PATENT SPECIFICATION

592,190

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COMPLETE SPECIFICATION

Improved Method of carrying out Catalytic Reactions

We, INTERNATIONAL CATALYTIC OIL PROCESSES CORPORATION, a Corporation of the State of Delaware, 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 or gaseous phase in contact with catalytic or non-catalytic granular solids in which the solid contact material needs reconditioning after the reaction. There are accordingly two steps in the process, the reaction proper and the reconditioning of the solids. The invention is characterized by the fact that the solids are present in a different form of distribution in the two steps and that the two steps are carried out in a cycle.

In order to show the nature of the invention in examples two processes of very different character may be mentioned in which the invention may be advantageously employed. They are the catalytic cracking of hydrocarbons and the manufacture of acetylene from hydrocarbon gases.

There are processes known in the refining of hydrocarbons in which the hydrocarbon vapors are cracked in the presence of a granular catalyst. In such processes the granular catalyst descends in the form of a compact bed in the reaction chamber and the hydrocarbon vapors to be cracked are passed countercurrently in an upward direction. The reaction zone is maintained at an appropriate temperature and usually under slightly superatmospheric pressure whereby the desired cracking of the hydrocarbons takes place. The cracked vapors are then fractionated and the granular catalyst is regenerated in the form of a compact bed or layer by burning off the coke, after which it is returned to the top of the cracking chamber. In the presently known processes of such nature the transportation of the catalyst, such as its elevation to the top of the reaction chamber, is carried out by mechanical conveyor which is inconvenient. Furthermore, such processes do not have the desired flexibility.

The present invention eliminates the inconvenient mechanical method of transporting the catalyst to higher levels and is furthermore characterized by great flexibility. In one method of carrying out catalytic cracking processes according to the present invention the granular catalyst descends through the reaction chamber in the form of a compact bed or layer and the hydrocarbon vapors are passed countercurrently to the catalyst or concurrently therewith. The fouled catalyst is then regenerated in a regeneration zone and simultaneously elevated to the desired height by passing it to the bottom of the regeneration chamber with sufficient oxygen-containing regeneration gas such as air to provide a so-called fluidized state of the catalyst in the regeneration chamber. The regenerated catalyst together with the regeneration gases in which it is distributed is then passed to a separator from which it is fed to the top of the reaction chamber.

There are processes known for the manufacture of acetylene from hydrocarbon gases in which solid particles are used as heat carriers. Such a process may be carried out according to the present invention as follows:—

The highly heated granular heat carrier is passed as a compact bed in downward direction through the reaction chamber countercurrently to or concurrently with the hot hydrocarbon gases, then removed from the bottom of the reaction chamber and passed in fluidized condition to the bottom of a vertical reconditioning and reheating chamber with highly heated combustion gases. The latter should have enough oxygen to effect the combustion of the carbon which deposited on the granular carrier during the reaction. The regenerated contact material in the fluidized state is again passed to a separator and returned to the descending bed of contact material at the top of the reaction chamber.

Figure 1 attached to the Specification is a vertical elevation partly in section of an

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appropriate apparatus for catalytic hydrocarbon reactions such as catalytic cracking according to one method of carrying out the present invention. The catalyst is present in the form of a compact bed in the reaction zone and in the fluidized form in the regeneration zone.

Figure 2 is a vertical elevation of the principal parts of an apparatus for carrying out the catalytic cracking of hydrocarbons according to that modification of the invention in which the catalyst is present in the fluidized form in the reaction zone and in the form of a descending bed or layer in the regeneration zone.

The apparatuses and the 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 in line 3 through heat exchanger zones 4 and 5 to the heating coils 6. The latter are located in the furnace 7 which may be heated by means of gaseous, liquid or solid fuel. The hydrocarbon oil is vaporized during its passage through the heating coils and heated to an appropriate reaction temperature of say 950° F. It will be understood that the reaction temperature may vary within broad limits say between 900—1150° F., or even within broader limits according to the type of products and the nature of the catalyst. The heated hydrocarbon vapors are then fed through transfer line 8 to the bottom of reaction chamber 9 in which they ascend upwardly and countercurrently to the descending bed of granular catalyst 10. The cracking of the hydrocarbons takes place in the reaction chamber in contact with the catalyst which becomes fouled through deposition of carbon thereon. The cracked vapors leave the reaction chamber through overhead line 11 and are passed into the fractionating column 12. The latter is of conventional design, the above mentioned heat transfer coil 4 being placed in its upper part for purposes of refluxing. The cracked hydrocarbons may be fractionated in the fractionating zone, usually called bubble tower, into three fractions, namely a residue which is removed through bottom line 13, a heavy naphtha fraction which is collected in pan 14 and removed therefrom through line 15 and vapors comprising light naphtha and hydrocarbon gases which pass over the heat transfer coils 4 through the overhead line 16 into the condenser 17. The condensed light naphtha and the hydrocarbon gases are then discharged into the separator 18, the light naphtha leaving the separator through line 19 and the hydrocarbon gases through overhead line 20. These gases will contain a considerable amount of light but condensible hydrocarbons such as pentanes, pentenes, butanes, butenes, propane, propene, which are recovered by conventional methods such as, for example, in an absorption tower.

Turning our attention to the reaction chamber, the bottom part thereof ends in a long drawoff line 21 of enlarged cross section which serves as a purging zone. The fouled catalyst contains a considerable amount of adsorbed hydrocarbons which are preferably removed before regeneration. The purging is carried out by means of an appropriate inert gas such as steam. The purging gas is introduced through line 22 and is removed through line 23.

The purged catalyst is passed from the purging zone 21 into the line of enlarged cross section 24 through the slide valve or star feeder 25. A sufficient amount of air or of an inert gas such as nitrogen is introduced through line 26 to fluidize the granular catalyst passing through the transefer line 24 and to transport the catalyst to the bottom of the regeneration chamber 27. The regeneration gas such as air is admitted into the bottom of the regeneration chamber through line 28 and the distributor (not shown). It will be understood that the regeneration gas may be admitted into the regeneration chamber at several levels. The amount of air admixed with the granular catalyst is regulated so as to maintain the latter in the so-called fluidized condition throughout the regeneration zone.

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 in unit volume of gas. It is usual to differentiate between two types of fluidized state, the dense phase and the dilute phase. In the dense phase there is a considerable amount of slippage between the solid particles and the gas due to which the solid particles accumulate in the zone and are in a vehemently agitated condition. In the dilute phase there is less slippage between the solid particles and the gas and the solid particles are present in a considerably lower density in the zone. By the proper selection of gas or vapor velocities through the regeneration zone it is possible to attain that the solid particles are present both in the dense phase and in the dilute phase in the zone and the height to which the dense phase reaches in the regeneration zone can also be regulated. The thorough agitation in the dense phase equalizes any local temperature differences which may arise due to the burning of the coke.

In the drawing the meniscus 29 shows the height at which the dense and dilute phase are in contact with each other. The regeneration gases together with the suspended catalyst leave the regeneration zone through overhead line 30 discharging into the cyclone separator 31. The temperature in the regeneration zone is usually maintained below about 1100—1200°F. because a higher regeneration temperature may result in a deterioration and deactivation of most catalysts. For the purpose of temperature regulation the regenerator may be equipped with appropriate circulating lines (not shown) leading through heat exchangers wherein the catalyst is cooled.

The cyclone separator is a conventional apparatus for separating solids from gases or vapors, the separation being aided by a tangential introduction of the solid containing gases which produces a centrifugal force. Inert gas such as steam, nitrogen or carbon dioxide, is introduced into the bottom part of the cyclone separator or into the leg 32 thereof by means of line 33 in order to strip the adsorbed regeneration gas from the catalyst. The regeneration gas still contains some oxygen and the introduction of any substantial amount of oxygen with the catalyst into the reaction zone would be injurious as it is easily understood. The stripped granular catalyst particles are then discharged through leg 32 and the slide valve 34 to the top of the reaction zone. A distributor 35 may be provided in the upper part of the reaction chamber for the incoming granular catalyst. A hopper (not shown) may be provided between the cyclone separator and the reaction chamber to insure an even and adequate supply of the catalyst to the reactor. The level of the solid bed of catalyst in the reaction chamber is shown at 36.

The gases leaving the cyclone separator through line 37 have been freed of most of the solid particles but they still contain some catalyst, especially fines, which have been produced by attrition both in the reaction and in the regeneration zones. Such catalyst fines are sometimes allowed to become lost with the off gases but under other conditions it may be important to recover them in order to avoid an undue loss of catalyst. This recovery may be effected either by use of one or more cyclone separators followed, if necessary, by a Cottrell precipitator or by any other means known to the art. In the drawing there is shown a method of recovering catalyst fines in water. To attain this purpose the gases from line 37 are first cooled by passing the same over the previously mentioned heat exchange coils 5 located in heat exchanger 38. They are then discharged through line 39 into the tower 40 in which they are brought in contact with water admitted into the top of the tower through spray 41. The regeneration gases leave the tower through line 42 while the slurry of water and catalyst fines is removed through line 43. The catalyst fines are separated from the slurry by filtration or by some other means such as Dorr thickeners, then are submitted to agglomeration or otherwise worked up into coarse catalyst to be reused in the process.

In catalytic cracking processes the reaction and the regeneration zones may be maintained between a pressure of 1—2 atmospheres.

Referring to Figure 2, the heated oil vapors from line 8 shown in Figure 1 are discharged through line 44 together with the fluidized catalyst into the reaction chamber 45. The catalyst is present in the dense fluidized state in the greater part of the reaction chamber up to the level shown at 46. The cracked vapors with catalyst fines in suspension are discharged through the vapor line 47 into the cyclone separator 48 where the catalyst is separated from the oil vapors and returned through leg 49 into the reaction chamber. Line 50 serves for the introduction of a sufficient amount of an inert gas to keep the catalyst in leg 49 in the fluidized condition. The cracked oil vapors are led through transefer line 11 into the fractionating tower 12, both mentioned in the description of Figure 1.

The bulk of the catalyst is removed through the bottom of the reaction chamber through the stripping section 51 and leg 52 into the catalyst transfer line 53 of enlarged cross section. An inert gas such as steam is introduced into 52 by means of line 54, passed through leg 52 and stripping section 51, and is then removed through line 55. This inert gas has the double purpose of stripping the hydrocarbon vapors from the catalyst and of simultaneously keeping the latter in the fluidized state. The main purpose of the line 53 is to allow the transport of the catalyst in the fluidized state from the bottom of the reaction chamber to the top of the regeneration chamber. In order to facilitate this, air is admitted from the compressed air line 56 into 53 at several levels as shown in Figure 2. The fouled catalyst may be discharged from the transfer line 53 directly into the top part of the regeneration chamber 57. Catalyst fines from the latter may be passed through line 58 into the cyclone separator 59 and hence through leg 60 back into the regeneration chamber 57. Any catalyst fines which are not separated from the regeneration gases in cyclone separator 59 may be passed through line 37 into the catalyst recovery system 38, 40 previously described in connection with Figure 1.

The regeneration chamber 57 may consist of one or more sections. In the drawing we have shown it as having sections defined by the perforated plates 61 and 62 over which the catalyst descends in the form of a compact layer. Air is introduced below the perforated plates at points 63 and 64 through distributors (not shown) from the air line 56 in order to burn the carbonaceous deposits off the descending catalyst. The distributors 65 and 66 serve to direct the catalyst to the uppermost periphery of the perforated plates. They are shown to be provided with high pressure steam coils for the purpose of cooling the catalyst between the regeneration sections. The steam is introduced from steam line 67 and removed through another line (not shown). The rate of regeneration in any section may be further controlled by recirculation of nearly spent and cooled regeneration gas, e.g. from line 42 of Figure 1.

The regenerated catalyst is stripped from air in the stripping section 68 and the standpipe of enlarged cross section 69 by means of steam or other inert gas introduced from line 70. The stripping gas is removed through line 71. The catalyst is kept in a fluidized form in the standpipe 69 and is discharged after stripping into the transfer line 44 to be introduced into the reaction chamber 45 together with the heated hydrocarbon vapors.

The catalyst in the catalytic cracking of hydrocarbon oils as described in connection with Figures 1 and 2 may be any of the usual catalysts employed in catalytic cracking. Activated bentonites, montmorillonite, synthetic impregnated or plural gels, etc. may be mentioned as appropriate catalysts for cracking hydrocarbon oils. Catalyst deposited on a granular carrier may also be used.

The following example will illustrate the invention in its application to the catalytic cracking of hydrocarbon oils as carried out according to the modification shown in Figure 2.

East Texas gas oil of gravity 31.2° A.P.I. and aniline point 184°F. with an initial boiling point of 386°F. and 50% off at 675°F. was submitted to catalytic cracking in the dense phase under the following conditions:—

Average temperature in the reaction zone, 912°F.;

Average gauge pressure on the reaction chamber, 8.2 pounds per square inch;

Catalyst to oil ratio by weight, 3;

Approximate contact time, 10 seconds;

Nature of catalyst: acid treated clay;

Size of catalyst: passing between 6 and 8 meshes of the standard screen scale;

Linear vapor velocity: about 4 feet per second;

The following yields were obtained on the gas oil feed: 400°F. end point gasoline of 10 lb. R.V.P. 43.0% by volume;

Excess butanes 5.5% by volume;

Gas oil 51.2% by volume;

Dry gas of 29 average molecular weight —4.9% by weight;

Coke—3.1% by weight;

Inspection of the gasoline:—

Aniline point, 86°F.;

Octane number, 80 CFRM;

It contained 5.7% by volume of C_4 hydrocarbons.

Inspection of the gas oil obtained in the cracking:—

Gravity, 30° A.P.I.;

Initial boiling point, 476°F.;

50% off at 585°F.;

Aniline point, 158°F.;

Carbon on fouled catalyst, 1.53% by weight;

Carbon on regenerated catalyst, 0.5% by weight.

The present invention may be advantageously employed in the catalytic cracking, isoforming, reforming, hydroforming, aromatization, polymerization, dehydrogenation, hydrogenation and treatment of hydrocarbon oils for the removal of sulphur compounds or unsaturates, also in the so-called Fischer-Tropsch process for the production of hydrocarbons from carbon monoxide and hydrogen in the presence of a catalyst.

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 needs reconditioning after the reaction.

The expression "granular catalyst" in the Specification and claims is meant to designate a course catalyst which will not pass through a 10 mesh screen. (P.2489, 27th Ed. (1943) Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., 2310, Superior Av., N.E. Cleveland, Ohio). Such catalyst particles have a minimum diameter of about 2 mm. It is found that granular catalyst which does not pass through a 10 mesh screen and has particle sizes between

2 and 15 mm. is essentially advantageous for carrying out the present invention because it is appropriate for handling both in the form of a descending compact column or layer and in the fluidized form. The expression " granular catalyst " or " contact material " is meant to designate a granular catalyst or contact material of the above-defined size whether of irregular or of regular geometric shape, such as spheres, pellets, etc.

The linear gas or vapour velocities through the reaction and regeneration zones respectively 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 which is easily realized at the reaction or regeneration temperatures involved. Thus, for example, if it is found that a 3 mm. diameter catalyst requires a linear vapor velocity of about four feet per second for the maintenance of a dense phase in a zone the linear velocity must be increased to about eight feet per second if catalyst of approximately 12 mm. diameter is to remain in the dense phase in the same zone when other factors such as temperature, pressure, nature of the catalyst, etc. remain unchanged. The necessary linear vapor velocities will also depend among other things, on the shape of the catalyst, on the viscosity of the gases and vapors, on the relative density of the solid to the gases or vapors, and on the size distribution of the solid particles. The necessary velocity is best determined experimentally.

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

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.

In the process described in connection with Figure 1 the regeneration may have been carried out in the dense phase with downflow in the regeneration zone and in that described in connection with Figure 2 the reaction may have been carried out in the dense phase with downflow in the reaction zone. The modifications necessary for this purpose will be obvious to those skilled in the art.

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 granular contact material as hereinbefore defined which needs reconditioning after the reaction by means of gases in a reconditioning zone which comprises moving the contact material as a descending compact bed through one of said zones and in the fluidized state through the other of said zones, and effecting the elevation of the contact material from a lower to a higher level in the fluidized state for transfer from one zone to the other.

2. The method according to claim 1 in which the contact material is of catalytic nature and either the reaction products or both the reacting vapors and the reaction products are predominantly hydrocarbons.

3. The method of carrying out the conversion of hydrocarbon vapors comprising catalytic cracking, isoforming, reforming, hydroforming, dehydrogenation, aromatization and treating hydrocarbon oils for the removal of sulphur compounds or unsaturated compounds, which comprises passing the hydrocarbon vapors through a reaction zone in contact with a granular catalyst as hereinbefore defined maintained in the form of a descending compact column, removing the hydrocarbon vapors after the desired conversion has taken place from the reaction zone, removing the catalyst from the reaction zone and stripping the same from hydrocarbon vapors, fluidizing the catalyst by means of a gas and passing it in the fluidized state through a regeneration zone together with an oxygen-containing regeneration gas, removing the regeneration gas from the regeneration zone, removing the regenerated catalyst from the regeneration zone, separating and stripping it from regeneration gas in a separating and stripping zone, and returning the stripped regenerated catalyst to the upper part of the reaction zone.

4. The method according to claim 3 in which the regeneration gas removed from the separating zone is free of catalyst fines in a catalyst recovery zone.

5. The method according to claim 3 in

which the catalyst is maintained in the dense phase in at least part of the regeneration zone.

6. The method of cracking hydrocarbon vapors according to claim 3 in which the reaction zone is maintained at a temperature between 900—1150°F. and at an absolute pressure of between 1 and 2 atmospheres.

7. The method of carrying out conversion of hydrocarbon vapors comprising catalytic cracking, isoforming, reforming, hydroforming, dehydrogenation, aromatization and treating hydrocarbon oils for the removal of sulphur compounds or unsaturated compounds, which comprises passing the hydrocarbon vapors through a reaction zone in contact with a granular catalyst as hereinabove defined and maintained in the fluidized state, removing the hydrocarbon vapors from the reaction zone after the desired conversion has taken place, removing the fluidized catalyst from the reaction zone and stripping it from hydrocarbon vapors, transferring the stripped catalyst in the fluidized state to the upper part of a regeneration zone, passing the catalyst downwardly through the regeneration zone in the form of a compact bed or layer, passing an oxygen-containing regeneration gas through the descending bed of catalyst, removing the regeneration gas from the regeneration zone, removing the regenerated catalyst from the regeneration zone and stripping it from the regeneration gas, fluidizing the stripped regenerated catalyst and introducing it into the reaction zone.

8. The method according to claim 7 in which the removed regeneration gas containing catalyst particles in the fluidized state is passed into a separation zone, separated catalyst is returned to the regeneration zone and further amount of catalyst is recovered from the regeneration gas leaving the separation zone in a catalyst recovery zone.

9. The method according to claim 7 in which the regeneration zone is subdivided into a plurality of sub-zones and the catalyst is cooled during its passage from one sub-zone to the next.

10. The method according to claim 7 in which the catalyst is maintained in the dense phase in at least part of the reaction zone.

11. The method of cracking hydrocarbon vapors according to claim 7 in which the reaction zone is maintained at a temperature between 900°-1150°F. and an absolute pressure of between 1 and 2 atmospheres.

Dated this 2nd day of January, 1945.
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592,190 COMPLETE SPECIFICATION

2 SHEETS
SHEET 1

[This Drawing is a reproduction of the Original on a reduced scale]

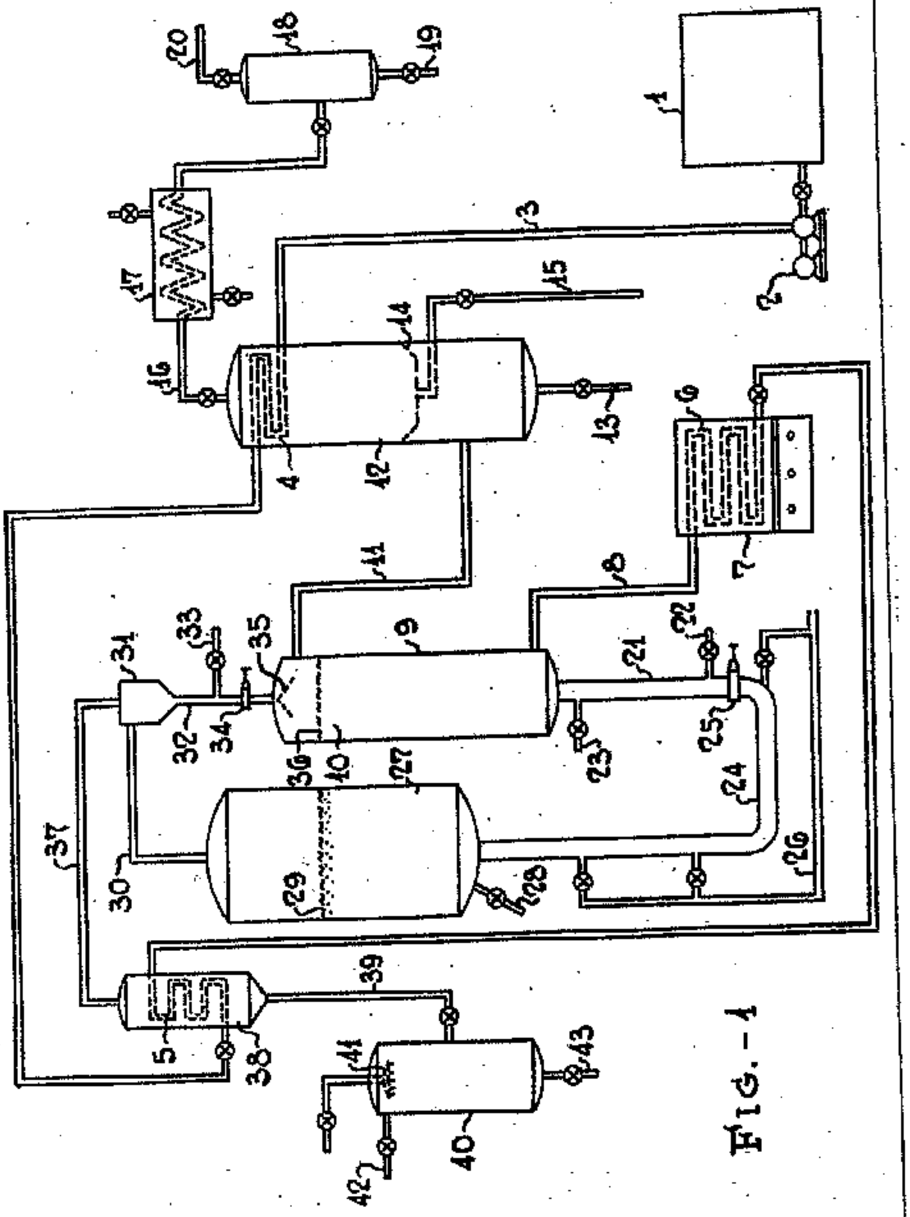

FIG. 1

[This Drawing is a reproduction of the Original on a reduced scale.]

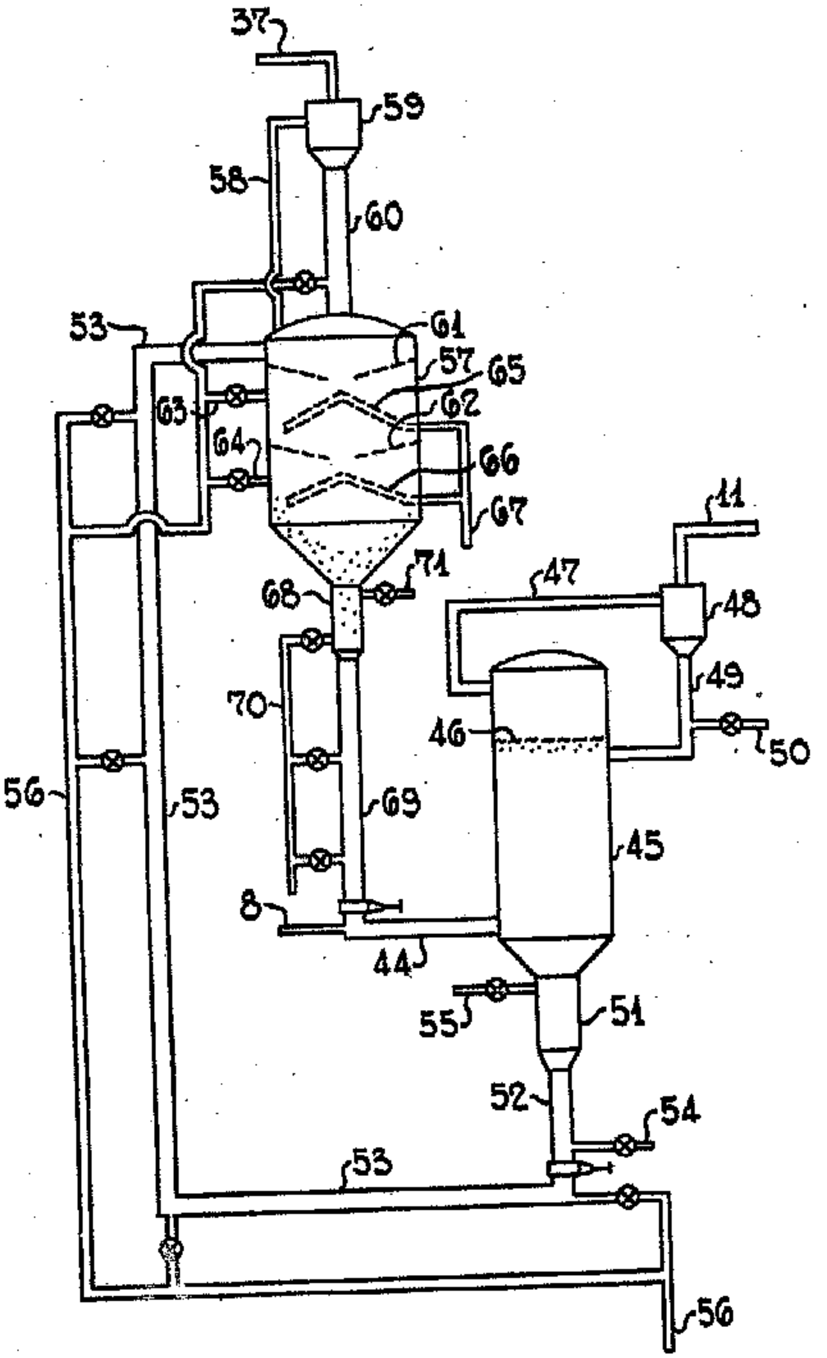

FIG. - 2