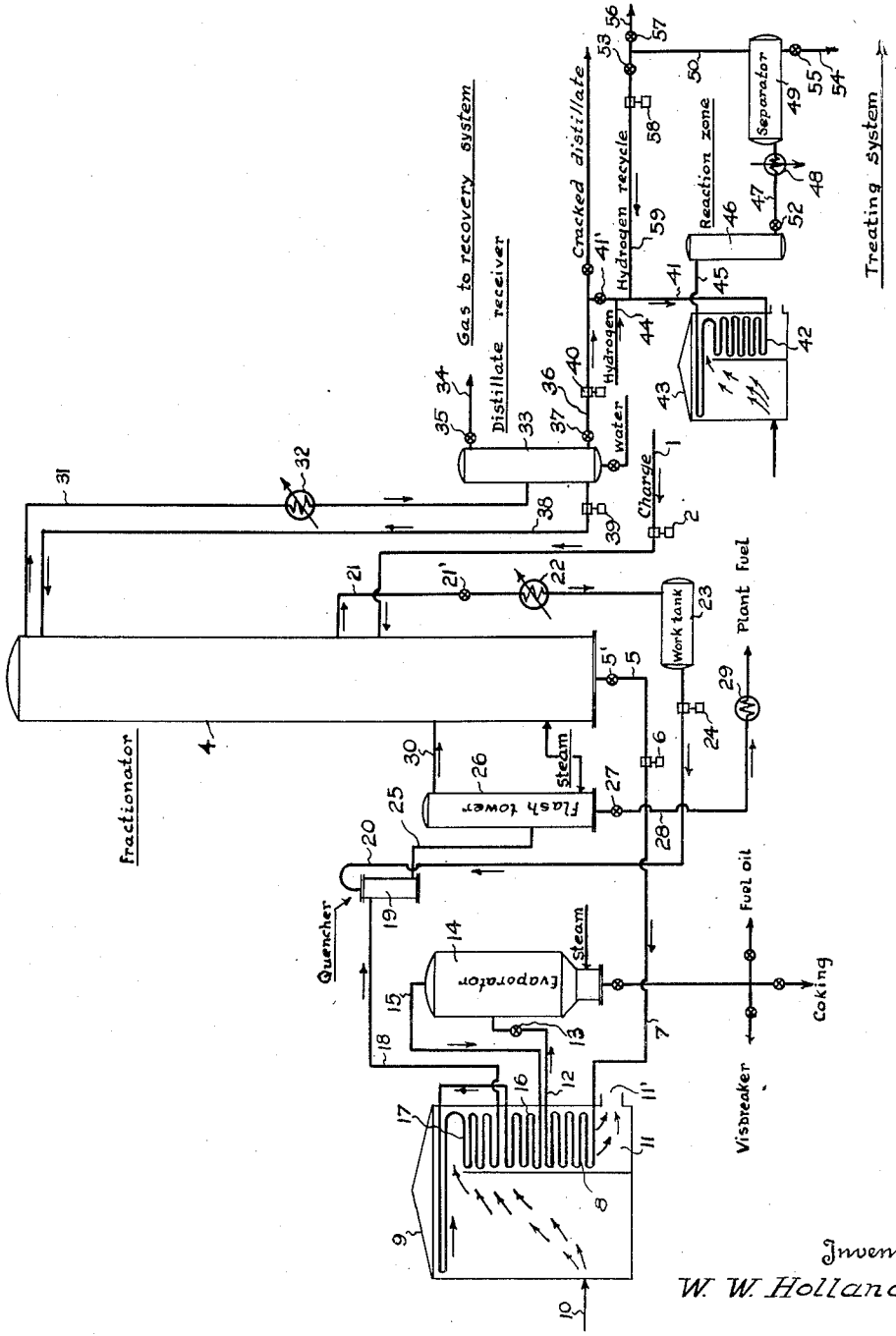
Dec. 26, 1950 W. W. HOLLAND 2,535,418

PROCESS FOR THE PRODUCTION OF VAPOR PHASE CONVERTED HYDROCARBONS

Filed July 17, 1947



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Patented Dec. 26, 1950

2,535,418

UNITED STATES PATENT OFFICE

2,535,418

PROCESS FOR THE PRODUCTION OF VAPOR PHASE CONVERTED HYDROCARBONS

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Application July 17, 1947, Serial No. 761,516

6 Claims. (Cl. 196—61)

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This invention relates to improvements in the methods of refining hydrocarbons, and is directed primarily to the vapor phase conversion of heavy oils into lighter products, certain of which having the characteristics of high grade motor fuel.

The present invention is adapted particularly to the conversion of hydrocarbons in the vapor phase at temperatures within the range of 1000° to 1550° F., wherein the oil is first charged to a primary heater coil in which its temperature is raised until it reaches a state of vaporization, without appreciable cracking. The vapors are then separated from the unvaporized portions of the oil admixed with steam, if desired, and are directed to a secondary heater coil maintained at a higher temperature than the primary coil and in which any entrained vesicular particles are converted into dry vapors. The thoroughly dried vapors are next conducted to a still higher temperature conversion coil wherein molecular decomposition of the vaporous hydrocarbons is effected under temperature and pressure conditions suitable to the grade or character of the hydrocarbons under treatment and so regulated as to produce maximum yields of the end products desired. Usually the lighter grades of oil, such as kerosene, for example, require higher conversion temperatures than the heavier charging stocks, such as topped crude, gas oil or the like. Also the conversion temperature depends largely upon the character of the final products desired, the flexibility of the process lending itself readily to the molecular decomposition of any grade of hydrocarbons, whether in the solid, liquid or gaseous state under normal temperature and pressure conditions, or whether the final products are to be used as motor fuel or for the synthesis of chemical compounds or for both. Thus, the process is readily adapted not only to the cracking of wax or liquid petroleum but also to the pyrolysis of hydrocarbons normally in the gaseous state, such as natural gas from the oil fields or refinery by-product gas, for the production of unsaturated hydrocarbons so widely used in the field of chemical synthesis. When it is desired to produce a high yield of cracked normally gaseous hydrocarbons, conversion temperatures of the order of 1400° to 1550° F. may be employed. However, the present invention deals primarily with the conversion of hydrocarbons normally in the liquid state, for the production of motor fuels of high anti-knock value in which case conversion temperatures of the order of 1050° to 1150° F. are usually employed. It also relates to improvements in the methods of cracking, and to separating and fractionating the condensable and non-condensable fractions released from the conversion zone, together with treatment of the liquid fractions without undue loss in volume or octane number.

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In carrying out the present invention, vaporized hydrocarbons are charged to a vapor-phase cracking coil where their conversion is effected, and after which they are immediately and substantially instantaneously quenched by intimate contact with a relatively cool oil. A heavy unvaporized oil fraction, withdrawn from the bottom of an evaporator ahead of the cracking coil, may be reduced to coke for the production of additional charging stock, or it may be subjected to a viscosity-breaking operation for the production of other materials such as road oil or bunker C fuel, or it may be "cut" with lighter material for other grades of fuel oil. The cracked vapors leaving the quenching chamber are flashed in a tower preferably with the aid of steam, the overhead from which passes directly to a fractionating column. The relatively small amount of bottoms withdrawn from the bottom of the flash tower usually contains some tar formed in the cracking operation, rendering it unsuitable for recycle charging stock. This material, however, is quite suitable for plant fuel, for which purpose it is generally used.

The raw charging stock enters the system at an intermediate point in the fractionating column, which is preferably of the bubble tower type of construction, where it serves as a cooling medium for the heated cracked vapors entering the column at a somewhat lower level, each flowing in counter-current direction to the other, insuring intimate contact between the two. The liquid accumulating in the bottom of the tower, consisting of a mixture of fresh feed and cycle stock condensed within the column, comprises the charge to the primary heating and vaporizing coil of the system. The uncondensed vapors leaving the top of the fractionating column are the products of the conversion reaction and consist primarily of motor fuel fractions, both saturated and unsaturated hydrocarbons, and fixed gases, each of which are subjected to appropriate refining means hereinafter referred to.

A noteworthy feature of this invention is the method employed in checking the hydrocarbon decomposition reaction in the cracking operation by shock chilling the highly heated cracked

vapors with a clean quenching hydrocarbon of intermediate boiling point range, selected from a tray in the bubble tower at a point somewhat above the introduction of the fresh feed stock. The fraction withdrawn from the tower for this purpose must be free from sediment and carbonaceous material and sufficiently low in boiling point range to evaporate substantially completely when brought into contact with the hot oil vapors, and it should contain no fractions readily susceptible to coking. This material is directed through a cooler and collected in a working tank from which it is pumped to the top of the quenching chamber where, by appropriate means, it is brought into intimate contact with the hot vapor, the temperature of which is reduced almost instantly to a degree below the critical temperature at which coking takes place, usually between about 600° and 650° F. As the cracking of the hydrocarbon charge proceeds, certain fractions peculiarly adapted to the quenching operation collect on the bubble tray selected for the purpose, so that this material or its equivalent is alternately vaporized and condensed as it circulates through its prescribed course, while the overall operation progresses smoothly.

Another feature in the practice of the present invention resides in the treatment of the cracked distillate following fractionation thereof. In some vapor phase cracking processes, the practice of filtering the distillate through fuller's earth under high pressure and at elevated temperatures is employed for the removal of gum-forming constituents and compounds which tend to discolor the finished product. However, such methods of treatment have not proven altogether effective in rendering the finished gasoline from vapor phase cracking operations entirely stable against gum formation and loss of color. This is due mainly to the presence of unsaturated hydrocarbons, both olefins and diolefins, in the cracked distillate which under favorable conditions polymerize to form gum. Yet, the complete removal of these unsaturated compounds would seriously affect the high anti-knock properties of the gasoline. For this reason, it is not practical to subject the distillate to conventional methods of treatment with reagents such as sulfuric acid without first having taken steps to guard against over-treatment and excessive losses in volume and octane rating.

I have discovered that mild hydrogenation of vapor phase cracked distillate, or fractions thereof, not only reduces the degree of unsaturation sufficiently to permit of its treatment with sulfuric acid but that its octane rating may actually be improved by the resultant structural rearrangement of the hydrocarbon molecule, effecting conditions which favor the addition of branched-chain groups to the straight chain compounds, together with a partial shifting of the multiple bonds from the end positions to the middle of the molecule, thereby reducing the number of olefinic linkages.

I have also observed that any of the well known catalytic hydrogenation processes may be used to this end, although I prefer those which employ iron, nickel, cobalt or copper, or their salts or oxides, as the active catalytic agent because of the lower operating temperatures required in such hydrogenation processes. A catalyst which appears to be particularly well adapted to the partial or non-destructive hydrogenation of vapor phase cracked distillate, for example, comprises a mixture of activated catalytic black iron and powdered activated nickel sulphide, which mixture apparently is less susceptible to the poisonous effects of impurities such as oxygen and sulphur normally found in cracked distillates. Furthermore, hydrogenation with the so-called "fluid" catalysts in the liquid phase is preferred when hydrogenating vapor phase cracked distillate, in which case temperatures of the order of 300° to 400° F. will suffice, whereas when operating in the vapor phase with the catalyst in the form of pellets, temperatures of 600° to 800° F. may be required to effect the desired hydrogenation reaction, resulting generally in rapid deterioration of the catalyst and necessitating frequent reactivation. However, I do not specify any particular catalyst or hydrogenation process as forming a part of these specifications, the selection of same being left to the choice of the individual refiner.

Vapor phase cracked distillate responds readily to partial or limited non-destructive hydrogenation, and since sufficient saturated hydrocarbons are usually present, acting as a diluent, to prevent rapid and excessive rises in temperature as a result of the heat of reaction, the control conditions may be readily established by one skilled in the art.

This invention will be clearly understood by reference to the accompanying simplified flow diagram forming a part of these specifications and representing in partial section a side elevation of apparatus and equipment adapted to the continuous operation and performance of the methods and processes herein described.

Referring to the drawing, the numeral 1 represents a pipe line leading from a bulk supply of relatively heavy feed or charging stock such as topped crude, gas oil, kerosene or the like, which is delivered by means of pump 2 through line 3 into a fractionating tower or column 4 where it is mixed with the reflux condensate formed within the column. This mixture is withdrawn from the bottom of the column through line 5, controlled by valve 5', and is charged by means of pump 6 through line 7 into a primary heating coil 8 located in the convection section of a furnace 9. Heat is supplied to the furnace by means of burner 10, raising the temperature of the oil in coil 8 somewhat above the vaporization point but not sufficiently high to cause appreciable cracking. This temperature may range from 650° to 800° F., depending upon the character of charging stock, but the flue gases 11 usually leave the furnace through outlet 11' at a temperature of about 850° to 875° F.

The heated oil leaving the primary coil 8 passes through line 12, controlled by valve 13, and is discharged into an evaporator 14, into the bottom of which steam may be admitted to assist in the vaporization of the oil under partial pressure conditions. A heavy residue oil, withdrawn from the bottom of the evaporator, may be disposed of in any manner suitable to the economic operation of the process. For example, it may be run to coke for the production of additional charging stock, or it may be further processed in a viscosity-breaking operation or "cut" with lighter stock for road oil or bunker C fuel. The vapors leaving the top of evaporator 14 pass through line 15 into a secondary heating coil 16, also preferably located in the convection section of the furnace, where they are further heated and thoroughly dried before entering the vapor phase cracking coil 17, the latter being

positioned partly in the radiant section of the furnace. In this coil, the actual vapor phase cracking takes place under temperature conditions ranging from 1000° to 1550° F., depending upon the character of the charge and the end products desired, although the normal operating temperature for the production of motor fuel is usually within the range of 1100° to 1250° F.

The cracked vapors leaving coil 17 are directed through line 18 into a quenching chamber 19 where they are brought into direct and intimate contact with a relatively cooler oil supplied through line 20, suddenly reducing the temperature of the vapors to a degree below that required for cracking. The quenching medium is normally a clean tar-free distillate withdrawn from an intermediate point in the fractionating tower 4 through line 21 controlled by valve 21'. Passing through cooler 22 into a working tank 23, the quench oil is delivered to the quenching chamber by means of pump 24. In this operation, the relatively light quench oil is practically completely vaporized, although the cracked vapors are not appreciably condensed. The mixture of cracked vapors and substantially vaporized quench oil leaving the bottom of the quenching chamber is then directed through line 25 into a flash tower 26 where a second vaporization step is effected under partial pressure conditions with the aid of steam injected into the bottom of the flash tower, which is maintained at a lower pressure than the cracking coil so that almost complete vaporization takes place. There is, however, a small amount of bottoms containing a little tar produced in the cracking operation. This material is unsuitable for recycle charging stock because of the tar, and it may be disposed of in any convenient manner. It is withdrawn from the flash tower through line 28 controlled by valve 27, passing through cooler 29, and is generally used as a part of the plant make-up fuel.

The overhead vapors from the flash tower pass through line 30 into the fractionating column 4 at a point of entry below that of the charging line 3, the charging stock acting as a reflux for the ascending vapors. Steam is introduced preferably into the bottom of the fractionating tower, acting as a stripping medium in effecting separation of the light and heavy fractions under partial pressure conditions. The vapors passing upwardly through the fractionating column are contacted repeatedly in a plurality of bubble trays with the descending liquid reflux, produced in part by condensation of the heavier fractions within the tower, while additional reflux is supplied in the form of condensed overhead vapors, a portion of which is pumped back to the top tray of the tower as a temperature control medium. The overhead vapors leaving the top of the tower through line 31 are directed through a condenser 32 and the liquid distillate is collected in a receiver 33, which is provided with a gas release line 34 controlled by valve 35, and a distillate line 36 controlled by valve 37. Provision is also made for withdrawing water, resulting from condensation of the steam, from the bottom of the distillate receiver.

The temperature of the top tray in the fractionating column is governed by the amount of liquid distillate returned to the top of the tower through line 38 by means of pump 39, which in turn governs the boiling points of the distillate produced. The uncondensed gases leaving the top of the distillate receiver 33 are conducted to a gas recovery system, which through the agencies of absorption, compression, polymerization and other gas recovery means, contributes to the overall gasoline yield.

The vapor phase cracked distillate withdrawn from the bottom of receiver 33 (or any portion or fraction thereof within any range of boiling points resulting from rerunning or other fractionating operations) through line 36 controlled by valve 37 is delivered by means of pump 40 through line 41 controlled by valve 41' to a heating coil 42 located in a furnace 43. Simultaneously hydrogen is injected into the distillate stream through line 44, and the two are heated together to a temperature suitable for catalytic hydrogenation. The effluent from the heater coil 42 is conducted through line 45 into a catalytic reaction zone 46 maintained under hydrogenating conditions, the hydrogenated product being withdrawn from the bottom thereof through line 47 controlled by valve 52, passing through cooler 48 into a separator 49. Hydrogen leaving the top of the separator through line 50 is recycled to the hydrogenating system by means of pump 58 through line 59 controlled by valve 53, any excess of hydrogen being conducted to storage through line 56 controlled by valve 57. The hydrogenated distillate, now in suitable condition for treatment by conventional means, such as sulphuric acid, without undue loss in volume or octane number, is withdrawn from the separator through line 54 controlled by valve 55, and sent to a continuous treating system, not shown on the drawing.

It is to be clearly understood that all or any portion or fraction of the vapor phase cracked distillate produced in accordance with the above described methods, within any range of boiling points resulting from rerunning, distilling or refractionating the distillate, may be subjected to hydrogenation for the purpose of reducing the degree of unsaturation and at the same time improving its anti-knock characteristics, without departing from the spirit and scope of this invention. It is also specifically understood that the terms charging stock, feed stock, raw feed and the like, as variously used in these specifications, are employed in a descriptive rather than a limiting sense, and do not define the scope or breadth of this invention with respect to the physical characteristics of the charge, whether it be in the solid, liquid or gaseous state, as typified by waxes, liquid hydrocarbons or hydrocarbons normally in the gaseous state; nor are limitations to be placed upon the boiling points of such charging stocks.

Obviously certain variations in furnace design and the arrangement of heating elements within the furnace may be desirable for certain grades of charging stock. For example, if the charge is in the gaseous state under normal conditions of temperature and pressure, the primary coil 8 which serves the purpose of vaporizing a liquid charge may be eliminated, together with the evaporator and feed line 3, under which conditions the gaseous charge would be admitted directly into the system through the secondary coil 16, which would then serve as a preheater for the conversion coil 17. Other minor changes and additions, such as means for recirculating uncracked gases through the heating elements, will be readily apparent from a consideration of the flow diagram.

In the production of gaseous products from a gaseous charge, such as the production of ethylene from normally gaseous saturated hydrocarbons, additional equipment involving the steps

of reheating, refrigeration, compression, fractionation and the like, as followed in conventional practice, is necessary, but is commonly known to the art, and therefore requires no special mention in this connection.

I claim:

1. A process of converting hydrocarbons into other hydrocarbons of generally lower boiling points and initially of a higher degree of unsaturation, comprising the steps of charging a hydrocarbon to a primary heating element located in a convection section of a furnace and therein heating it to a vaporization temperature, separating the vaporizable and unvaporizable fractions under partial pressure conditions with the aid of steam injected into the bottom of the vaporization zone, diverting the liquid residue from the bottom of the vaporization zone, drying and superheating the separated vapors in a secondary heating element also located in the convection section of said furnace, cracking the dried vapors in a third heating element located partially in the convection section and partially in a radiant heat section of said furnace, immediately thereafter and substantially instantaneously shock-chilling the cracked vapors to a temperature below that at which active vapor phase cracking takes place by quenching said vapors through intimate contact with a relatively cooler sediment-free and carbon-free liquid hydrocarbon not readily susceptible to coking, flashing the mixture of quenched vapors and unvaporized quench oil in a flash zone maintained at reduced pressure and operating under partial pressure conditions with the aid of steam introduced into the bottom of said flash zone, withdrawing the unvaporized oil from the bottom of the flash zone and diverting it from the system, fractionating the separated vapors, condensing the fractionated vapors into a highly unsaturated distillate, reducing partially the degree of unsaturation by subjecting at least part of the distillate to mild non-destructive hydrogenation and treating the hydrogenated distillate with sulphuric acid to remove undesirable gum-forming and color imparting compounds therefrom.

2. A process of converting hydrocarbons into other hydrocarbons of generally lower boiling points and initially of a higher degree of unsaturation, comprising the steps of charging a hydrocarbon to a primary heating element located in a convection section of a furnace and therein heating it to a vaporization temperature, separating the vaporizable and unvaporizable fractions under partial pressure conditions, diverting the liquid residue from the bottom of the vaporization zone, drying and superheating the separated vapors in a secondary heating element also located in the convection section of said furnace, cracking the dried vapors in a third heating element located partially in the convection section and partially in a radiant heat section of said furnace, immediately thereafter and substantially instantaneously shock-chilling the cracked vapors to a temperature below that at which active vapor phase cracking takes place by quenching said vapors through intimate contact with a relatively cooler sediment-free and carbon-free liquid hydrocarbon not readily susceptible to coking, flashing the mixture of quenched vapors and unvaporized quench oil in a flash zone maintained at reduced pressure and operating under partial pressure conditions, withdrawing the unvaporized oil from the bottom of the flash zone and diverting it from the system, fractionating the separated vapors, condensing the fractionated vapors into a highly unsaturated distillate, reducing partially the degree of unsaturation by subjecting at least part of the distillate to mild non-destructive hydrogenation and treating the hydrogenated distillate to remove undesirable gum-forming and color-imparting compounds therefrom.

3. A process for converting hydrocarbons, comprising passing vapors of the hydrocarbons to be converted through a converter zone in which the vapors are heated to temperatures within the range of 1000° to 1550° F., immediately thereafter and substantially instantaneously shock-chilling the cracked vapors to a temperature below that at which active vapor phase cracking takes place by quenching said vapors through intimate contact with a relatively cooler sediment-free and carbon-free liquid hydrocarbon not readily susceptible to coking, flashing the mixture of quenched vapors and unvaporized quench oil in a flash zone maintained at reduced pressure and operating under partial pressure conditions with the aid of steam introduced into the bottom of said flash zone, withdrawing the unvaporized oil from the bottom of the flash zone and diverting it from the system, fractionating the separated vapors, condensing the fractionated vapors into a highly unsaturated distillate, reducing partially the degree of unsaturation by subjecting at least part of the distillate to mild non-destructive hydrogenation and treating the hydrogenated distillate with sulphuric acid to remove undesirable gum-forming and color-imparting compounds therefrom.

4. A process for converting hydrocarbons, comprising passing vapors of the hydrocarbons to be converted through a converter zone in which the vapors are heated to temperatures within the range of 1000° to 1550° F., immediately thereafter and substantially instantaneously shock-chilling the cracked vapors to a temperature below that at which active vapor phase cracking takes place by quenching said vapors through intimate contact with a relatively cooler sediment-free and carbon-free liquid hydrocarbon not readily susceptible to coking, flashing the mixture of quenched vapors and unvaporized quench oil in a flash zone maintained at reduced pressure and operating under partial pressure conditions, withdrawing the unvaporized oil from the bottom of the flash zone and diverting it from the system, fractionating the separated vapors, condensing the fractionated vapors into a highly unsaturated distillate, reducing partially the degree of unsaturation by subjecting at least part of the distillate to mild non-destructive hydrogenation and treating the hydrogenated distillate to remove undesirable gum-forming and color-imparting compounds therefrom.

5. A process for converting hydrocarbons, comprising passing vapors of the hydrocarbons to be converted through a converter zone in which the vapors are heated to temperatures within the range of 1000° to 1550° F., immediately thereafter and substantially instantaneously shock-chilling the cracked vapors to a temperature below that at which active vapor phase cracking takes place, fractionating the vapors and subjecting the same to condensation to produce a highly unsaturated distillate of motor fuel boiling range and cracked hydrocarbon gases under normal conditions of temperature and pressure, reducing partially the degree of unsaturation by subjecting the unsaturated distillate to mild non-

destructive hydrogenation, and thereafter treating the hydrogenated products with sulphuric acid to remove therefrom objectionable gum-forming and color-imparting compounds.

6. A process for converting hydrocarbons, comprising passing vapors of the hydrocarbons to be converted through a converter zone in which the vapors are heated to temperatures within the range of 1000° F. to 1550° F., immediately thereafter and substantially instantaneously shock-chilling the cracked vapors to a temperature below that at which active vapor phase cracking takes place by quenching said vapors through intimate contact with a relatively cooler sediment-free and carbon-free liquid hydrocarbon not readily susceptible to coking, distilling the mixture of quenched vapors and unvaporized quench oil at reduced pressure under partial pressure conditions, fractionating the separated vapors in a fractionator in which raw charging stock enters and serves as a cooling medium for the cracked vapors, withdrawing at a point above the entry of the charging stock in the fractionator a fraction of intermediate boiling point range constituting the aforesaid sediment-free and carbon-free quenching liquid, condensing the separated vapors from the fractionator into a highly unsaturated distillate, hydrogenating the unsaturated distillate to partially reduce its degree of unsaturation, and treating the hydrogenated product with sulphuric acid to remove undesirable gum-forming and color-imparting compounds therefrom.

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