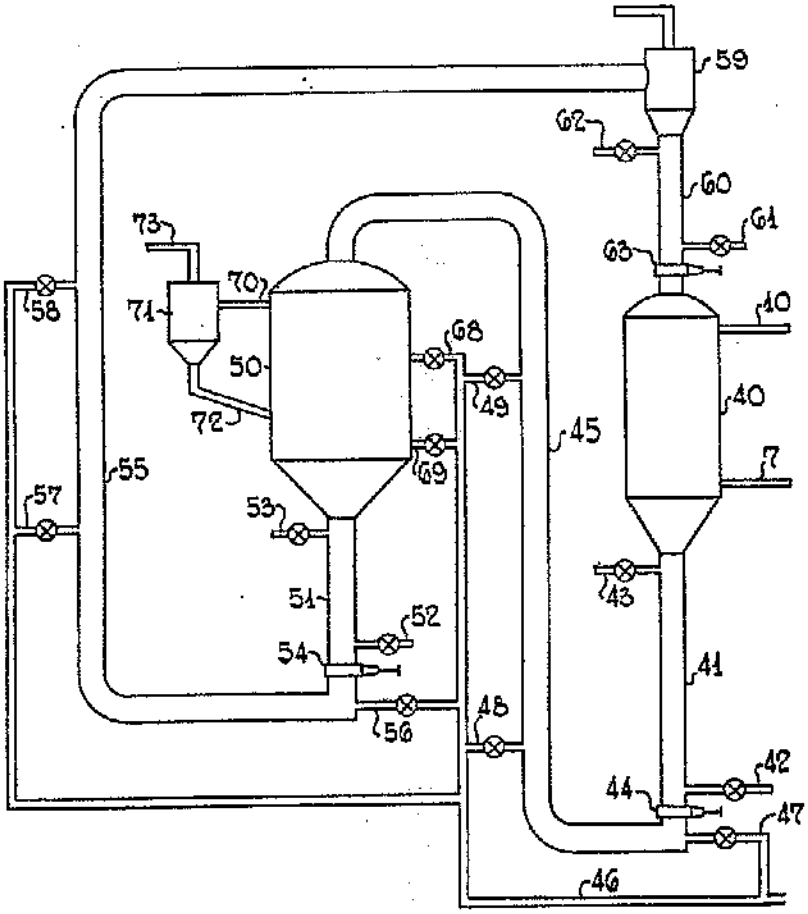
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FIG. - 2

596,870 COMPLETE SPECIFICATION

2 SHEETS
SHEET 1
SHEET 2

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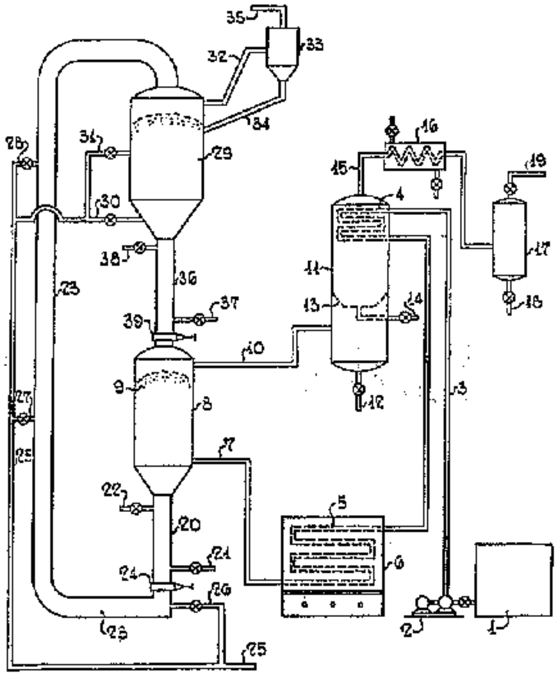

FIG.-1.

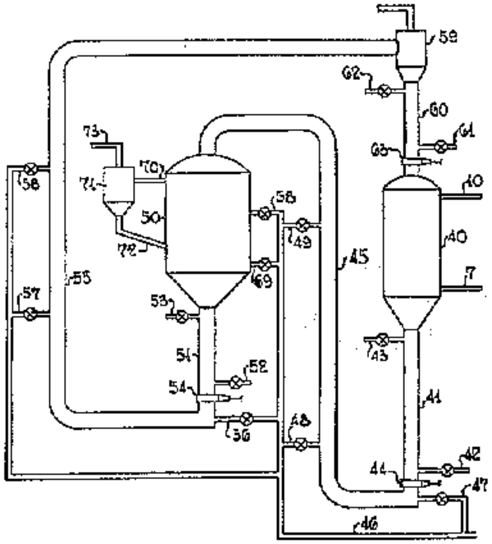

FIG.-2

H.M.S.O.(Ty.P.)

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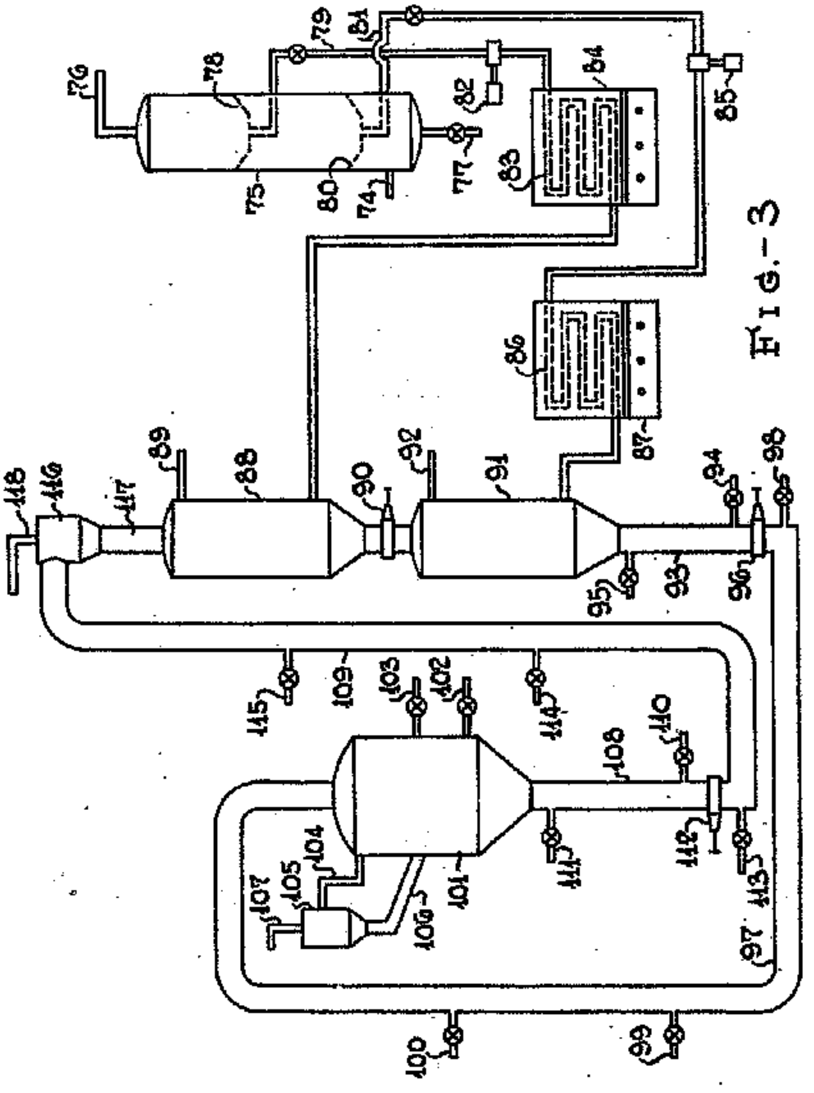

FIG. 3

H.M.S.O. (Ty.P.)