Feb. 2, 1937. J. D. SEGUY 2,069,392

CRACKING OF HYDROCARBON OILS

Original Filed Feb. 8, 1930 2 Sheets-Sheet 1

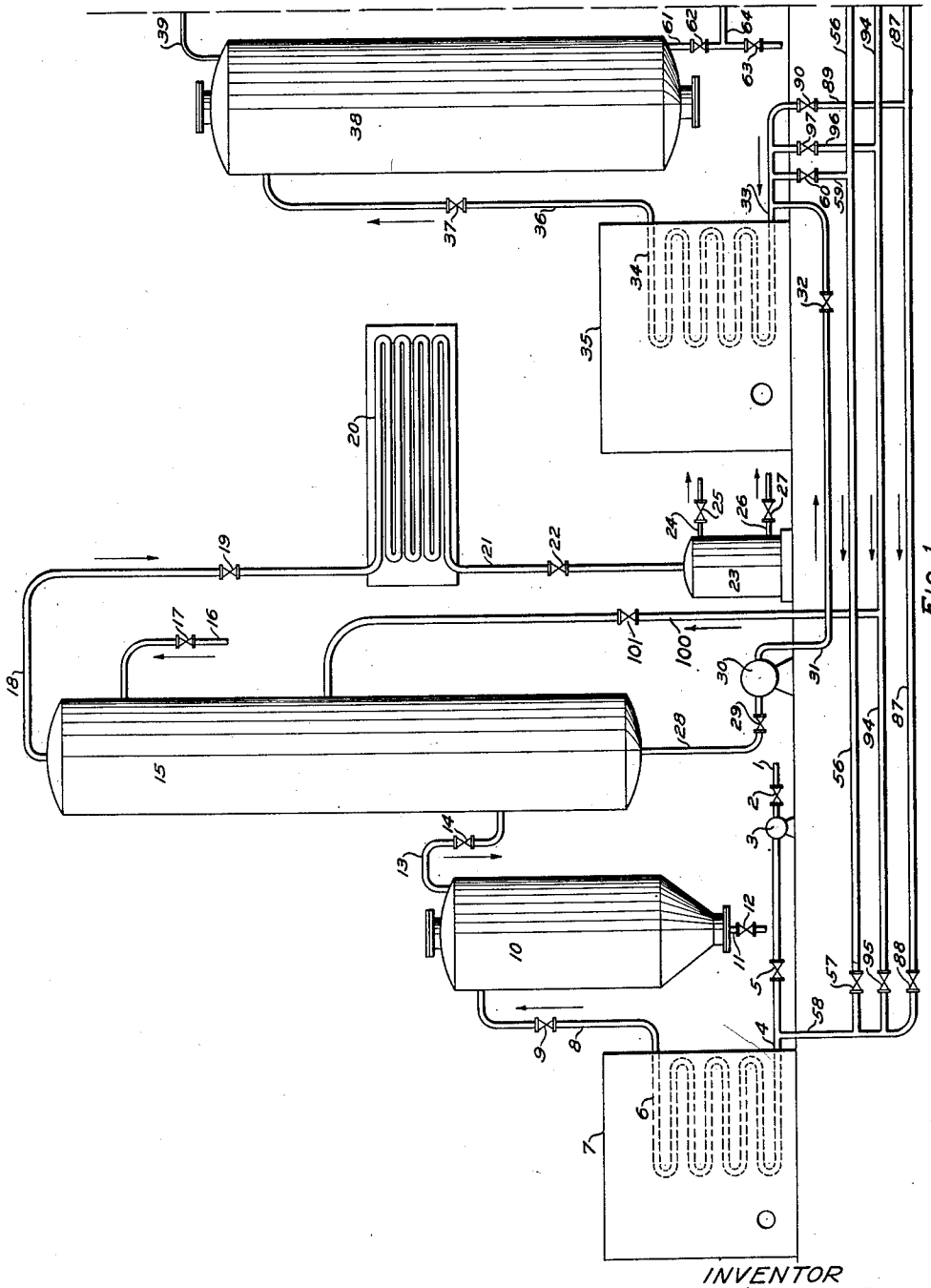


FIG. 1

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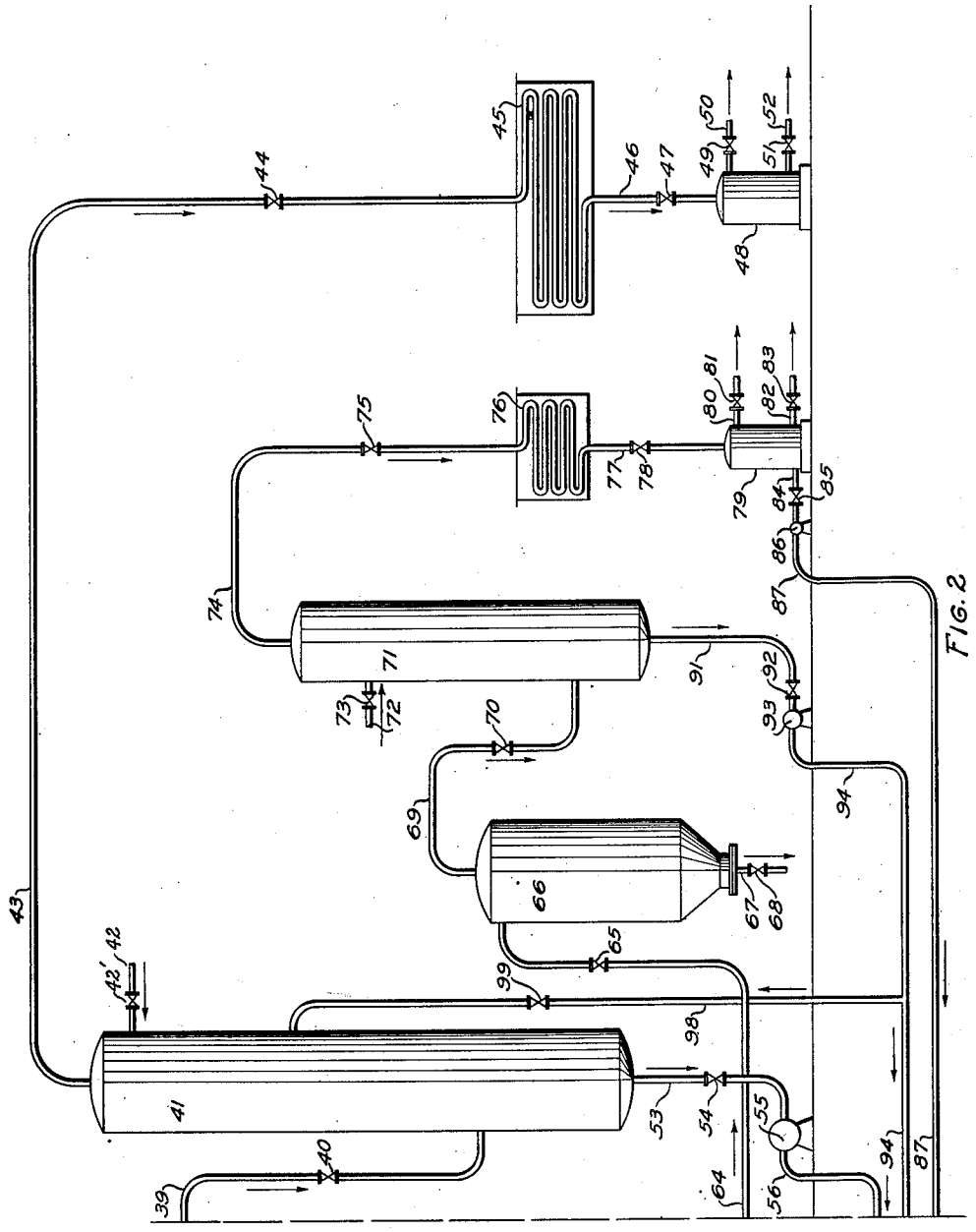


FIG. 2

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Patented Feb. 2, 1937 2,069,392

UNITED STATES PATENT OFFICE

2,069,392

CRACKING OF HYDROCARBON OILS

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Application February 8, 1930, Serial No. 426,805
Renewed September 20, 1934

1 Claim. (Cl. 196—60)

In so-called liquid-phase or low temperature cracking processes wherein hydrocarbon oils are subjected to conversion temperatures under superatmospheric pressures in a coil and enlarged reaction zone in which the vaporized and unvaporized products are separated, the vapors subjected to fractionation to effect separation of the desired light products from the heavier insufficiently converted portions, and these heavier insufficiently converted products returned as reflux condensate to the heating coil for retreatment, it is known that this reflux condensate is ordinarily lighter and more refractory to cracking reaction than the raw oil charged to the process. This reflux will thus require more prolonged or more severe treatment than that to which the raw oil is best suited and, in the system mentioned wherein this reflux is returned to the heating coil for reconversion under the same conditions as those to which the raw oil is subjected, two undesirable conditions may arise; either the conversion conditions are so severe that overdecomposition of the raw oil (with a resulting high coke and gas formation) may occur or the conversion conditions are too mild for the proper reconversion of the reflux, necessitating repeated recycling of this product, the ratio of reflux to raw oil sometimes running as high as five to one, or even higher, thus imposing an excessive load on the furnace and other parts of the apparatus.

It has been proposed to subject this refractory reflux condensate to reconversion in a separate heating zone under conditions of temperature, pressure and time better suited for the production of a maximum yield of motor fuel therefrom. The conditions of reconversion employed are often of the higher order known as high temperature, or so-called vapor-phase cracking.

The fact that reflux condensate from the fractionating zone of a so-called vapor-phase or high temperature cracking process handling refractory charging stock may be, under some conditions, heavier and/or less refractory to cracking than the charging stock to this process does not seem to be recognized.

It is among the purposes of this invention to provide an improved system of cracking employing respectively relatively mild and relatively severe conversion conditions, subjecting the more refractory hydrocarbons to the relatively severe conversion conditions best suited to the desired degree of their decomposition and subjecting the less refractory products to reconversion under the relatively mild conditions best suited for the desired degree of their decomposition.

One method of realizing the purposes of my invention may be to first subject a relatively refractory charging stock to conditions commonly known as vapor-phase or high temperature cracking. These conditions may comprise heating the oil to temperatures of the order of 1000° to 1200° F., more or less, under relatively low pressure which may range from atmospheric pressure to a few hundred pounds per square inch. The heated mass may be discharged into an enlarged zone where any unvaporized products such as carbon and heavy coke-like or pitchy materials are precipitated and separated from the vapors, the latter passing from this separating zone into a fractionating zone.

Well known means of cooling and fractionation may be employed in the fractionating zone, the desired light products (which may consist of material boiling within the range of motor fuel) being condensed, cooled and collected after leaving the fractionating zone and the heavier portions of the vapors not boiling within the required range of motor fuel being cooled and condensed in the fractionating zone and collected as reflux condensate from the so-called vapor-phase system. This reflux condensate may be heavier and less refractory to cracking conditions than the oil used as charging stock to the vapor-phase or relatively high temperature heating element and may be fed to another heating element employing milder conversion conditions such as are commonly employed in so-called liquid-phase cracking systems. These milder conditions may comprise subjecting the oil to reconversion at temperatures between 800° F. and 950° F., more or less, and under pressures of say 100 to 1500 pounds per square inch, more or less. The reconverted products leaving the low temperature heating element may be introduced into an enlarged reaction zone wherein separation of the vaporized and unvaporized products occurs.

The vapors from this reaction zone may be removed and subjected to fractionation, the desired light products from the fractionating zone being separately cooled, condensed and collected and the heavier insufficiently converted products from the fractionating zone being returned as reflux condensate to either the low temperature or the high temperature heating element, depending on their composition and the conditions best suited for their desired reconversion. The unvaporized products from the reaction chamber of the low temperature system may be withdrawn from the system or may be subjected to a further vaporization of their lighter portions in

a zone of substantially reduced pressure. The unvaporized products from this zone of reduced pressure may be withdrawn from the system and the vaporized products may be subjected to fractionation. The lighter portions of these flashed vapors may leave the fractionating zone to be condensed, cooled and collected as flash distillate; the heavier portions of the flashed vapors may be condensed as reflux condensate from the flashing part of the system. Either or both the flash distillate and reflux condensate from the flashing system may be returned to either the high temperature or the low temperature heating zone, depending upon which conditions are best suited for their desired reconversion.

It will be understood that any of the intermediate products from the process such as reflux condensate from the high temperature system, reflux condensate from the low temperature system, reflux condensate from the flashing system, residual or unvaporized products from the reaction zone of the low temperature system and flash distillate may be isolated wholly or in part from the process as desired. It will be also understood that any of the well known means of cooling and assisting fractionation may be employed in any and in all of the various fractionating zones and that substantially uniform, reduced or increased pressures of a wide range may be employed betwen the various component parts of the process. It will also be understood that well known means for controlling the reaction in the various elements of the system may be used such as cooling the oil discharging from the heating coils or in the reaction zones to the proper temperature.

Many salient features not enumerated will be apparent from the foregoing general description of one embodiment of my improved process.

In the attached drawings, Figs. 1 and 2 comprise a diagrammatic view in elevation, not to scale, of one of the many types of apparatus in which my process may be carried out.

Referring more in detail to the drawings, raw oil charging stock, introduced through line 1 and valve 2 to pump 3, may be fed through line 4 and valve 5 into the high temperature heating element 6 which is located in a suitable furnace setting 7 and after being brought to the desired outlet temperature the heated mass may pass through line 8 and valve 9 into reaction chamber 10. In chamber 10 the carbon and other undesirable solid, semi-solid or liquid products are separated from the vapors and removed from the chamber through line 11, controlled by valve 12. The vapors from chamber 10 may pass through line 13 and valve 14 into the fractionating zone 15. Any suitable cooling medium such as distillate from the process may be introduced through line 16 and valve 17 into the fractionating zone 15 to assist fractionation therein. By maintaining the proper outlet temperature, at the top of fractionating tower 15 only the desired light products, which may be those falling within the boiling range of motor fuel, will remain as vapors at the top of this fractionating tower, and these vapors may be removed through line 18 and valve 19, condensed and cooled in condenser 20 and, after passing through line 21 and valve 22, collected in receiver 23. Uncondensed gas may be withdrawn from receiver 23 through line 24, controlled by valve 25 and the condensed distillate may be withdrawn through line 26, controlled by valve 27.

Reflux condensate from the fractionating tower 15 is temporarily collected in the bottom of this fractionating tower and may be fed as desired through line 28, valve 29, pump 30, line 31, valve 32 and line 33 to the low temperature heating element 34 which is located in a suitable furnace setting 35. The heated and reconverted products from the heating element 34 may pass through transfer line 36 and valve 37 into the reaction chamber 38. A separation occurs in reaction chamber 38 between the vaporized and unvaporized products, said vapors being removed through line 39 and valve 40 to the fractionating tower 41. In this fractionating tower a suitable cooling medium may be employed either in direct or in indirect contact with the ascending vapors to assist their fractionation, and this cooling medium may be introduced through line 42, controlled by valve 42'. Vapors of the desired boiling range are withdrawn from the fractionating tower 41 through line 43 and valve 44 and, after being cooled and condensed in condenser 45, may pass through line 46 and valve 47 into the receiver 48 from which uncondensed gas may be withdrawn through valve 49 and line 50. The distillate from this receiver may be withdrawn through valve 51 and line 52.

Reflux condensate from the fractionating tower 41 of the low temperature system may be returned through line 53, valve 54, pump 55, line 56, valve 57, line 58 and line 4 to the high-temperature heating element 6 for reconversion. All or a portion of this product may, however, when so desired, be diverted from line 56 through line 59 and valve 60 into line 33 from which it may be supplied to the low-temperature heating element 34 for reconversion.

Unvaporized residual products from reaction chamber 38 of the low-temperature system may be withdrawn through line 61 and valve 62 and may be either withdrawn from the system through valve 63 or may pass through line 64 and valve 65 into the flash chamber 66. The pressure on the hot residual product is reduced in passing through valve 65 and the latent heat liberated by this pressure reduction will serve to vaporize light portions of the residual oil introduced into the flash chamber 66. The unvaporized final residual product from this flash chamber may be withdrawn from the system through line 67 and valve 68. The vapors from flash chamber 66 may pass through line 69 and valve 70 into the flash dephlegmator 71 where the desired light portions of the vapors are separated from the heavier portions, the separation being assisted, if desired, by a cooling medium introduced through line 72 and valve 73.

That portion of the flash vapors remaining uncondensed at the temperature maintained at the top of flash dephlegmator 71 may be withdrawn therefrom through line 74 and valve 75 and, after being condensed and cooled in condenser 76, pass through line 77 and valve 78 into the receiver 79. Uncondensed gases may be withdrawn from receiver 79 through line 80, controlled by valve 81 and the condensed distillate may be withdrawn through line 82, controlled by valve 83. A portion or all of this distillate may, if desired, be returned by means of line 84, valve 85, pump 86, line 87, valve 88, line 58 and line 4, to the high-temperature heating element 6 for reconversion. Any portion or all of this recycled material may, at will, be diverted from line 87 through line 89, valve 90 and line 33 for reprocessing in the low temperature heating element 34. The reflux condensate from flash dephleg-

mator 71 is withdrawn therefrom through line 91 and valve 92 and may be fed by means of pump 93 through line 94, valve 95, line 58 and line 4 to undergo reconversion in the high temperature heating element 6. A portion or all of this product may likewise be diverted from line 94 as desired and by passing through line 96, valve 97 and line 33 may be fed to the low temperature heating element 34 for reconversion therein. Any portion or all of this reflux condensate from the flash dephlegmator may be fed overhead to the fractionating tower 41 through line 98, controlled by valve 99, or it may be fed overhead to the fractionating tower 15 through line 100, controlled by valve 101. By feeding this material overhead either to fractionating tower 15 or to fractionating tower 41, or in part to both, all but its lightest portions will eventually be returned through the pumps 30 and/or 55 to either the high temperature heating element 6 or to the low temperature heating element 34, as the case may be, or if fed in part to both fractionating towers the product will be reconverted in a like proportion in the high-temperature heating element 6 and the low-temperature heating element 34, respectively.

As a specific example of one particular operation incorporating my method of cracking as carried out in the above described process, a 32° A. P. I. gravity intermediate product, commonly known as pressure distillate bottoms, produced, for instance, from a separate so-called liquid-phase cracking process, or from any other source, may be fed to the high-temperature or so-called vapor-phase heating element 6, in which it may be heated under a pressure of about fifty pounds per square inch to a final temperature of about 1100° F. A small portion of heavy pitchy material may be withdrawn from the bottom of separating chamber 10 which is also maintained under a pressure of approximately fifty pounds per square inch. The temperature at the top of fractionating tower 15 may be maintained at about 350° F. by recirculating a portion of the product from receiver 48 to control cooling. The vapor-phase cracked product collected from receiver 23 will thus fall within the boiling range of motor fuel and may amount to approximately 25% of the raw oil charged to the process.

The reflux condensate from the fractionating tower 15 may be fed through the low-temperature heating element 34 maintained at a pressure of approximately 150 pounds per square inch, and may be heated in this coil to an outlet temperature of approximately 850° F. The reaction chamber 38 may also be held at about this same pressure, but in this case the pressure in the fractionating tower 41 may be reduced to approximately fifty pounds per square inch by the control of valve 40. Vapors withdrawn from the top of fractionating tower 41 may be at a temperature of about 350° F. and the distillate collected in receiver 48 will thus meet the boiling range requirements for commercial motor fuel and this product may amount to approximately 45% based on the raw oil.

Residual oil may be withdrawn from the reaction chamber 38 and fed into the flash chamber 66 at a reduced pressure of approximately thirty pounds per square inch. Substantially this same pressure may be maintained on the flash dephlegmator 71 and the distillate removed from this dephlegmator and collected in receiver 79 may be returned to the dephlegmator 41 through line 42 and valve 42' to assist cooling therein and after combining with the reflux condensate from this dephlegmator may be fed by means of pump 55 back to the high temperature heating element 6 where the combined product may undergo reconversion together with the charging stock. A portion of the flash distillate from the receiver 79 may be recirculated through line 72 and valve 73 to the top of the flash dephlegmator 71 to control cooling in this zone and the reflux condensate from dephlegmator 71 may be returned to the low temperature heating element 34, there to undergo reconversion, together with the reflux condensate from the fractionating tower 15.

The final residual liquid formed in flash chamber 66 may amount to about 12% of the raw oil and may be removed from the system through line 67.

It is evident from the foregoing that by the use of my improved process it is possible to convert a relatively refractory charging stock with a reduced coke and gas formation and with consequently lower process losses than are ordinarily experienced in the vapor-phase cracking of oil of this character. It will also be noted that a higher yield of motor fuel is obtainable from this process than could be obtained by a vapor-phase conversion alone and in many instances this product will be of a much more stable nature than the usual run of vapor-phase cracked distillate, and yet have an anti-knock rating comparable with the high rating characteristic of a product made by the vapor-phase method, at the same time the gas loss may be materially decreased by the use of my process.

It is to be noted that the process is not limited to the treatment of so-called pressure distillate bottoms, but other suitable charging stocks may be treated according to the process of my invention.

I claim as my invention:

A process for producing gasoline from hydrocarbon charging oil which is relatively light and refractory to cracking, said process comprising subjecting such charging oil while substantially in the vapor phase to cracking treatment at a temperature in excess of 1000° F. and converting the same into a vaporous mixture containing gasoline-like hydrocarbons and hydrocarbons of higher boiling point than said charging oil, dephlegmating said vaporous mixture and condensing therefrom the hydrocarbons which are of higher boiling point than the charging oil, subjecting resultant condensate to a cracking treatment at lower temperature than that of the first-mentioned cracking treatment, while under sufficient pressure to maintain a substantial portion thereof in the liquid phase, separating the reaction products of the last-named cracking treatment into vapors and unvaporized oil, recovering gasoline-like hydrocarbons from said vapors, flash distilling said unvaporized oil by pressure reduction and dephlegmating the flashed vapors independently of said vaporous mixture, introducing resultant flash reflux into contact with said vaporous mixture undergoing dephlegmation to assist the dephlegmation and to be supplied with said condensate to the second-mentioned cracking treatment, and condensing the vapors uncondensed by said dephlegmating steps.

JEAN DELATTRE SEGUY.