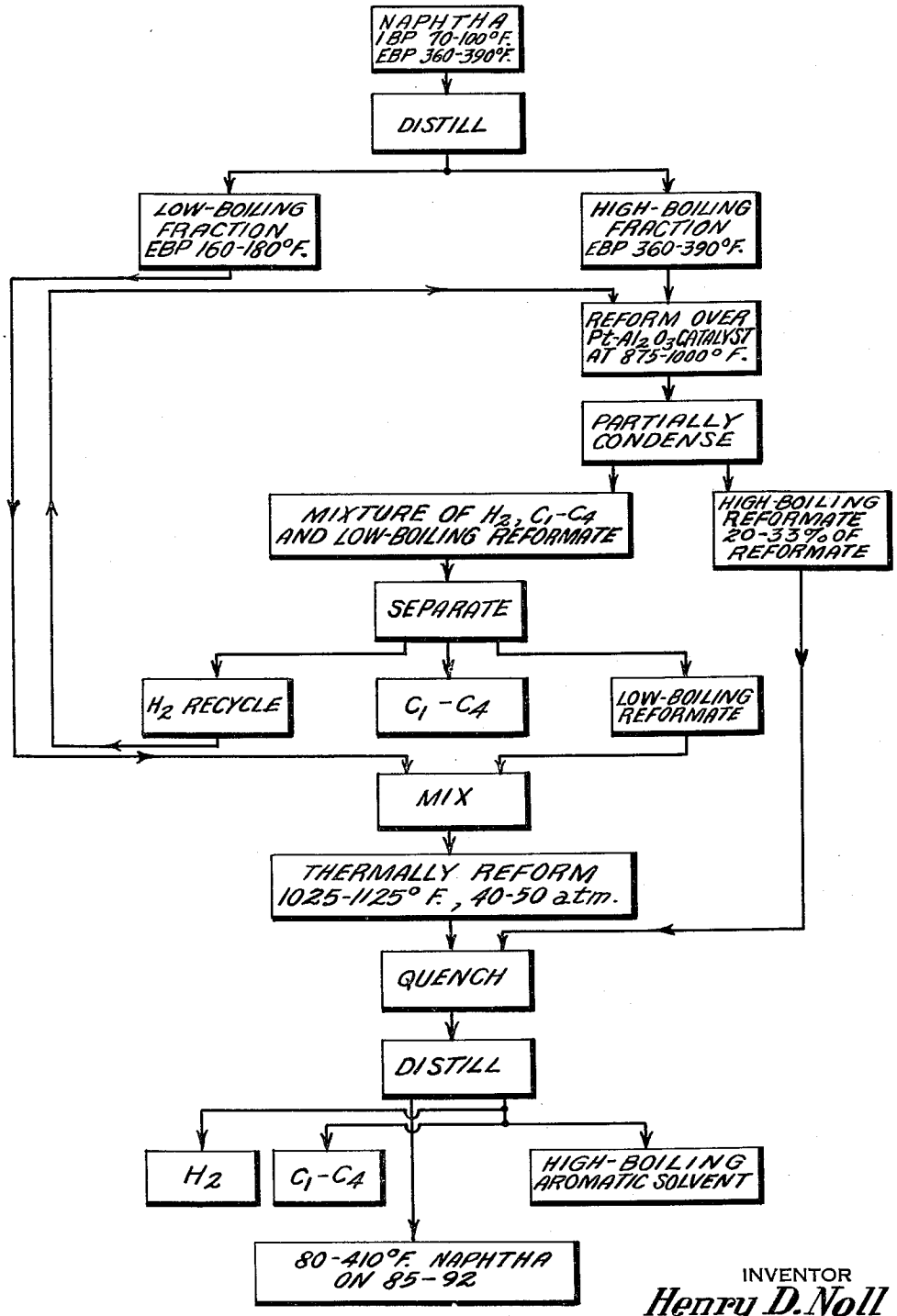
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REFORMING GASOLINE

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REFORMING GASOLINE

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This invention relates to the upgrading of naphtha to provide a flexible arrangement for the production of desirable products in advantageous yields with a minimized investment in petroleum refinery apparatus.

Heretofore, it has been known that a limited amount of octane improvement could be achieved by the use of inexpensive equipment required for thermal reforming of a naphtha fraction boiling in or near the gasoline range. By the use of expensive catalyst and equipment, naphtha has been catalytically reformed in the presence of hydrogen by methods conveniently designated as hydrogenative aromatizing processes. It has also been proposed that all or part of the reformate from a hydrogenative aromatizing zone be subjected to thermal reforming, but such procedures have been suggested only for the preparation of extremely high octane number products.

During the investigations leading to the development of the present invention, it was discovered that the yields for a given octane are advantageously high and the total plant investment for achieving a particular octane level in the moderate octane range (85–92 F–1 clear) is advantageously low when the method comprises subjecting to the hydrogenative aromatizing zone only those fractions of hydrocarbons particularly beneficiated by the hydrogenative aromatizing treatment, and subjecting to the thermal reforming zone only those hydrocarbons particularly beneficiated by the thermal reforming step.

In accordance with the present invention, naphtha is upgraded by the method which comprises the steps of: distilling a naphtha having an initial boiling point within the range of from about 70° F. to about 100° F. and a final boiling point within the range from about 360° F. to about 390° F. to separate a low boiling fraction boiling from about 80° to an end boiling point within the range from about 160° to about 180° F. and a high boiling fraction having an initial boiling point near said end boiling point of the low-boiling fraction and having an end boiling point within the range from about 360° F. to about 390° F.; hydrogenatively aromatizing said high boiling fraction in the presence of several mols of hydrogen per mol of hydrocarbon at superatmospheric pressure at a temperature within the range from 875° F. to 1000° F. over a platinum-alumina catalyst to form a highly aromatic reformate, some of which may boil higher than the effluent from the hydrosulfurization step; partially condensing the effluent from the hydrogenative aromatizing zone to separate a liquid constituting from about 20 to about 33% of the reformate; mixing the remaining portion of the reformate with said low boiling fraction of the naphtha, and passing said mixture through a thermal reforming zone at a temperature within the range from about 1025° F. to 1125° F. at a pressure of from about 40 to about 50 atmospheres at a soaking factor within the range from about 1 to 10 ft.^{3}/BSD; withdrawing and immediately quenching and cooling the effluent from the thermal reforming zone by contact with said hydrocarbon fraction separated by the partial condensation of the effluent from the hydrogenative aromatizing zone; and passing the thus prepared mixture of the quench oil and the effluent from the thermal reforming zone to a fractional distillation step from which there are recovered products comprising a minor amount of heavy aromatic solvent, and a major amount of naphtha

having an F–1 octane number within the range from about 85 to 92. The heavy aromatic solvent may be contaminated by tar formed during the thermal reforming step. Gases including hydrogen and C_1–C_4 hydrocarbons may also be separated from the effluent from the thermal reforming step.

The self-explanatory flow sheet in the accompanying drawing illustrates some of the relationships among the steps whereby reformate having an octane number of moderate level (F–1 clear 85–92) may be obtained at a combination of advantageously low plant investment and advantageously low operating cost.

The invention is further clarified by reference to an example.

Example I

A straight run gasoline having an endpoint within the range from about 360° F. to about 390° F. represents a suitable starting material. If the gasoline contains troublesome amounts of sulfur, it may be hydrodesulfurized by any appropriate procedure, such as by passing it, together with an appropriate amount (e.g. about 0.5 mol of hydrogen per mol of gasoline) at 750° F. at 400 pounds per square inch gauge pressure at a space rate of 1.5 liquid volumes per volume of catalyst per hour through a pretreating reactor containing a cobalt molybdate on alumina catalyst. Sulfur is usually the most abundant contaminant in a straight run naphtha, but the hydrodesulfurization pretreatment may sometimes also remove measurable amounts of nitrogen, oxygen, metals, and other contaminants.

The distillation of the naphtha is subsequent to the hydrodecontamination if the hydrodecontamination step is necessary. By the distillation, a low boiling fraction comprising hydrocarbons having a low (e.g. 80° F.) initial boiling point and an end boiling point within the range from about 160° F. to about 180° F. is withdrawn from the fractional distillation and sent directly to the mixing zone for the preparation of the feed to the thermal reforming zone, thereby bypassing the hydrogenative aromatizing zone, the partial condenser and the high pressure flash distillation zone. There is also withdrawn from the initial fractional distillation a high boiling fraction boiling above said low boiling fraction (i.e. an initial boiling point within the range from about 160° F. to 180° F.) and having an end boiling point within the range from about 360° F. to about 390° F., which fraction is subjected to the hydrogenative aromatizing zone in the presence of a catalyst comprising about 0.5% platinum on alumina. The hydrogenative aromatizing is conducted at a pressure from about 10 to 50 atmospheres and at a temperature of from about 875° F. to 1000° F., there being a high molar ratio, e.g. 10 to 1, of hydrogen to naphtha. In the hydrogenative aromatizing zone, the boiling points of the c_6 naphthenes are increased from about 10° to about 50° F. as a result of the aromatization. The effluent from the hydrogenative aromatizing zone is passed through a partial condensation zone adapted to condense from about 20% to about 35%, desirably about 25% of the liquid hydrocarbon effluent from the aromatizing zone. The thus condensed material consists predominantly of $R_xC_6H_{6-x}$, that is, high boiling mononuclear aromatic hydrocarbons. The high boiling aromatic fraction thus separated by the partial condensation step has an octane number sufficiently high to meet market demands. The gaseous effluent from the partiol condenser is passed to a high pressure separation zone in which a hydrogen-rich recycle gas is separated from the normally liquid hydrocarbon components. This hydrogen-rich recycle gas is of sufficient purity that it may be recycled without purification, a portion of the gas being withdrawn to maintain in the hydrogenative re-

forming system a reasonably constant inventory of recycle gas. Some of the thus withdrawn hydrogen can be employed in th hydrodesulfurization pretreatment over the cobalt molybdate catalyst. The liquid hydrocarbons recovered in the high pressure separation zone are mixed with the volatile fraction (boiling between about 80° F. and 160° F.) of fresh naphtha and this mixture is passed through a thermal reforming zone containing no catalyst at a pressure of from about 40 to 50 atmospheres pressure and at a temperature of from about 1025° F. to about 1125° F., preferably 1050–1085° F. and desirably 1070° F. at a Soaking Factor of from about 1 to 10. As in other thermal reforming operations, the desired severity may be achieved in a relatively shorter reaction time by using relatively higher temperature. It is sometimes convenient to refer to the severity of the time-temperature conditions as the "Soaking Factor," which designates the product of the ratio of the volume of the thermal reforming zone (measured in cubic feet) to the throughput capacity of the unit (measured in barrels per standard day) multiplied by the ratio of the reaction rate of said reforming temperature to the reaction rate of 800° F. Various combinations of temperature and reaction time may be equivalent for a particular severity, and would all be expressed by the same Soaking Factor. The thermal reforming is conducted at a Soaking Factor of from about 1 to about 10. The selective fraction of the hydrogenative reformate is upgraded in octane number by reason of the conversion of the paraffinic components of the aromatic reformate to olefins and by reason of other thermal reforming reactions. Moreover, there is an unexpectedly advantageous upgrading of the volatile virgin naphtha, and a hypothesis has been proposed that such advantages may be attributable in part to the diluent effect, whereby there is a lower pressure of virgin naphtha in the cracking zone and may be attributable in part to the ability of the high concentration of aromatic molecules to promote conversion of paraffins to olefins and to repress the conversion of virgin naphtha to coke and/or C_1–C_4 hydrocarbons.

The effluent from the thermal cracking zone is instantaneously cooled in a quench tower by contact with a quench oil consisting of the high boiling aromatic reformate separated by the partial condensation step. Substantially all of the liquid hydrocarbon products of the over-all process are thus brought together again in the quench tower and move together in the stream of hydrocarbons subjected to the final fractional distillation step. Final distillation of the thus prepared mixture of products is reasonably precise and thus overcomes any of the inadequacies of the separations of earlier stages of the over-all process. There is recovered from the product distillation tower: light gasses comprising hydrogen; C_1C_4 hydrocarbons; a gasoline fraction having appropriate volatility and an appropriate end boiling point; and a fraction boiling above the normal gasoline range, which high boiling fraction has a sufficiently high content of aromatic hydrocarbons to be marketable as a heavy aromatic solvent. If desired, the heavy aromatic solvent may be purified by distillation. The gasoline fraction constitutes most of the product, and because of its upgraded octane number and other favorable properties, is the valuable product sought more than any of the by-products.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

What I claim is:

1. The method of upgrading naphtha to provide high boiling aromatic solvent, upgraded gasoline and gaseous hydrocarbons which method comprises the steps of: fractionally distilling a naphtha having an initial boiling point within the range from about 70° F. to about 100° F. and an end boiling point within the range from about 360° F to about 390° F. to separate a low boiling fraction having an initial boiling point within the range of from about 70° F. to about 100° F. and an end boiling point within the range from about 160° to about 180° F. and a high boiling fraction having an initial boiling point near said end boiling point of the low boiling fraction and having an end boiling point within the range from about 360° F. to about 390° F.; hydrogenatively aromatizing said high boiling fraction in the presence of several mols of hydrogen per mol of hydrocarbon at superatmospheric pressure at a temperature within the range from 875° F. to 1000° F. over a platinum-alumina catalyst to form a highly aromatic reformate; partially condensing the effluent from the hydrogenative aromatizing zone to separate a liquid constituting from about 20% to about 33% of the reformate; mixing the remaining portion of the reformate with said low-boiling naphtha fraction, and passing said mixture through a thermal reforming zone at a temperature within the range from about 1025° F. to 1125° F. at a pressure of from about 40 to about 50 atmospheres at a soaking factor within the range from about 1 to 10 cu. ft./BSD; withdrawing and immediately quenching and cooling the effluent from the thermal reforming zone by contact with said hydrocarbon fraction separated by the partial condensation of the effluent from the hydrogenative aromatizing zone; and passing the thus prepared mixture of the quench oil and the effluent from the thermal reforming zone to a fractional distillation step from which there are recovered products comprising a minor amount of heavy aromatic solvent, and a major amount of naphtha having an F–1 octane number within the range from 85 to 92.

2. The method of upgrading naphtha which comprises the steps of: fractionally distilling the naphtha to provide a low boiling fraction and a high boiling fraction, said high boiling fraction having an initial boiling point within the range from about 160–180° F. and an end boiling point within the range from about 360° F. to about 390° F.; hydrogenatively aromatizing said high boiling fraction in the presence of several mols of hydrogen per mol of hydrocarbon at super-atmospheric pressure at a temperature within the range from about 875° F. to about 1000° F. in a hydrogenative aromatizing zone containing platinum on alumina catalyst particles; withdrawing effluent from said hydrogenative aromatizing zone; partially condensing the effluent from the hydrogenative aromatizing zone to separate a liquid condensate constituting from about 20% to about 33% in said effluent; mixing the remaining portion of the normally liquid components of said effluent with said low boiling naphtha fraction end passing said mixture through a thermal reforming zone at a temperature within the range from about 1025° F. to about 1125° F. at a pressure of from about 40 to about 50 atmospheres at a soaking factor within the range from about 1–10 cubic feet/BSD; withdrawing the effluent from said thermal reforming zone and immediately quenching and cooling said effluent by contact with said liquid condensate partially condensed from the effluent from the hydrogenative aromatizing step; and passing the thus prepared mixture of the effluent from the thermal reforming zone and the quenching liquid to a fractional distillation zone; fractionally distilling said mixture to recover a minor amount of heavy aromatic solvent and a major amount of naphtha having an octane number higher than the octane number of the naphtha initially separated into low boiling and high boiling fractions.

3. In a method of upgrading naphtha by subjecting at least a portion of the naphtha to hydrogenative aromatizing over a catalyst comprising platinum and alumina, and by subjecting at least a portion of the liquid hydrocarbon reformate from the hydrogenative aro-

matizing step to thermal reforming, the improvement which comprises the steps of: fractionally distilling the naphtha to provide a low boiling fraction and a high boiling fraction, said high boiling fraction having an initial boiling point within the range from about 160–180° F., and an end boiling point within the range from about 360° F. to about 390° F.; hydrogenatively aromatizing said high boiling fraction in the presence of several mols of hydrogen per mol of hydrocarbon at superatmospheric pressure at a temperature within the range from about 875° F. to about 1000° F. in a hydrogenative aromatizing zone containing platinum on alumina catalyst particles to prepare a catalytic reformate; withdrawing effluent from said hydrogenative aromatizing zone; partially condensing the effluent from the hydrogenative aromatizing zone to separate a liquid condensate constituting from about 20% to about 33% of the normally liquid components in said effluent; mixing the remaining portion of the normally liquid components of said effluent with said low boiling naphtha fraction and passing said mixture through a thermal reforming zone to prepare a thermal reformate at a temperature within the range from about 1025° F. to about 1125° F. at a pressure of from about 40 to about 50 atmospheres at a soaking factor within the range from about 1–10

cubic feet/BSD; withdrawing the effluent from said thermal reforming zone immediately quenching and cooling said effluent by admixture with said liquid condensate partially condensed from the effluent from the hydrogenative aromatizing step; and passing the thus prepared mixture of the effluent from the thermal reforming zone and the liquid condensate portion of the catalytic reformate to a fractional distillation zone; fractionally distilling said mixture to recover a minor amount of heavy aromatic solvent and a major amount of naphtha having an octane number higher than the octane number of the naphtha initially separated into low boiling and high boiling fractions.

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