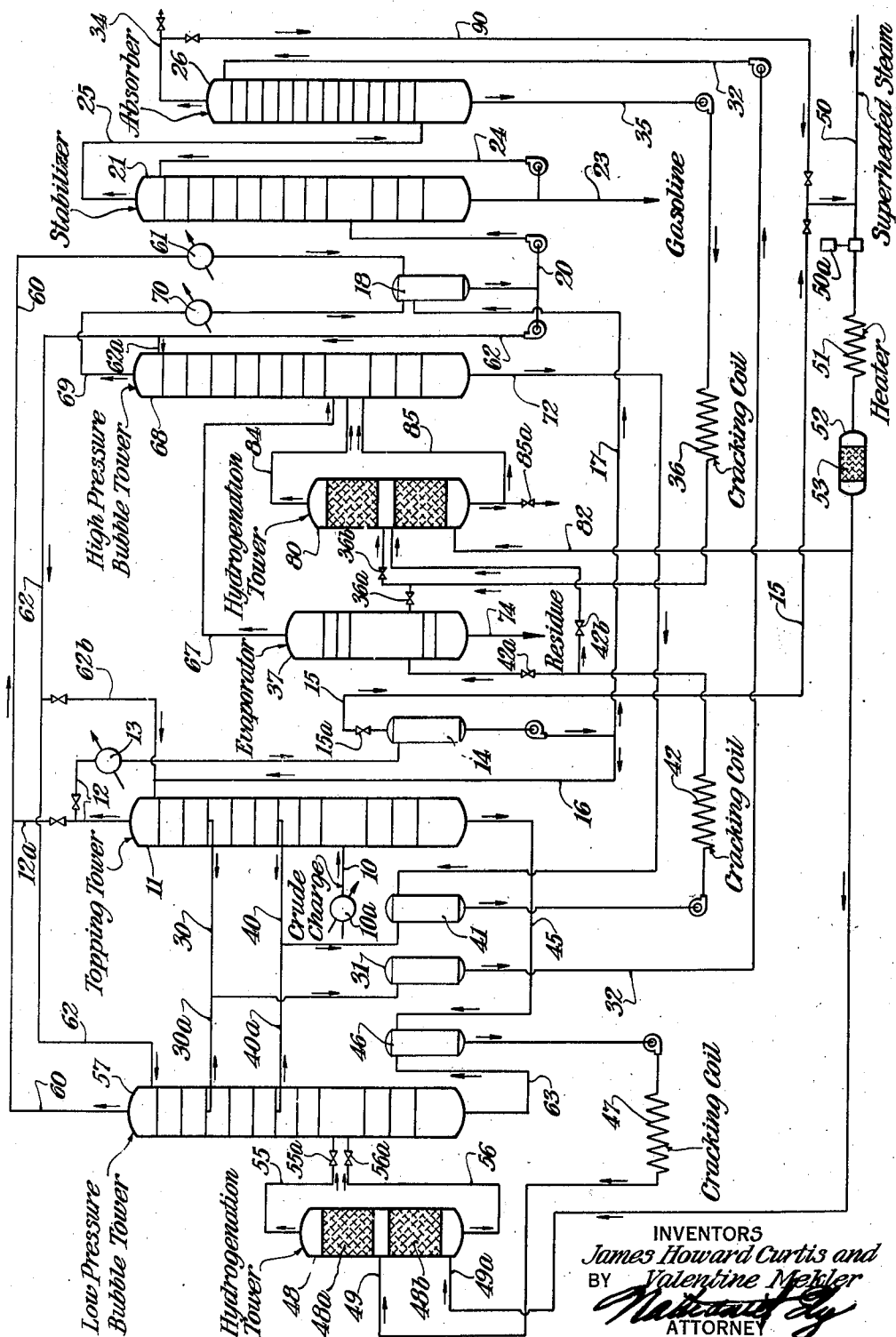


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REFINING HYDROCARBONS

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## REFINING HYDROCARBONS

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This invention relates to an improved method of treating petroleum oil for the production of a high yield of gasoline of a high octane rating. More specifically, this invention relates to a process of hydrogenation by means of which a substantial portion of the heavy or high boiling fractions occurring in crude petroleum, cracked stocks, and the like is converted into high octane gasoline.

It is customary to process a residual stock, such as a reduced crude, for conversion into lighter products by subjecting it to suitable cracking conditions of temperature and pressure, continuing the cracking reaction in an evaporator or reactor, separating the cracked vapors from the liquid conversion products, and fractionating these vapors to obtain gasoline. The cracking reaction decomposes the heavy hydrocarbons comprising the residual stock into lighter saturated and unsaturated hydrocarbons. In the continuation of the cracking reaction these unsaturated hydrocarbons tend to polymerize, thereby forming tarry materials and coke. These heavy polymerized hydrocarbons represent an unsatisfactory conversion of the reduced crude and a consequent loss in yield of the more valuable lighter products, such as gasoline.

It has also been the practice to use a suitable stock for admixture with the cracked products as they issue from the cracking coil, to prevent the polymerization of the unsaturated cracked hydrocarbons from continuing beyond a desired point, such operation being known as quenching. This method is not entirely successful, however, in arresting the formation of undesirable polymerized products, since a considerable amount of tarry residue or the like is almost always formed.

It is the principal object of this invention to provide a method of treating crude petroleum by means of which the maximum yield of gasoline is obtained from the petroleum by suitable conversion thereof, and in which the production of other materials is held to a minimum.

A more specific object of this invention is to provide a method of treating residual hydrocarbon material, such as a reduced crude, by a combination of cracking and hydrogenation operations, whereby the residual material is substantially converted into lower boiling material and polymerization of the cracked residual material to heavier tarry and coky substances is substantially prevented.

Further objects and advantages of this in-

vention will be apparent from the following description of a preferred form of embodiment thereof, taken in connection with the attached drawing, which is a diagrammatic flow sheet showing one arrangement of flow.

It is known that, when a heavy hydrocarbon is heated under suitable cracking conditions of temperature and pressure, the molecule usually breaks up into a lower boiling saturated hydrocarbon and a lower boiling unsaturated hydrocarbon. For example, a heavy paraffinic hydrocarbon, when cracked under mild conditions of temperature and pressure, splits into a lower boiling paraffin and a low boiling olefin. Furthermore, as the length of the hydrocarbon chain increases, the tendency of the molecule to split in the middle of the chain becomes greater. Hence the reaction that takes place when a heavy paraffinic hydrocarbon is cracked, as in a viscosity-breaking operation, is such that it breaks up into a lower boiling paraffin and a corresponding olefin.

If the reaction is continued in an evaporator or reactor of some sort, as is usually practiced, the cracked olefins, being unsaturated, tend to polymerize and form heavy tarry hydrocarbons. The cracked paraffins, being saturated, undergo no such polymerization reaction.

In accordance with a preferred form of embodiment of our invention, a residual material, such as a reduced or topped crude, is subjected to mild cracking conditions of temperature and pressure, such as in a viscosity-breaker, for such a time that only a portion of the hydrocarbons is cracked. Immediately thereafter the partially cracked hydrocarbons are subjected to hydrogenation under suitable conditions in the presence of a hydrogen-containing gas, whereby the unsaturated products of cracking are saturated by the addition of hydrogen thereto and polymerization of these unsaturated compounds to heavy tarry hydrocarbons is prevented. The partially converted hydrocarbons are then fractionated into gasoline, several intermediate cuts suitable for further thermal or catalytic conversion to gasoline, and a residue, representing substantially the unconverted portion of the original charge, which is recycled to the above-mentioned cracking unit.

The nature of the hydrogenation reaction is such that the partially cracked hydrocarbons are subjected to conditions of simple hydrogenation; destructive hydrogenation, in which cracking is combined with hydrogenation, does not take place. The reaction merely involves the

addition of hydrogen to the unsaturated cracked products without further cracking of the partially cracked hydrocarbons.

For convenience, our invention will be described in connection with a system in which a combination of topping, cracking, hydrogenating, and polymerizing operations is so utilized that a substantial portion of the crude petroleum undergoing treatment is converted to gasoline.

In accordance with the preferred form of embodiment of our invention, a crude petroleum is charged at 10 to topping tower 11, after having been raised to the desired distilling temperature in heater 10a. In the topping tower the crude petroleum is separated into a gasoline fraction, a naphtha fraction, a gas oil fraction, and a residual bottoms.

Gasoline vapors from tower 11 are removed overhead in line 12, condensed in condenser 13, and collected in receiver 14. Valve 15a in line 15 maintains such a pressure in receiver 14 that substantially only propane and lighter gases are allowed to escape through line 15. Part of the condensate from receiver 14 is returned for refluxing purposes to tower 11 through line 16. The remainder of the condensate is pumped through line 17 to receiver 18, in which it is mixed with other gasoline condensates obtained as hereinafter described.

Mixed gasoline condensate from receiver 18 is pumped through line 20 to stabilizer 21, in which the normally gaseous hydrocarbons having four carbon atoms per molecule or less are stripped from the gasoline. Stabilized gasoline is removed at 23 and sent to storage. Reflux for stabilizer 21 is supplied by recirculating a portion of the stabilized gasoline through line 24. The stripped normally gaseous hydrocarbons are removed from stabilizer 21 at 25 and passed to absorber 26.

The naphtha fraction withdrawn from topping tower 11 in line 30 is collected in receiver 31 and pumped through line 32 to absorber 26, in which it is brought into countercurrent contact with the normally gaseous hydrocarbons from stabilizer 21 for the purpose of absorbing those gaseous hydrocarbons having three to four carbon atoms per molecule. The gases leaving absorber 26 at 34 consist primarily of those gaseous hydrocarbons having two carbon atoms per molecule or less.

Enriched naphtha is withdrawn from absorber 26 at 35 and is passed to high temperature cracking coil 36, in which the absorbed gaseous hydrocarbons and the constituents of the naphtha fraction react under suitable temperature and pressure conditions to form a substantial amount of gasoline hydrocarbons. The cracked products from coil 36 are then passed through pressure reducing valve 36a to evaporator 37, in which they are separated into vapors and liquid.

The gas oil fraction removed from topping tower 11 at 40 is collected in receiver 41, in which it is mixed with other gas oil streams obtained as hereinafter described. Gas oil from receiver 41 is pumped to high temperature cracking coil 42, in which it is substantially converted into lower boiling material. The cracked products are passed through pressure reducing valve 42a to evaporator 37 for separation into vapors and liquid.

The bottoms from topping tower 11 is removed through line 45 and collected in receiver 46, from which it is pumped to low temperature cracking coil 47, wherein it is subjected to essentially a

viscosity-breaking operation. The cracking conditions in coil 47 are such that the bottoms is only partially decomposed into lighter materials.

In accordance with our invention, the partially cracked products from coil 47, containing unsaturated hydrocarbon constituents that have a tendency to polymerize to heavy tar-like materials, are then immediately passed to hydrogenation tower 48, in which hydrogenation of these unsaturated hydrocarbons is effected. Although the hydrogenation may be accomplished under appropriate conditions of temperature and pressure only, the reaction is preferably carried out in the presence of a suitable hydrogenating catalyst, so that the temperature in tower 48 may be maintained sufficiently low to prevent further cracking of the material undergoing conversion. Metals, such as nickel, chromium, cobalt, molybdenum, or the like, or the oxides or sulfides thereof, or any other substance capable of effecting the desired reaction, may be employed as the catalyst.

Hydrogenation tower 48 preferably contains two catalyst masses 48a and 48b. The partially cracked hydrocarbons from coil 47 are conveniently introduced into tower 48 at 49, intermediate the two catalyst masses, hydrogen being introduced at 49a. By means of this arrangement, separation of the vaporous portion from the liquid portion of the partially cracked hydrocarbons is effected; and hydrogenation of the unsaturated components therein is independently accomplished.

The reaction is carried out under such conditions that the hydrogenation is non-destructive in nature; hydrogen is added to the unsaturated cracked products only, and the heavy uncracked hydrocarbons are not further converted. Hydrogenation of the unsaturated components materially arrests their tendency to polymerize to heavy tarry and coky substances, so that the formation of heavy hydrocarbon polymers as a result of the cracking operation is negligible.

Hydrogen for the hydrogenation reaction in tower 48 is produced by mixing the gaseous hydrocarbons removed from receiver 14 through line 15 with superheated steam introduced at 50, compressing the mixture by means of compressor 50a, heating the mixture in heater 51 to a high temperature, and passing the heated, compressed mixture to a hydrogen-producing unit 52 containing a catalyst 53 which effects a reaction of the steam with the gaseous hydrocarbons to form hydrogen. It will be understood that unit 52, though conventionally shown, comprises the necessary equipment to carry out the reaction and to purify the hydrogen produced. Catalyst 53 may consist of any of various metals or metal oxides, such as nickel oxide and the like. The hydrogen mixture is then introduced into hydrogenation tower 48 at 49a in conjunction with the partially cracked products from viscosity-breaker 47.

The cracked and hydrogenated hydrocarbons from tower 48 are introduced into the low pressure bubble tower 57, vapors in line 55 and liquid in line 56. Lines 55 and 56 are respectively provided with pressure reducing valves 55a and 56a. As in topping tower 11, the vapors and liquid are fractionated in tower 57 into a gasoline fraction, a naphtha fraction, a gas oil fraction, and a residuum.

The gasoline fraction is removed overhead at 60, condensed in condenser 61, and collected in receiver 18. Condensate from receiver 18 is re-

turned to bubble tower 57 through line 62 as reflux. The naphtha fraction is removed at 30a and combined in receiver 31 with the naphtha fraction removed from topping tower 11 at 30. Similarly, the gas oil fraction is removed at 40a and combined in receiver 41 with the gas oil fraction from topping tower 11. The residuum is removed at 63 and is collected in receiver 46, from which it is recycled to cracking coil 47. Inasmuch as cracking coil 47 does not accomplish a complete cracking of the hydrocarbons therein, the material in line 63 represents substantially those hydrocarbons which were not cracked during passage through coil 47.

Vapors from evaporator 37 are removed at 67 and are fractionated in high pressure bubble tower 68 into a gasoline fraction, removed at 69, and a gas oil fraction, removed at 72. The gasoline fraction is condensed in condenser 70 and is collected in receiver 18, condensate from which is returned through lines 62 and 62a to bubble tower 68 as reflux. The gas oil fraction is sent to receiver 41 and is mixed with the gas oil fractions from topping tower 11 and low pressure bubble tower 57. The liquid residue withdrawn at 74 from evaporator 37 consists of the heavy hydrocarbon polymers produced in cracking coils 36 and 42 and is suitable for use as a fuel oil.

It will be appreciated that, if desired, the cracked hydrocarbons issuing from cracking coils 36 and 42 may be subjected to hydrogenation to prevent the formation of any high boiling polymeric hydrocarbons. In this case these cracked hydrocarbons are passed, immediately after leaving cracking coils 36 and 42 respectively, through pressure reducing valves 36b and 42b to catalytic hydrogenation unit 80, wherein the unsaturated constituents are hydrogenated. Hydrogen is introduced into tower 80 through line 82. Hydrogenation unit 80 is similar to tower 48 in construction and operation. The converted and substantially fully saturated hydrocarbons are then passed through lines 84 and 85 to bubble tower 68 for separation into light and heavy fractions. If desired, the liquid from hydrogenation tower 80 may be withdrawn from the system through line 85a. Substantially complete conversion of a crude petroleum into gasoline is possible, since the amount of liquid that would be withdrawn through line 85a is small.

It is also possible to utilize the gaseous hydrocarbons leaving absorber 26 at 34 for the production of hydrogen, since these hydrocarbons are similar in character to those released from receiver 14 through line 15. For this purpose the gaseous hydrocarbons are passed through line 90 to be mixed with superheated steam at 50. When these hydrocarbons are so used, it is desirable to pass the gasoline fraction from topping tower 11 through lines 12a and 60 direct to receiver 18, thereby dispensing with receiver 14. Reflux for tower 11 is then supplied through lines 62 and 62b.

It will be understood that the operation of our invention is not limited to the method of producing hydrogen described above and that any other suitable process of converting these unabsorbed normally gaseous hydrocarbons into hydrogen may also be utilized.

By way of example only, our invention may be described in connection with the treatment of a Mid-Continent (Van Zandt) crude. The crude is fractionated in topping tower 11 into gasoline, naphtha, and gas oil fractions, and a residuum containing hydrocarbons boiling substantially

above 650° F. The gasoline fraction is stabilized to remove the normally gaseous hydrocarbons having four carbon atoms per molecule or less. These hydrocarbons are then subjected to absorption by the naphtha fraction for the recovery of those hydrocarbons having three to four carbon atoms per molecule. The unabsorbed gaseous hydrocarbons are mixed with superheated steam, and the mixture is subjected to the action of an appropriate catalyst for the production of hydrogen. Pressures of from 400 to 600 lbs./sq. in. and temperatures of from 1500 to 1600° F. are found suitable for carrying out this latter reaction.

The naphtha enriched by the absorbed gaseous hydrocarbons is passed to cracking coil 36, in which it undergoes a reforming operation for conversion into gasoline. Cracking coil 36 is preferably operated at a temperature of from 1050 to 1150° F. and a pressure of from 1100 to 1200 lbs./sq. in. The gas oil fraction is cracked in coil 42, at a temperature of approximately 1000° F. and a pressure of from 1000 to 1200 lbs./sq. in. Evaporator 37, to which the cracked products from coils 36 and 42 are passed, is maintained at a pressure of from 300 to 500 lbs./sq. in.

The residuum from tower 11 is subjected to a viscosity-breaking operation in cracking coil 47, in which a temperature from 825° to 875° F. and a pressure from 400 to 600 lbs./sq. in. are maintained. As soon as the partially cracked residuum leaves coil 47, it is subjected to a non-destructive hydrogenation in tower 48 in order to convert the unsaturated products of cracking to saturated compounds and to prevent the formation of heavy polymeric hydrocarbons. The pressure in hydrogenation tower 48 is approximately the same as that maintained in cracking coil 47; the temperature is somewhat lower, preferably below 800° F., so that further cracking will not take place. The pressure in bubble tower 57, to which the products of conversion from tower 48 are passed, is kept at about 50 lbs./sq. in. or lower.

By means of the process disclosed in our invention, crude petroleum may be substantially entirely converted into gasoline. Production of fuel oil or other heavy residua and gas is materially reduced, as these substances are utilized to increase the yield of gasoline.

While we have described a preferred form of embodiment of our invention, we are aware that there may be modifications thereto, and we, therefore, desire a broad interpretation of our invention within the scope and spirit of the description herein and the claims appended hereinafter.

We claim:

1. The method of converting heavy hydrocarbons boiling above the range of gas oil into a hydrocarbon mixture from which a maximum amount of lighter hydrocarbons boiling within the range of gasoline may be obtained, which comprises the steps of subjecting said heavy hydrocarbons to low temperature, and low pressure cracking conditions to accomplish a viscosity breaking thereof, thereafter immediately non-destructively hydrogenating all of said partially cracked hydrocarbons in the presence of hydrogen and a hydrogenating catalyst, whereby the heavy unsaturated products of cracking are converted into saturated compounds and the polymerization of said unsaturated products of cracking to heavy tar-like materials is substantially prevented, and fractionating said converted hydrocarbons to obtain an additional cracking stock

for conversion into gasoline and a fraction boiling within the range of gasoline.

2. The method of converting heavy hydrocarbons boiling above the range of gas oil into lighter hydrocarbons boiling within the range of gasoline, which comprises the steps of subjecting said heavy hydrocarbons to low temperature and low pressure cracking conditions to accomplish a viscosity breaking thereof, thereafter immediately non-destructively hydrogenating all of said partially cracked hydrocarbons in the presence of hydrogen and a hydrogenating catalyst, whereby the heavy unsaturated products of cracking are converted into saturated compounds and the polymerization of said unsaturated products of cracking to heavy tar-like materials is substantially prevented, separating the products of conversion into a gasoline fraction, a fraction containing predominantly saturated hydrocarbons of intermediate boiling point as an additional cracking stock from which a high yield of gasoline can be obtained, and a residue composed of constituents boiling above the range of gas oil, and recycling said residue for further conversion in admixture with the initial heavy hydrocarbon charge.

3. The method of treating hydrocarbon oils, which comprises the steps of topping a crude petroleum to obtain a reduced crude, subjecting said reduced crude to a viscosity-breaking operation to effect a partial cracking thereof, immediately thereafter subjecting all of the partially cracked reduced crude to non-destructive hydrogenating conditions to convert the unsaturated products of cracking to fully saturated compounds, whereby polymerization of said unsaturated cracked products to heavy tar-like materials is substantially prevented, fractionating the cracked and hydrogenated hydrocarbons to obtain an additional saturated cracking stock and a fraction suitable for use as gasoline, and cracking said saturated cracking stock to obtain the maximum yield of gasoline boiling range hydrocarbons.

4. The method of converting heavy hydrocarbons boiling above the range of gas oil into a hydrocarbon mixture from which a maximum amount of lighter hydrocarbons boiling within the range of gasoline may be obtained, which comprises the steps of subjecting said heavy hydrocarbons to low temperature and low pressure cracking conditions to accomplish a viscosity breaking thereof, thereafter immediately non-destructively hydrogenating all of said partially cracked hydrocarbons in the presence of hydrogen and a hydrogenating catalyst, whereby the unsaturated products of cracking are converted into saturated compounds and the polymerization of said unsaturated products of cracking to heavy tar-like materials is substantially prevented, fractionating said converted hydrocarbons to obtain an additional cracking stock for conversion into gasoline and a fraction boiling within the range of gasoline, stabilizing said gasoline fraction to remove the normally gaseous hydrocarbons contained therein, separating from said normally gaseous hydrocarbons those constituents having two carbon atoms per molecule or less, reacting said separated hydrocarbons under appropriate conditions to produce hydrogen, and utilizing the hydrogen in said hydrogenating step.

5. The method of substantially converting a reduced crude into gasoline, which comprises the

steps of subjecting said reduced crude to a viscosity-breaking operation, immediately thereafter non-destructively hydrogenating all of said viscosity-broken reduced crude in the presence of a hydrogenating catalyst and hydrogen to convert the unsaturated products of cracking to saturated compounds, fractionating the converted reduced crude into a plurality of fractions including a gasoline fraction, a naphtha fraction, and a residue, admixing the residue with the reduced crude prior to the viscosity-breaking treatment, stabilizing said gasoline fraction to strip the normally gaseous components therefrom, treating said normally gaseous components with said naphtha fraction to absorb those hydrocarbons having from three to four carbon atoms per molecule, and cracking said enriched naphtha fraction under suitable cracking conditions to produce a further yield of gasoline.

6. The method of treating hydrocarbon material which comprises the steps of fractionating a crude petroleum into a gasoline fraction, a naphtha fraction, a gas oil fraction, and a reduced crude; viscosity breaking the reduced crude in a low temperature cracking coil; immediately thereafter subjecting all of the partially cracked reduced crude to a non-destructive hydrogenation to effect a saturation of the unsaturated products of cracking; fractionating the cracked and hydrogenated reduced crude into a gasoline fraction, a naphtha fraction, a gas oil fraction, and a residue; recycling the residue from the second fractionation for admixture with the reduced crude from the first fractionation; stabilizing the gasoline fractions to strip the normally gaseous components therefrom; scrubbing said normally gaseous components with said naphtha fractions to absorb the C<sub>3</sub> and C<sub>4</sub> components therein; reacting the unabsorbed gaseous components with superheated steam at an elevated temperature and pressure in the presence of a suitable catalyst to form hydrogen; utilizing the hydrogen in said hydrogenation step; separately cracking the enriched naphtha fractions and the gas oil fractions under relatively severe cracking conditions; separating the resultant cracked vapors from the cracked liquid; removing said cracked liquid as a fuel oil residue; fractionating said cracked vapors into a gasoline fraction and a gas oil fraction; and recycling said gas oil fraction for admixture with said other gas oil fractions for further cracking thereof.

7. The method of treating hydrocarbon material which comprises the steps of fractionating a crude petroleum into a gasoline fraction, a naphtha fraction, a gas oil fraction, and a reduced crude; viscosity breaking the reduced crude in a low temperature cracking coil; subjecting the partially cracked reduced crude to a non-destructive hydrogenation to effect a saturation of the unsaturated products of cracking; fractionating the cracked and hydrogenated reduced crude into a gasoline fraction, a naphtha fraction, a gas oil fraction, and a residue; recycling the residue from the second fractionation for admixture with the reduced crude from the first fractionation; stabilizing the gasoline fractions to strip the normally gaseous components therefrom; scrubbing said normally gaseous components with said naphtha fractions to absorb the C<sub>3</sub> and C<sub>4</sub> components therein; reacting the unabsorbed gaseous components with superheated steam at an elevated temperature and pressure in the presence of a suitable catalyst to form hydrogen; utilizing the hydrogen in the hydrogenation opera-

tions; separately cracking the enriched naphtha fractions and the gas oil fractions under relatively severe cracking conditions; immediately thereafter subjecting the cracked naphtha and gas oil to a non-destructive hydrogenation to saturate the unsaturated products of cracking and to prevent the polymerization of said unsaturated products of cracking to heavy tarry and coky materials; and fractionating the cracked and hydrogenated naphtha and gas oil into a gasoline fraction and a higher boiling fraction.

8. The method of converting a heavy petroleum residue boiling substantially above 650° F. into lower boiling materials, which comprises subjecting said residue to a partial conversion at a temperature between 825° and 875° F. and a pressure from 400 to 600 lbs. per square inch, immediately thereafter subjecting all of the partially cracked residue to a non-destructive hydrogenation at a temperature below 800° F. and at substantially the same pressure in the presence of hydrogen and a hydrogenating catalyst to saturate the unsaturated cracked products, whereby polymerization of said unsaturated cracked products to heavy tarry and coky materials is substantially prevented, and fractionating the cracked and hydrogenated hydrocarbons to obtain an additional cracking stock for con-

version into gasoline and a fraction suitable for use as gasoline.

9. A process for the treatment of hydrocarbon oils such as petroleum, which comprises the steps of distilling such oil to produce a gasoline distillate, a plurality of intermediate distillates, and a residual oil, subjecting the intermediate distillates to relatively severe cracking conditions whereby said distillates are converted into lower boiling materials, subjecting the residual oil to relatively mild cracking conditions in the nature of viscosity breaking to convert a portion thereof into lighter materials, separately subjecting the cracked intermediate distillates and the partially cracked residual oil to a non-destructive hydrogenation to effect a saturation of the unsaturated products of cracking, and fractionating the cracked and hydrogenated hydrocarbons to obtain an additional cracking stock for conversion into gasoline and a fraction boiling within the range of gasoline.

10. The method according to claim 7, in which the higher boiling fraction obtained in the last-mentioned fractionation is recycled for admixture with said gas oil fractions for further cracking thereof.

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