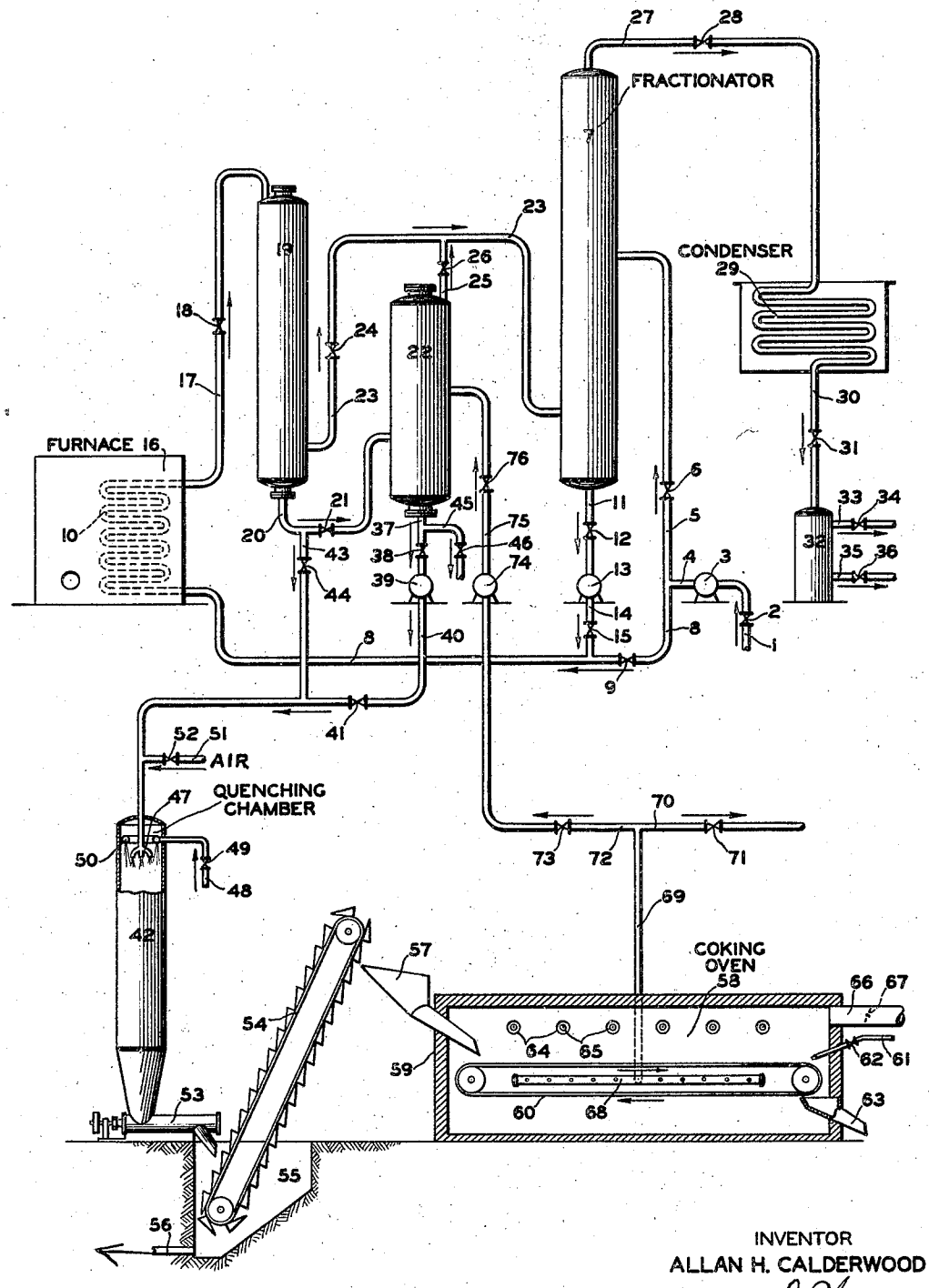
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TREATMENT OF HYDROCARBON OILS

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TREATMENT OF HYDROCARBON OILS

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This invention refers to an improved process for the treatment of relatively high boiling hydrocarbon oils, such as those resulting from pyrolytic conversion, whereby residual oil withdrawn hot from the cracking system is first quenched with water while in the form of a spray, whereby it is broken up into relatively small particles of a semi-solid asphaltic nature, followed by reduction of said semi-solid particles to substantially dry coke.

While the present invention is directed to the treatment of cracked residual oils obtained in heated state from a cracking system, it is not limited to the use of any particular type of cracking system for the production of said residual liquid, and the latter may be obtained from either a relatively high pressure cracking zone or may be the result of further vaporization, at substantially reduced pressure, of residual liquids produced at relatively high superatmospheric pressure.

The invention also contemplates, when desired, controlled partial oxidation of the cracked residue prior to quenching the same. This method of treatment has been found in some cases to assist the production of semi-solid asphaltic particles from the cracked residual liquid upon quenching, which state is highly desirable in order to facilitate handling of the residual material prior to the coking step.

Any desired method of coking the semi-solid asphaltic particles resulting from the treatment of the cracked residue in the manner provided by the present invention may be employed within the scope of the invention and, since it is possible to store the semi-solid asphaltic particles for a considerable length of time without their coalescing, it is not essential that the coking step be accomplished simultaneously with the other stages of the process. Preferably, however, the coking operation is simultaneous with the cracking, oxidation and quenching stages of the process in order to eliminate the necessity of providing storage facilities and in order that the vaporous hydrocarbons recovered from the coking stage may be returned for further treatment to the cracking stage of the system.

The accompanying diagrammatic drawing illustrates one specific form of apparatus in which the process of the invention may be accomplished.

Referring to the drawing, hydrocarbon oil charging stock for the cracking operation, which may comprise any desired type of hydrocarbon oil, is supplied through line 1 and valve 2 to a pump 3, by means of which it is fed through line 4 and may be directed, all or in part, through line 5 and valve 6 to fractionator 7, or it may be supplied, all or in part, through line 8 and valve 9 direct to cracking coil 10. Any charging stock supplied to the fractionator, as described, may commingle therein with the hot conversion products undergoing fractionation, serving to assist their fractionation and being thereby preheated and subjected to vaporization. The components of the charging stock supplied to the fractionator boiling above the range of the desired final light distillate product of the process collect, together with the reflux condensate formed in this zone by condensation of the insufficiently converted components of the vaporous conversion products supplied thereto, and the commingled materials are withdrawn from the lower portion of the fractionator through line 11 and valve 12 to pump 13, by means of which they are fed through line 14, valve 15 and line 8 to conversion in heating coil 10.

A furnace 16 of any suitable form supplies the required heat to the oil passing through heating coil 10 to subject the same to the desired conversion temperature, preferably at a substantial superatmospheric pressure, and the heated products are discharged from the heating coil through line 17 and valve 18 into reaction chamber 19.

Chamber 19 is also preferably maintained at a substantial superatmospheric pressure, which may be substantially the same or somewhat lower than the pressure employed at the outlet from the heating coil. Although not indicated in the drawing, chamber 19 is preferably insulated in order to prevent the excessive loss of heat therefrom by radiation so that conversion of the heated products supplied to this zone, and particularly their vaporous components, may continue therein. Both vaporous and liquid conversion products may be withdrawn in commingled state from the lower portion of chamber 19 through line 20 and may be directed through valve 21 into vaporizing chamber 22, wherein the liquid conversion products are subjected to appreciable further vaporization by a substantial reduction in the pressure imposed thereon. It is, however, entirely within the scope of the invention to withdraw substantially only liquid conversion products, or liquid conversion products and a regulated quantity of the vapors, from the lower portion of the reaction chamber, in the manner illustrated, and to separately remove substantially all of the remaining vaporous products from any desired point or plurality of points in the reaction chamber above the point of removal of the liquids. In the case herein illustrated provision

is made for separately removing vapors from chamber 19 through line 23, and directing the same through valve 24 in this line to fractionator 7, although a regulated portion or all of these vapors may, when desired, be introduced into chamber 22 at any desired point or plurality of points in this zone, by well known means not illustrated.

When both vaporous and liquid conversion products from chamber 19 are supplied to chamber 22 in the manner previously described, further vaporization of the liquids and final separation is accomplished in this zone. The vapors evolved in chamber 22, as well as any vaporous products supplied thereto from chamber 19, are directed from the upper portion of this zone through line 25, valve 26 and line 23, to fractionation in fractionator 7.

The components of the vaporous conversion products supplied to fractionator 7 boiling above the range of the desired final light distillate product are condensed in this zone as reflux condensate and are returned, in the manner previously described, to further conversion in heating coil 10. Fractionated vapors of the desired end boiling point are withdrawn, together with uncondensable gas produced by the process, from the upper portion of fractionator 7, through line 27 and valve 28, and are subjected to condensation and cooling in condenser 29. The resulting distillate and gas pass through line 30 and valve 31 to collection and separation in receiver 32. Uncondensable gas may be released from the receiver through line 33 and valve 34. Distillate may be withdrawn from receiver 32 through line 35 and valve 36, to storage or to any desired further treatment. When desired, a regulated portion of the distillate collected in receiver 32 may be recirculated, by well known means not illustrated in the drawing, to the upper portion of fractionator 7 to serve as a cooling and refluxing medium for assisting fractionation of the vapors and to maintain the desired vapor outlet temperature from the fractionator.

Residual liquid remaining unvaporized in chamber 22 is withdrawn from the lower portion of this zone through line 37 and may be directed, all or in part, through valve 38 to pump 39, by means of which it is fed through line 40 and valve 41 into quenching chamber 42. Provision is also made in the case here illustrated for directing residual liquid withdrawn from chamber 19 from line 20 through line 43 and valve 44 into line 41, and thence to quenching chamber 42. Provision is also made for withdrawing a regulated portion or all of the flash distilled residual liquid from chamber 22 to cooling and storage, or elsewhere as desired, by means of line 45 and valve 46.

The cracked residual liquid supplied, as described, to chamber 42 is preferably directed into this zone in the form of a spray by means of a suitable spray nozzle such as indicated, for example, at 47, and the spray of liquid residue is caused to intimately commingle in this zone with a spray of cold water which is supplied to chamber 42 through line 48, valve 49 and a suitable spray arrangement 50.

As previously mentioned, the present invention contemplates controlled partial oxidation of the hot residual liquid prior to its introduction into chamber 42. This may be accomplished, for example, by the introduction of controlled amounts of air into the stream of hot residual oil passing through line 41, by means of line 51 and valve 52. Other air inlet lines not illustrated may be provided at suitable intervals along line 40 in order that the amount of oxidation produced in the cracked residue may be controlled not only by the temperature of the residue and the amount of air commingled therewith but also varying by the point of introduction of the air and the consequent time of contact between the two prior to quenching.

The product of the treatment of the cracked residue in the manner above described is a mass of individual particles of semi-solid material of more or less asphaltic nature, ranging for example from one-eighth to three-eighths of an inch or thereabouts in diameter. These individual particles have a relatively hard outer crust and do not readily coalesce even when allowed to stand under ordinary atmospheric conditions for a period of several months. I am thereby enabled to produce by this method of treatment a cracked residual oil in semi-solid state and in relatively finely divided form which may be readily handled by ordinary methods without the danger of coking so often encountered when it is attempted to convey heavy cracked residues in heated fluid state. The present method of treatment also eliminates leakage and the usual mess attendant with the handling of heavy residual oils in ordinary conveying equipment. It is therefore possible, in conjunction with the other features of the present invention, to employ practically any of the various satisfactory methods of coking for the semi-solid residual particles.

In the case here illustrated residual material may be allowed to accumulate in the lower portion of chamber 42, together with the water supplied to this zone, from which the water and residual particles are conveyed through a suitable helical conveyor, or the like, indicated at 53, the residual particles passing onto a suitable belt type conveyor 54, while the water, which collects within pit 55, may be withdrawn therefrom through line 56. The residual particles are discharged from the upper end of conveyor 54 into hopper 57 of coking oven 58.

The coking oven in the particular case here illustrated comprises suitable refractory walls 59 housing a continuous conveyor 60, preferably constructed of suitable metallic alloys capable of withstanding high temperatures. The particles of semi-solid residual material pass from hopper 57 onto one end of the upper surface of conveyor 60, moving thereon through the coking oven to the opposite end of the conveyor and being reduced to relatively dry coke during their travel through the oven. Jets of water may be directed by suitable means, indicated for example by line 61 and valve 62, against the surface of the coke at the discharge end of the conveyor in order to crack and loosen the same from the surface of the conveyor belt, or it may be otherwise removed in any suitable well known manner, such as for example by means of a scraper, not illustrated, and is discharged from the coking oven through a suitable discharge device 63 to storage or elsewhere, as desired. Suitable burner ports, such as indicated for example at 64, are provided in the side walls of furnace 59, and burners, the tips of which are indicated at 65, preferably direct a combustible fuel and air mixture upward at an angle against the roof of the coking oven so that a major portion at least of the heat required for coking of the semi-solid residual particles is supplied thereto by radiation from the roof of the coking oven and, in order to minimize

mixing of the combustion gases and the hydrocarbon vapors evolved from the material undergoing coking, a combustion gas outlet is preferably provided near the roof of the furnace, for example, flue 66 controlled by damper 67, while a hydrocarbon vapor outlet is provided at a relatively remote point or plurality of points in the oven. In the case here illustrated a vapor collecting header 68 is provided beneath the upper surface of conveyor 60. The hydrocarbon vapors evolved during the coking operation are withdrawn from the coking oven through line 69 and may be directed therefrom through line 70 and valve 71 to condensation and collection by well known means not illustrated, or they may be directed through line 72 and valve 73 to pump or compressor 74 and thence through line 75 and valve 76 into vaporizing chamber 22. In case chamber 22 is operated at relatively low pressure and substantially the same or somewhat higher pressure is employed in the coking oven, pump or compressor 74 may be dispensed with. This is not contemplated, however, in case the type of coking oven illustrated in the drawing is employed.

In case vaporous products from the coking operation are returned as described to chamber 22, any entrained heavy liquid particles or high boiling components of the vapors unsuitable for conversion in the heating coil may be collected with the residual liquid conversion products in chamber 22 for further treatment therewith in the manner described, while the remaining lower boiling components of the vapors are directed to fractionation in fractionator 7, whereby any components thereof boiling within the range of the desired final light distillate product of the process are collected as such, while their higher boiling components are condensed as reflux condensate and returned to heating coil 10 for further conversion.

As a specific example of the operation of the process of the invention, the charging stock supplied to the cracking system comprises a California gas oil of about 32° A. P. I. gravity which is subjected, together with the reflux condensate recovered from within the system, to a conversion temperature, measured at the outlet from the heating coil, of approximately 960° F. at a superatmospheric pressure of about 350 pounds per square inch. This pressure is substantially equalized in the reaction chamber and is reduced in the vaporizing chamber to a pressure of approximately 50 pounds per square inch, the succeeding fractionating, condensing and collecting equipment being operated at substantially the same pressure. Non-vaporous residual liquid of about 3° A. P. I. gravity is withdrawn from the vaporizing chamber of the cracking system at a temperature of approximately 760° F. and the heated oil is introduced through atomizing nozzles into a chamber wherein it is contacted with a cold water spray. A relatively small amount of air is commingled with the stream of hot residual oil shortly before the oil is quenched by contact with the water. The resulting product is a mass of relatively small particles of semi-solid material having a specific gravity of approximately 1.1399, a melting point of approximately 307° F., which contains approximately 66.81% by weight of volatile matter, approximately 32.81% fixed carbon and about 0.38% ash and has a solubility of petroleum ether of approximately 20.4% by weight. This material is of a relatively hard nature showing no penetration at 77° F. and is passed by means of conveyors from the lower portion of the quenching zone to a coking oven wherein it is reduced to low volatile coke at a temperature of approximately 1200° F. Vaporous products from the coking oven are returned to the vaporizing chamber of the cracking system. This operation will yield, per barrel of charging stock, approximately 65 per cent of motor fuel of good antiknock value and approximately 70 pounds of low volatile good quality coke, the remainder being chargeable, principally, to uncondensable gas.

I claim as my invention.

1. A process for the treatment of residual liquid resulting from the pyrolytic conversion of hydrocarbon oils which comprises withdrawing said residual liquid in heated state from the conversion process wherein it is produced, admixing an oxidizing gas with the residual liquid while the latter is at a sufficient temperature to be partially oxidized and passing the heated oil through a spray nozzle into a quenching drum, contacting the oil spray in the drum with relatively cold water, whereby to quench the oil and cause the formation of relatively small particles of semi-solid residual material which do not readily coalesce, passing said semi-solid residual particles from the quenching zone to a coking zone, reducing same therein to substantially dry coke, and returning hydrocarbons evolved during the coking operation to the conversion process for further treatment.

2. In a process for the treatment of hydrocarbon oils wherein the oil is subjected to conversion conditions of cracking temperature and superatmospheric pressure in a heating coil and communicating reaction chamber, the resulting vaporous and liquid conversion products separated, the latter subjected to further vaporization in a zone of substantially reduced pressure relative to that employed in the reaction chamber, the vaporous conversion products, including those evolved by said further vaporization of the liquids, subjected to fractionation resulting in the formation of reflux condensate, the reflux condensate returned to the heating coil for further conversion, fractionated vapors of the desired end-boiling point subjected to condensation and the resulting distillate recovered, the improvement which comprises withdrawing non-vaporous residual liquid in heated state from said zone of reduced pressure vaporization, passing the same in the form of a relatively fine spray into a quenching chamber, commingling oxidizing gas in relatively small regulated quantities with the stream of hot residual liquid passing from said reduced pressure zone to the quenching chamber, contacting said spray with a spray of relatively cold water for the purpose of quenching the same and causing the formation of relatively small particles of semi-solid residual material, removing the latter from the quenching zone and introducing the same into a coking zone, subjecting same in the coking zone to a high temperature whereby to reduce same to substantially dry coke, and returning the hydrocarbon vapors from the coking zone to said reduced pressure vaporizing zone.

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