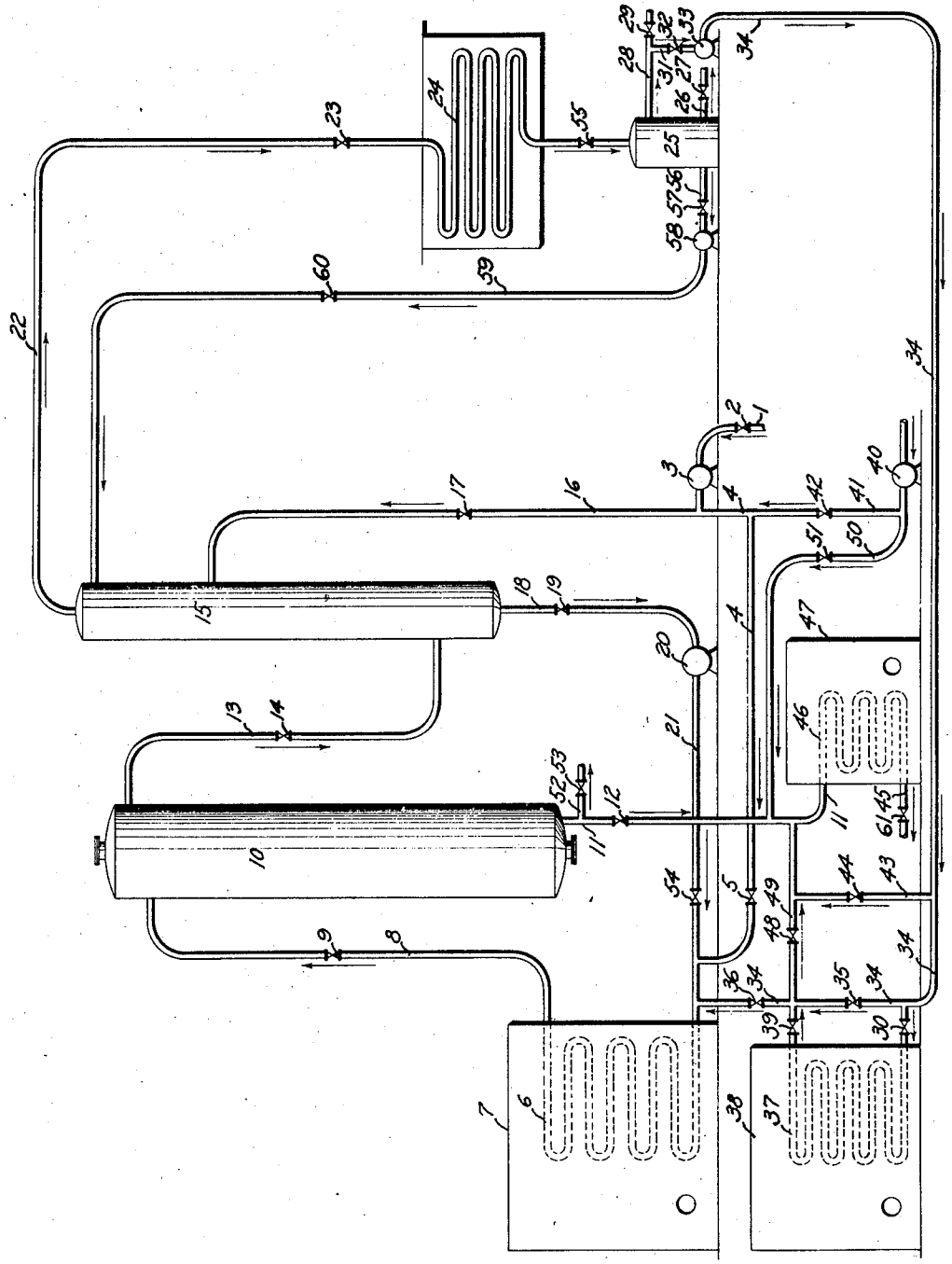
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CRACKING OF HYDROCARBON OIL

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CRACKING OF HYDROCARBON OIL

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This invention relates to the conversion of hydrocarbon oils, and refers more particularly to hydrogenation of hydrocarbon oils, particularly those which are formed during the cracking process and which are deficient in hydrogen with respect to saturation.

In the conversion of higher boiling hydrocarbons into lower boiling hydrocarbons at elevated temperatures, and usually under pressure, pitchy material or heavy asphaltic residue may be formed under certain conditions of operation in addition to a carbonaceous product and a gaseous product. Analysis of the gaseous product shows it to contain considerable elementary hydrogen, as well as combined hydrogen. When the process is operated to produce a heavy fuel oil, this product contains a much higher ratio of carbon and hydrogen than the motor fuel product, and it is possible by the addition of hydrogen to the heavier hydrocarbon to supply this hydrogen deficiency and convert the same into a lower boiling product suitable for motor fuel; otherwise the chief product of further reaction or cracking of the heavy residue is coke and gas.

It is not the object of this invention necessarily to completely saturate the motor fuel product with respect to hydrogen, that is, to have all the carbon atoms of the molecules of the gasoline hydrocarbons contain all of the hydrogen which the quadrivalent character of the carbon atom demands. So far as the motor fuel product is concerned, it is quite desirable that some of the components be unsaturated, and particularly belong to that group of unsaturated carbons known as the mono-olefins. However, it is desirable that the reaction be carried out in such manner as to convert an otherwise heavy asphaltic product deficient in hydrogen into lower boiling hydrocarbons and to prevent the formation of carbon by causing the same to enter into combination with hydrogen before separating out as such.

In carrying out my invention I aim to effect a balance so that the hydrogen which separates out in the gas, either as such or in combined form, will enter into combination with components of a pitchy or asphaltic nature, or will prevent their formation, with the object of producing a greater yield of liquid products, particularly gasoline. In carrying out the operation of the process of my invention, the gaseous product of the process is returned either directly or after heat treatment to convert it further into elementary hydrogen and is contacted with the oil undergoing treatment, preferably in the presence of a hydrogenating catalyst. This catalyst may be a metal, examples of which are potassium, sodium, calcium, barium, strontium, magnesium, aluminum, zinc, tin, iron, chromium, nickel, manganese, copper, silver, platinum, palladium and osmium. Oxides of the metals may also be used, as well as other compounds of the said metals.

Referring to the accompanying drawing diagrammatically illustrating the process, the raw oil is charged through line 1, controlled by valve 2, and is forced by means of pump 3 into line 4, controlled by valve 5, and thence into heating coil 6 located in furnace setting 7. The heated oil leaves the heating coil 6 through transfer line 8, controlled by valve 9, and is discharged into reaction chamber 10 maintained under conversion and hydrogenation conditions of temperature and pressure. The non-vaporized liquid residue from reaction chamber 10 is withdrawn through line 11 and may be removed from the system through line 52 and valve 53. Preferably, however, the liquid residue is passed through valve 12 to further treatment in a manner which will hereinafter be described.

The vapors separated in reaction chamber 10 pass through vapor line 13, controlled by valve 14, and enter dephlegmator or fractionating column 15. A portion or all of the raw oil can be pumped through line 16, controlled by valve 17 into dephlegmator 15 where it undergoes heat exchange with the ascending vapors, condensing a portion thereof and becoming heated. The reflux condensate from dephlegmator 15 together with unvaporized raw oil is returned to the heating coil 6 for reconversion through line 18, controlled by valve 19, and through hot oil pump 20 and line 21, controlled by valve 54. The sufficiently converted vapors leaving dephlegmator 15 pass through line 22, controlled by valve 23, into cooler and condenser 24, the condensate being collected in receiver 25. Valve 55 assists in controlling the flow of the fluids into the receiver, as well as to control the pressure upon the condenser.

The distillate collected in receiver 25 is passed through line 26, controlled by valve 27, to storage. A portion of this distillate, however, is preferably withdrawn through line 56 and valve 57 and by means of pump 58 may be returned through line 59 and valve 60 to the dephlegmator 15 to assist in the cooling of the vapors therein and to assist in controlling the character of the distillate passing into receiver 25. The uncondensed gas is removed through line 28, controlled by valve 29, which valve may also be used to control pressure upon the entire system. A portion of the gas may then be passed to storage or diverted for other

uses and this portion may be scrubbed or otherwise treated to remove the condensable material therefrom. Any desired amount of gas is recirculated to the process through line 31, controlled by valve 32, and is boosted to any desirable pressure by pump or compressor 33. The gas may be returned directly to the heating element 6 through line 31, valve 32, pump 33, line 34 and valves 35 and 36, or it may be passed, all, or in part, by the manipulation of valves 30 and 35, prior to injection to heating coil 6, into the heating element 37 located in furnace setting 38 to be heated to a temperature which will cause both cracking and polymerization, increasing the hydrogen content of the gaseous product entering heating coil 6, as well as increasing the total liquid product formed from the process by the polymerization of a portion of said gases. The temperature to which the gases may be heated in heating element 37 may vary between 800 and 1500° F., more or less. The gases leaving heating element 37 pass through valves 39 and 36 and line 34 into heating coil 6.

The catalyst, preferably in suspension in the charging oil, is introduced into heating coil 6 by means of pump 40 through line 41, valve 42, and line 4 and valve 5.

The liquid residuum, including any vapors leaving reaction chamber 10 through line 11, controlled by valve 12, may be passed into heating element 46 located in furnace setting 47 for separate treatment with the gas which may enter line 11 directly from line 34 through line 43, controlled by valve 44, and through line 49, or from the heating element 37 through valves 39 and 48 and line 49. The catalyst for assisting in the hydrogenation of the residuum is introduced into line 11 through pump 40, line 50 and valve 51. The residual material treated together with gas and catalyst in heating element 46 is preferably passed to a vaporizing vessel and associated dephlegmating and condensing equipment (not shown) through line 45 and valve 61 for recovery of the vapors evolved and the final liquid residue may be removed to storage. A portion or all of the residuum may be withdrawn through line 52, controlled by valve 53, and may be passed to storage or into a chamber (not shown) under reduced pressure where it may undergo flashing or vaporization. The distillate resulting from the vaporization of the residue so treated may be returned for further conversion into the heating element 6, and the residue from this flashing zone may be returned to heating element 46 for treatment in the manner described for the non-vaporized liquid residue leaving reaction chamber 10.

As examples of operating conditions, the pressure upon heating element 6 and on reaction chamber 10 may vary from 100 pounds per square inch, more or less, to several thousand pounds. Differential pressures may be maintained upon these elements which in the case of heating element 6 and reaction chamber 10 will be controlled by valve 9. Likewise, the pressure on heating elements 37 and 46 may be controlled over a wide range varying from 100 pounds per square inch, more or less, to several thousand pounds. The pressure upon any of these heating elements may be independently controlled by means of pumps (not shown). The temperatures in heating elements 6, 37 and 46 may vary from 800° F., more or less, to 1400° F., more or less.

As examples of the yields of products obtained by my process: Mid-Continent topped crude was treated, which would normally produce, by non-residuum operation, 60% gasoline; 50 pounds of coke per barrel; 650 cubic feet of gas per barrel, and the remainder a gas oil known as pressure-distillate bottoms; whereas, by my process I may be able to obtain 70% gasoline, 30 pounds of coke per barrel and 300 cubic feet of gas per barrel, in addition to the pressure-distillate bottoms, the most desirable product, gasoline, being increased, while the least desirable products, namely, gas and coke, are decreased. The results will vary depending upon the manner of treatment; for example, preheating the gas will increase the yield of liquid products as will also the heat treatment of the residuum oils while passing the gas therethrough or varying the conditions of treatment on the reflux condensate passing through heating element 6, e. g., increasing the temperature will increase the anti-knock value of the gasoline produced. It is obvious that increased temperature and pressure on heating element 46 will increase the conversion of the residual oil passing therethrough and increase the overall yield of low boiling products.

It will be understood that the above examples are purely illustrative, and that the results obtained will vary according to the conditions of treatment and kinds of charging stock used, and that my invention is not limited in any manner by the examples cited.

What I claim as my invention is:

1. A process which comprises subjecting hydrocarbon oil in a cracking zone to cracking conditions of temperature and sufficient pressure to maintain a substantial portion thereof in liquid phase and separating the same into vapors and unvaporized oil, passing said unvaporized oil, without substantial cooling thereof, to a hydrogenating zone, dephlegmating said vapors to condense insufficiently cracked fractions thereof and returning resultant reflux condensate to the cracking zone, finally condensing the dephlegmated vapors and separating the distillate thus formed from the incondensible gases produced in the process, introducing at least a portion of said gases to said hydrogenating zone, introducing another portion of said gases to said cracking zone to saturate unsaturated constituents of the light cracked product, subjecting the unvaporized oil in the hydrogenating zone to hydrogenating conditions of temperature and pressure adequate to form lower boiling hydrocarbons therefrom in the presence of the gases introduced thereto, the last named pressure being sufficient to maintain a substantial portion of the unvaporized oil in liquid phase in the hydrogenating zone and recovering the resultant hydrogenated products.

2. The process as defined in claim 1 further characterized in that the incondensible gases, prior to introduction to the cracking and hydrogenating zones, are heated to temperature adequate substantially to increase the free hydrogen content thereof.

3. A conversion process which comprises subjecting hydrocarbon oil in a cracking zone to cracking temperature under sufficient pressure to maintain a substantial portion thereof in liquid phase, separating the heated oil into vapors and unvaporized oil, passing at least a portion of the separated unvaporized oil, without substantial cooling thereof, to a hydrogenating zone, condensing said vapors and separating therefrom the incondensible gases produced in the process, introducing separate portions of said gases to the

cracking zone and to the hydrogenating zone, subjecting the unvaporized oil in the hydrogenating zone, in the presence of the gases introduced thereto, to hydrogenating conditions of temperature and pressure adequate to form lower boiling hydrocarbons therefrom and to maintain a substantial portion of the unvaporized oil in liquid phase, and recovering resultant hydrogenated products.

4. A conversion process which comprises subjecting hydrocarbon oil in a cracking zone to cracking temperature under sufficient pressure to maintain a substantial portion thereof in liquid phase, separating the heated oil into vapors and unvaporized oil, passing at least a portion of the separated unvaporized oil, without substantial cooling thereof, to a hydrogenating zone, condensing said vapors and separating therefrom the incondensible gases produced in the process, heating such gases to a temperature adequate substantially to increase the free hydrogen content thereof and then introducing separate portions thereof to the cracking zone and to the hydrogenating zone, subjecting the unvaporized oil in the hydrogenating zone, in the presence of the gases introduced thereto, to hydrogenating conditions of temperature and pressure adequate to form lower boiling hydrocarbons therefrom and to maintain a substantial portion of the unvaporized oil in liquid phase, and recovering resultant hydrogenated products.

CARBON P. DUBBS.