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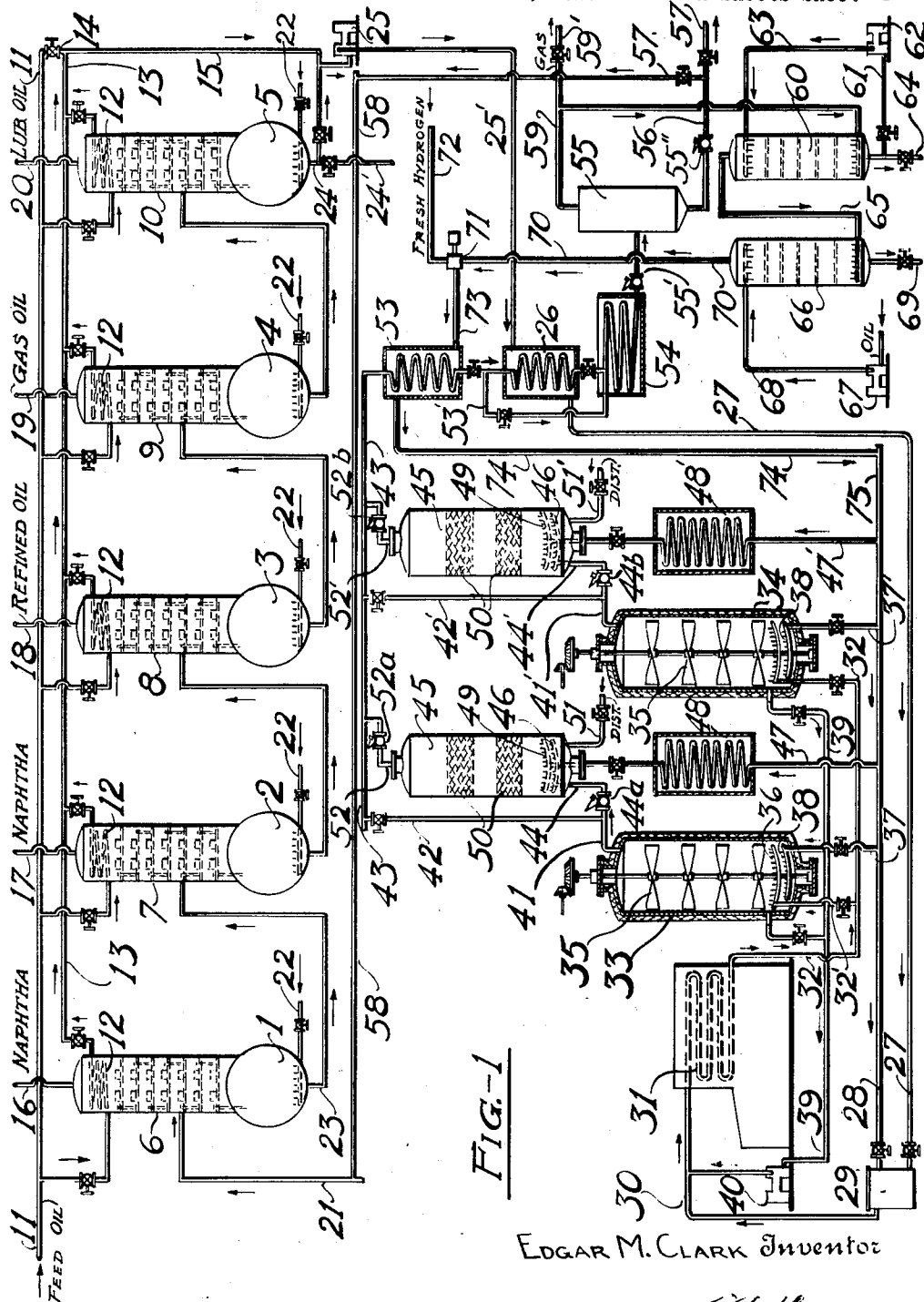
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METHOD AND APPARATUS FOR HYDROGENATION AND DISTILLATION

Filed Jan. 26, 1928

2 Sheets-Sheet 1



By His Attorney *W. W. Wain*

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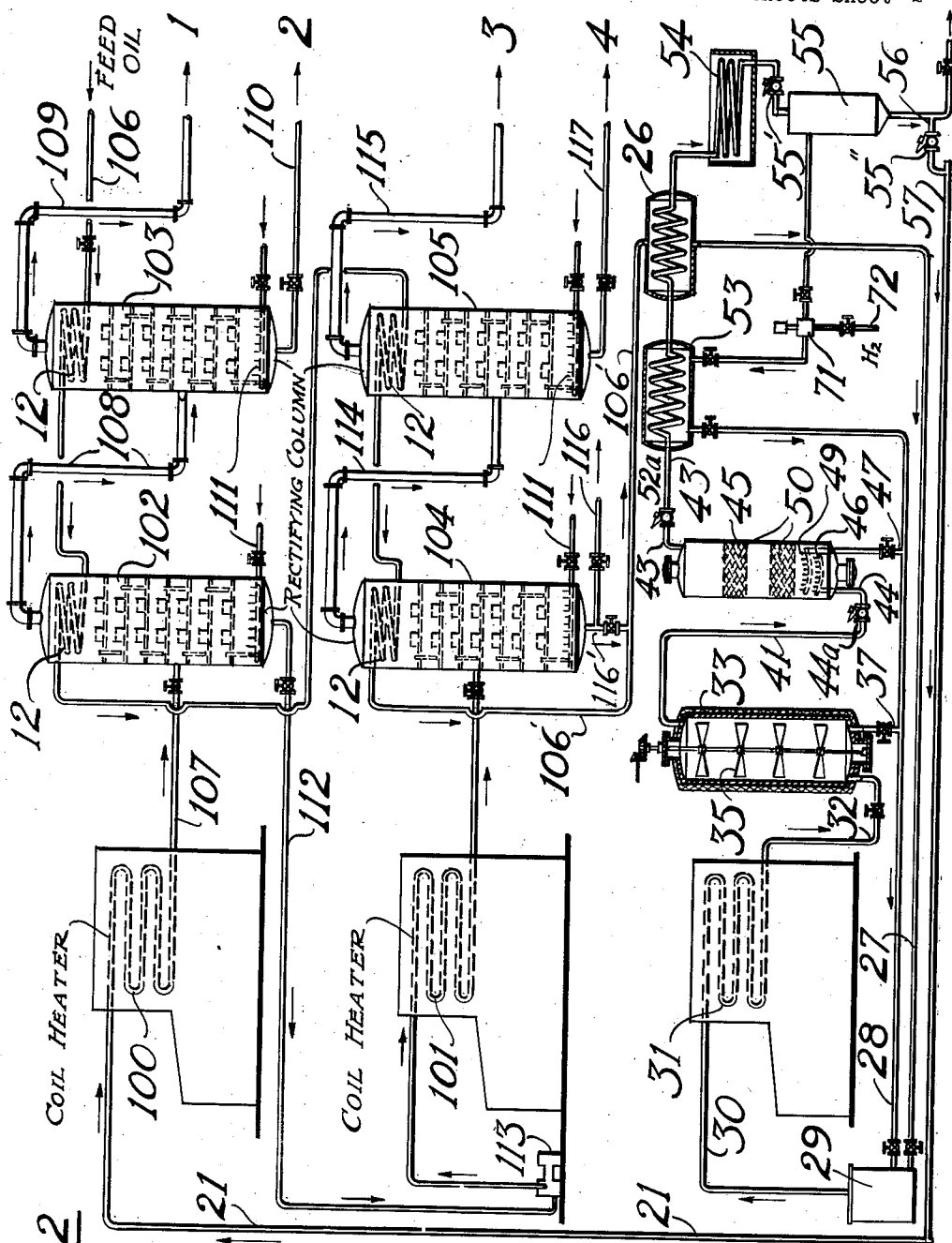


FIG. 2

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METHOD AND APPARATUS FOR HYDROGENATION AND DISTILLATION

Application filed January 26, 1928. Serial No. 249,584.

The present invention relates generally to the art of hydrogenating hydrocarbon oils. More specifically, it comprises an improved process and apparatus for producing large yields of valuable products from oils such as crude petroleum or reduced crude, with or without other carbonaceous matter. The invention will be fully understood from the following description and the drawings which illustrate preferred methods and apparatus.

Fig. 1 is a semi-diagrammatic view in elevation of a continuous battery of shell stills, in combination with high pressure hydrogenation equipment, and illustrates the flow of materials through the apparatus; and

Fig. 2 illustrates a modification in which pipe or coil stills are substituted for the shell stills.

Referring to Fig. 1 of the drawings, stills 1, 2, 3, 4, and 5 are arranged as a continuous battery and it is to be understood that either a greater or lesser number of such stills may be used. These stills are of the ordinary shell type, and each is preferably fitted with a rectifying column 6, 7, 8, 9, and 10 respectively, of any suitable design. Bell-cap plate columns are perhaps most satisfactory. Each column is provided with a refluxing coil 12, which also serves as a means for preheating the oil which is fed by a line 11 to the coils 12. Preheated oil is collected in a hot oil line 13 and the coils 12 are preferably arranged so that each may be fed with a regulated quantity of oil in accordance with the cooling desired in each column. There is a by-pass line 14 connecting the cold oil line 11 with the hot oil line 13. The total feed is collected in line 15.

Towers 6, 7, 8, 9, and 10 are fitted with vapor lines 16, 17, 18, 19, and 20, respectively, and each vapor line communicates with a condenser, not shown, so that a separate distillate may be obtained from each still. Oil is fed to tower 6 by line 21, as will be described below, and distillate is removed from the tower 6 by vapor line 16. Bottoms or unvaporized oil collects in still 1, which is heated by combustion gas or otherwise. Steam may be injected into the still by spray pipe 22, if desired. The unvaporized oil is

fed to tower 7 by a flow line 23 which may be provided with a pump, but it is preferable to inject a small quantity of steam into the line to induce the flow. The oil flows to remaining stills in series, as will be understood, each still producing a cut or fraction of oil. Residuum from still 5 is withdrawn by line 24 and may be run to storage by line 24' or preferably combined with the oil from line 15 and conducted to a high pressure pump 25.

Pump 25 forces the oil under high pressure through a pipe 25' and, if desired, to a heat exchanger 26, in which the oil temperature is raised, and then into line 27. Hydrogen or a gas containing hydrogen is fed by line 28, as will be described below, into line 27 through a mixer 29. The mixer may be of any preferred design but it has been found satisfactory to feed the hydrogen into the oil through a perforated or porous plate so as to form a substantially homogeneous mixture, which then passes through pipe 30 into a coil 31, preferably heated by combustion gases.

Coil 31 discharges into a line 32 carrying the heated mixture of oil and hydrogen under high pressure into a plurality of high pressure reaction chambers or reactors for hydrogenation. Two reactors 33 and 34 are shown, but the number may be varied. They are similar in construction and preferably consist of heavy metal shells designed to withstand heat, pressure, and the action of hydrogen. The shells are preferably not heated externally but are heavily lagged against loss of heat. They may be fitted with internal electrical heaters (not shown) or may depend solely on heat carried by the oil and hydrogen from coil 31.

If desired, the temperature of the reactors 33 and 34 may be maintained by circulating a part of the charge through a line 39 and suitable means, such as a surge pump 40, to the inlet of coil 31. Coil 31 may be eliminated and the heat supplied by the internal heaters mentioned, but I prefer to heat by coil 31, as described above. Means for stirring or agitating, such as the paddles 35, or other means for obtaining intimate mixing in the reactors may be used. Pipe 32 discharges through a

branch pipe 32' and a spray head 36. Hot hydrogen-containing gas is fed by branch pipe 37 to a second spray head 38. Other methods of introducing the gas and oil may be used, such as nozzles, and the like.

Vapor is removed from reactors 33 and 34 by lines 41, 41' and may be conducted directly by lines 42, 42' to a vapor manifold 43. Alternatively, vapor may be conducted by lines 44, 44' into secondary reactors 45 and distributed therein, as by spray pipes 46. Chambers 33 and 34 may be considered as primary reactors. Pressure control valves 44a and 44b are installed in lines 44, 44', respectively. An additional quantity of hydrogen-containing gas may be fed to secondary reactors 45 by lines 47, 47'. This gas is preferably heated by heaters 48, 48', before entering the secondary reactors, in which it may be distributed and thoroughly mixed, as by spray pipes 49. However, the reactors 45 may be heated internally, if desired. Catalytic masses 50 are provided in reactors 45 for promoting reaction between the oil and hydrogen. Distillate oils, preferably preheated, may be added by lines 51, 51'.

Vapor passes from the chambers 45 by lines 52, 52', into the vapor manifold 43, which conducts the vapor to a heat-exchanger 53, in which the incoming hydrogen-containing gas is preheated, as will be described. The hot products may then flow to a second exchanger 26, which is used to further preheat the incoming oil, as stated above, or this exchanger may be by-passed through valved line 53'. The vapor, with any condensates formed from it, flows thence to a cooler 54. Pressure control valves 52a and 52b are installed in lines 52, 52', respectively. The cooled products then pass to a drum 55 for separation of gas from liquid. The latter is continuously removed by line 56 and is conveyed by lines 57 and 58 into line 21 and thence to the tower 6 of still 1, as was described above, or out of the system through pipe 57'. Pressure control valves 55', 55'', respectively, are provided in the inlet and outlet lines connecting drum 55.

Gas from drum 55 flows by line 59 to a purifying tower 60, where it is washed to remove impurities, such as hydrogen sulfid. A water solution of caustic soda or carbonate of soda may be used and the liquid is preferably recirculated by line 61, pump 62, and line 63. Gas may be vented, when required, through line 59'. Spent purifying solution may be withdrawn by line 64 and revived if desired.

Gas from tower 60 passes preferably through line 65 to a tower 66 to be washed with a suitable medium, such as petroleum oil, for removal of methane or other light hydrocarbons and any remaining hydrogen sulfid. Wash oil is forced into the top of tower 66 by pump 67 and line 68 and with-

drawn by line 69 to apparatus (not shown) for removing the dissolved gas from the oil. The purified gas flows from the top of tower 66 by a line 70 to a booster pump 71. Fresh gas may be added by line 72 and the highly compressed mixture is fed to the heat exchanger 53, as described above, by line 73, and thence by line 74 to a manifold 75. Hydrogen-containing gas is distributed in regulated quantities to pipes 28, 37, 37' and 47, 47', as has been described, and through these pipes respectively to mixer 29, primary reactors 33 and 34, and secondary reactors 45.

Referring now to Fig. 2, it will be seen that the shell stills 1 to 5 have been replaced by coil heaters 100 and 101, each provided with two rectifying columns 102 and 103 for heater 100, 104 and 105 for heater 101. More than 2 heaters could obviously be used, but for illustrative purposes, two only are shown. The crude oil is fed by pipe 106 and is passed through the coils in towers 103, 102, 105 and 104 in the order named. By-pass lines (not shown) are preferably provided so that the cooling effect in each tower may be suitably regulated. Hot oil from coil 12 in tower 104 then passes by line 106' to hydrogenation equipment similar to that described in connection with Fig. 1, but shown in a somewhat simpler form, the gas purifying system in particular being omitted. In Fig. 2 only one primary reactor 33 and only one secondary reactor 45 are shown, for simplicity, but two or more may be provided as in Fig. 1. The flow of materials through the hydrogenating equipment need not be traced again.

A line 107 conveys oil from heater 100 to tower 102. Vapor lines 108 and 109 lead from towers 102 and 103, respectively. Bottoms or unvaporized oil may be withdrawn from tower 103 by line 110, after stripping by steam injected through line 111, if desired. Bottoms from tower 102 pass to coil 101 through line 112 and pump 113. Towers 104 and 105 are provided with vapor lines 114 and 115 respectively. Lines 116 and 117 conduct unvaporized oil from these towers. A by-pass 116' connects line 116 with line 106'.

In operation of my improved process with the equipment shown in Fig. 1, the preheated crude petroleum or reduced crude is usually mixed with heavy residuum from the stills and the mixture is passed into the hydrogenation zone. The oil in reactors 33 and 34, which may be used continuously, is held under pressure of 50 or 100 to 200 atmospheres or more (preferably about 200 atmospheres) and at a temperature of about 750-950° F. A catalyst, preferably finely pulverized metal oxids, may be suspended in the oil on starting up the unit and may be maintained in the reactors or circulated around through pipe 39 and coil 31. A catalyst such as 90%

chromium oxid and 10% molybdenum oxid has been satisfactorily used. The amount of catalyst may be widely varied. When using the catalyst described, it is desirable to have it present in amount about $\frac{1}{3}$ by volume of the oil in the reactor at any one time.

The hydrogen-containing gas is preferably substantially pure hydrogen and is usually forced into the reactors 33 and 34, at a rate of from 10,000 to 15,000 cu. ft. per bbl. of oil fed. Most of the asphaltic materials that may be in the oil appear to be converted into low-boiling distillates. From 60-80% of total sulphur is ordinarily converted into hydrogen sulfid. The equipment described is especially adapted for running high sulphur oils. In a copending application Serial No. 249,585 filed January 26, 1928, a system designed for low sulphur oils is described and claimed.

Gases and vapors from primary reactors 33 and 34 may be conducted into the secondary reactors 45. The latter operate preferably at 800°-950° F. and under the pressure maintained in the reaction chambers, although pressure in the secondary reactors may be satisfactorily reduced as low as 25 atmospheres. Catalytic materials, similar to those used in reactors 33 and 34, are preferably arranged on trays or otherwise to secure good contact with vapors.

It appears that the oil is hydrogenated mostly in liquid phase in the primary reactors 33 and 34, while the reaction in the secondary reactors 45 is doubtless mostly in the gas or vapor phase. Whatever the nature of the reaction, substantially increased yields of low-boiling products are obtained when the secondary reactors are used.

The temperature is raised in the secondary reactors 45 by forcing in a supply of highly heated hydrogen or hydrogen-containing gas through lines 47, 47' and heaters 48, 48'. The rate of flow of hydrogen may vary, but should ordinarily be about 30,000 cu. ft. per bbl. of gasoline formed. Distillate oils, heavier than gasoline, such as heavy naphtha, kerosene, gas oil and the like, or mixtures of these oils, may be passed into reactors 45 through lines 51, 51', either as liquid or vapor. Such distillates may be obtained from the various stills of the continuous battery, as will be discussed below. While it is often advantageous to provide secondary reactors 45, the use of reactors 33 and 34 alone, gives good results.

Vapor from reactors 45 and/or 33 and 34 is cooled in preheating the incoming crude oil and incoming hydrogen, in exchangers 26 and 53, respectively. Normally liquid products are condensed in coil 54 and separated in drum 55 from gases, which may contain low boiling hydrocarbons, hydrogen sulfid, etc., with residual hydrogen. The gas is purified in any satisfactory manner, such as

washing with alkali or water in tank 60 to remove hydrogen sulfid and with oil in tank 66 to remove hydrocarbons, and is then returned to the process. Condensation is usually under full pressure.

It will be understood that any desired degree of rectification may be substituted for the simple condensation in cooler 54 and gas release in drum 55. Lighter products may be recovered by such rectification and the hydrogenated residuum only returned to the stills.

The condensed hydrogenated oil, preferably as hot as may be without allowing any substantial quantity of gasoline to be carried off by the gas, is conveyed to the battery of stills where it is separated into fractions, such as gasoline, naphtha, kerosene, gas oil, and lubricating oils, which are removed from the stills in the order named. Pressure is substantially atmospheric and temperature is progressively increased from the first to the last still, as in an ordinary crude battery. The first still will be at a temperature between 350° F. and 470° F., or higher, depending on the boiling range of distillate desired, and the last still in the series may be as high as 700° F. The same general range of temperatures may be maintained in the coil heaters 100, 101, Fig. 2. Distillation takes place chiefly in towers 102, 103, 104 and 105. The method of operating the equipment shown in Fig. 2 will be obvious from the foregoing description.

If preferred, only gasoline, kerosene, and gas oil may be removed and the lubricating fractions, as well as the heavy residue, may be recirculated to the hydrogenation and cracking equipment.

The present method is applicable to all petroleum oils, whether crude, reduced crude, or heavy refinery residues, or shale oil and the like, and is particularly applicable to oils which contain large quantities of sulphur. Finely divided coal or similar carbonaceous material may be commingled with the oil to form a fluent mass for hydrogenation and/or distillation. The invention is not limited by any theory of the reaction nor by any illustrative example of either apparatus or process. Various changes and alternative arrangements may be made within the scope of the following claims, in which it is desired to include all novelty inherent in the invention.

I claim:

1. Process for obtaining valuable products from hydrocarbon oil, comprising forcing a mixture of the oil and hydrogen under high pressure through a heating zone, discharging the heated mixture into a reaction zone, maintained at a temperature in excess of about 750° F. and under a pressure above about 100 atmospheres, withdrawing a mixture of gases and vapors substantially free

- of liquid therefrom, cooling the same under full pressure, separating the condensate from the uncondensed gases, expanding said separated condensate into the first of a series of distillation zones, distilling under substantially atmospheric pressure, removing distillates from the distillation zones, and returning the undistilled residue to the reaction zone.
2. Process of continuously hydrogenating oil, comprising maintaining a supply of hydrogenated oil, distilling products from the hydrogenated oil in a series of distillation zones without hydrogenation, preheating feed oil by indirect heat exchange with vapors produced in said distillation zones, hydrogenating the preheated oil at a temperature above about 750° F. and under a pressure above about 50 atmospheres, separating hydrogen therefrom, passing the hydrogenated oil to the first distillation zone for progressive flow through the series, and commingling the residual oil from a later distillation zone with the preheated oil passing to the hydrogenation stage.
3. Continuous hydrogenation and distillation apparatus, comprising a heating coil adapted to raise oil under pressure in excess of 50 atmospheres to a temperature at which it reacts with hydrogen, a reactor, means for passing the hot oil into the reactor, means for supplying hydrogen at high pressure and temperature to the reactor for intimate admixture with the oil therein, means for segregating gases and normally liquid products from the reactor, means for expanding said liquid products to low pressure, means for distilling lower boiling fractions from said liquid products under substantially atmospheric pressure, and means for continuously returning residual liquid products with hydrogen to the heating coil and thence to the reactor.
4. Apparatus according to claim 3, in which means are provided for purifying the gases under high pressure therefor returning them to the reactor.
5. Hydrogenation and distillation apparatus, comprising means for mixing oil with hydrogen, means for heating said mixture under pressure in excess of 100 atmospheres, a primary reactor into which said heated mixture may be discharged, a secondary reactor, means for passing vapors from the primary reactor to the secondary reactor, means for supplying additional hot hydrogen to said secondary reactor, means for condensing normally liquid products from the vapors from said secondary reactor and means for separating said liquid products from uncondensed gases without substantial reduction in pressure, means for expanding said separated liquid products into the first of a series of distillation zones, and means for distilling and fractionating said liquid products under atmospheric pressure.
6. Process for obtaining valuable products from a fluent carbonaceous material which comprises heating the material in the presence of hydrogen at a pressure not substantially less than 50 atmospheres, withdrawing a mixture of gases and vapors substantially free of liquid, cooling the same without any substantial reduction in pressure, separating the condensate from uncondensed gases, continuously expanding the condensate into the first of a series of distillation zones and distilling under a materially lower pressure.
7. Process for obtaining valuable products from a hydrocarbon oil, which comprises heating the oil in the presence of hydrogen at a pressure not substantially less than 100 atmospheres, withdrawing a mixture of gases and vapors substantially free of liquid, cooling the same under substantially the same pressure, separating the condensate from uncondensed gases, continuously expanding the condensate into the first of a series of distillation zones and distilling under a materially lower pressure.
8. Process according to claim 7 in which the undistilled residue from one or more of the distillation zones is returned to the hydrogenation step.
9. Process for obtaining valuable distillate oils from heavy hydrocarbon oil, comprising heating the oil in the presence of hydrogen at a pressure not substantially less than 100 atmospheres, withdrawing a mixture of gases and vapors substantially free of liquid, condensing out normally liquid products from the gases and vapors, continuously expanding the liquid products into a distillation zone, distilling without hydrogen, collecting distillate oils from said zone, and returning the undistilled residue to the hydrogenation step.
10. Process for obtaining valuable distillates from petroleum oil, comprising suspending a catalytic material in the oil, maintaining a body of the suspension under a pressure not substantially less than 100 atmospheres, and temperature in excess of 750° F., forcing a gas rich in free hydrogen into the suspension, withdrawing a mixture of gases and vapor substantially free of liquid, condensing normally liquid products from the gases and vapors, releasing pressure on said liquid products, distilling the liquid products under substantially atmospheric pressure in a series of distillation zones, collecting distillates from the distillation zones, and returning the undistilled residue to the body of oil under high pressure.
11. Process for obtaining valuable distillates from petroleum oil, comprising suspending a catalytic material in the oil, maintaining a body of the suspension under a pressure not substantially less than 100 at-

mospheres, and temperature in excess of 750° F., forcing a gas rich in free hydrogen into the suspension, removing gases and vapors from said body of oil and subjecting them before being cooled to hydrogenation in vapor phase in a second reaction zone, withdrawing a mixture of gases and vapors substantially free of liquid from said second zone, condensing normally liquid products from the gases and vapors, releasing pressure on said liquid products, distilling the liquid products under substantially atmospheric pressure in a series of distillation zones, collecting distillates from the distillation zones, and returning the undistilled residue to the body of oil under high pressure.

12. Process according to claim 11 in which the vapors evolved from the body of oil are passed through the secondary reaction zone with an additional quantity of gas rich in free hydrogen.

13. Process according to claim 11 in which the secondary reaction zone is maintained at a temperature in excess of 800° F. and under a pressure above 25 atmospheres.

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