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[54] **COMBINATION CRACKING PROCESS FOR CONVERTING PARAFFINIC NAPHTHA INTO HIGH OCTANE GASOLINE**

[75] Inventors: **John C. Strickland; Dorrance P. Bunn, Jr.,** both of Houston, Tex.

[73] Assignee: **Texaco Inc.,** New York, N.Y.

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[58] **Field of Search** 208/78, 60; 260/683.43

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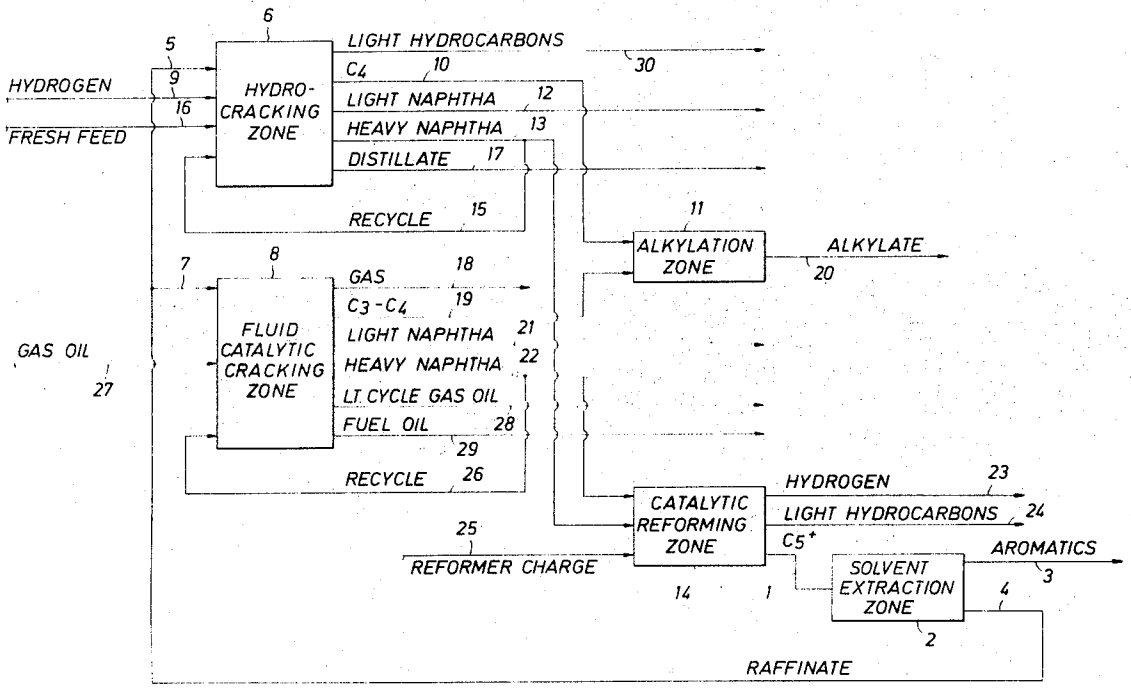
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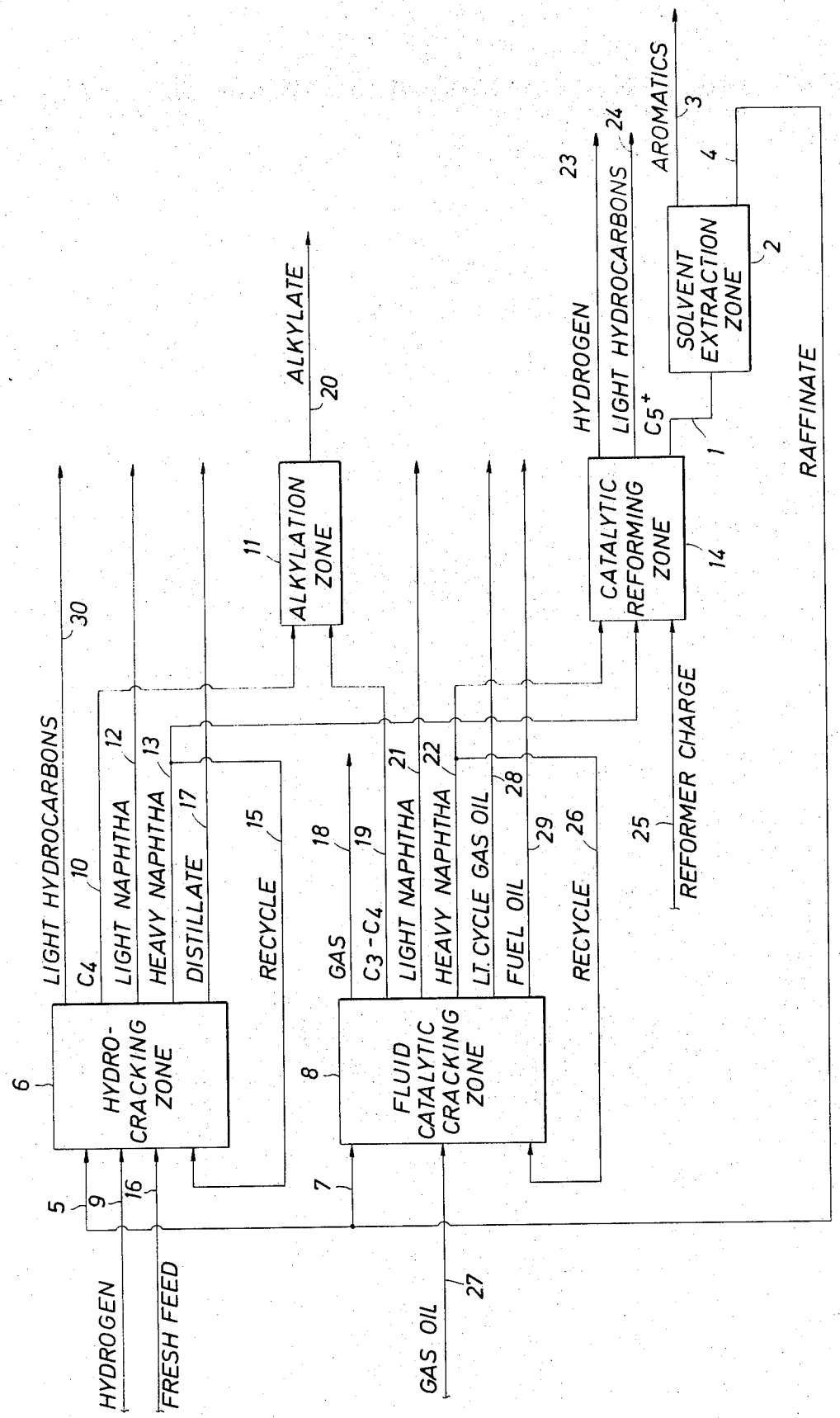
Primary Examiner—Delbert E. Gantz
Assistant Examiner—G. E. Schmitkons
Attorney—Thomas H. Whaley et al.

[57] **ABSTRACT**

A process for manufacturing high octane gasoline from a low octane paraffinic naphtha, which comprises hydrocracking a first portion of the naphtha to yield a C_4 fraction comprising isobutane and a hydrocracked light naphtha fraction having a relatively high octane number, catalytically cracking a second portion of the naphtha to yield a C_3-C_4 fraction comprising propylene, butylenes and isobutane and a catalytically cracked light naphtha fraction having a relatively high octane number, and reacting, in an alkylation zone the hydrocracked C_4 fraction and the catalytically cracked C_3-C_4 fraction to yield a high octane gasoline alkylate. The proportion of naphtha charged to the hydrocracking zone and the catalytic cracking zone are adjusted such that isobutane, butylene and propylene charge to the alkylation zone are in stoichiometric balance.

7 Claims, 1 Drawing Figure




HYDROGEN
FRESH FEED
GAS OIL
HYDRO-CRACKING ZONE
FLUID CATALYTIC CRACKING ZONE
ALKYLATION ZONE
CATALYTIC REFORMING ZONE
SOLVENT EXTRACTION ZONE
LIGHT HYDROCARBONS
C4
LIGHT NAPHTHA
HEAVY NAPHTHA
DISTILLATE
RECYCLE
GAS
C3-C4
LIGHT NAPHTHA
HEAVY NAPHTHA
LT. CYCLE GAS OIL
FUEL OIL
RECYCLE
ALKYLATE
HYDROGEN
LIGHT HYDROCARBONS
C5+
REFORMER CHARGE
AROMATICS
RAFFINATE
5
6
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COMBINATION CRACKING PROCESS FOR CONVERTING PARAFFINIC NAPHTHA INTO HIGH OCTANE GASOLINE

BACKGROUND OF THE INVENTION

The present invention relates to a method for converting low octane, gasoline range hydrocarbons into high octane gasoline. More particularly, the present invention relates to a method for converting a raffinate hydrocarbon comprising paraffinic hydrocarbons and having a very low octane number into high octane gasoline. The raffinate hydrocarbon is separated into two portions. The first portion is hydrocracked to yield a light naphtha fraction having a higher octane than the raffinate and a fraction comprising isobutane. The second raffinate portion is fluid catalytically cracked to yield a light naphtha fraction having an octane higher than the raffinate and a fraction comprising propylene, butylene, and isobutane. The hydrocracked isobutane fraction and the fluid catalytically cracked propylene-butylene-isobutane fraction are charged to a alkylation reaction from which a high octane alkylate is recovered. The hydrocracked light naphtha fraction, the fluid catalytically cracked light naphtha fraction, and the alkylate are recovered as gasoline products.

In the refining of petroleum, it is common that petroleum fractions comprising aromatic and paraffinic hydrocarbons and boiling in the gasoline boiling range are solvent extracted to recover the aromatic hydrocarbons. The aromatic hydrocarbons recovered from such a solvent extraction, such as for example benzene, toluene and xylene, are desirable for use as chemicals or as high octane gasoline blending components. The raffinate hydrocarbons recovered from such solvent extraction processes substantially comprise paraffinic hydrocarbons. Although such raffinate hydrocarbons may be utilized, such as in commercial hydrocarbon solvents or as charge stocks to processes for the recovery of straight chain hydrocarbons, it is a common occurrence that an excess of such paraffinic raffinates are available. Such excess paraffinic raffinates must be disposed of. One method is to blend these raffinates into the refinery gasoline pool. However, such raffinates have extremely low octane values and their addition to the gasoline pool lowers the octane rating of the pool. Consequently, the requirement for octane improvers, such as tetraethyl lead, for increasing the octane of the gasoline pool to a marketable value is substantially increased. Recently, with the advent of zeolitic fluid catalytic cracking catalyst, it is now possible to dispose of paraffinic raffinate by cracking in a fluid catalytic cracker to yield a high octane light naphtha fraction and a C_3–C_4 hydrocarbon fraction rich in olefins. The light naphtha fraction may be combined into the refinery gasoline pool and the C_3–C_4 hydrocarbon fraction may be utilized as charge stock to an alkylation reaction wherein the olefins are reacted with isoparaffins to yield a high octane alkylate product. However, when such raffinates are subjected to fluid catalytic cracking, the C_3–C_4 hydrocarbon fraction recovered therefrom contains insufficient isoparaffin hydrocarbon components to provide an alkylation charge stream containing a stoichiometric balance of isoparaffin and olefin hydrocarbons. Therefore, an excess amount of C_3–C_4 olefins suitable for alkylation feed may be produced without a concomitant production of isoparaffins. When such an excess production of olefins occurs, the ratio of olefin to isoparaffin hydrocarbon reactants charged to the alkylation reaction may become unbalanced, and without the acquisition of additional isoparaffin hydrocarbon from an external source the available olefin hydrocarbons cannot be converted into high octane alkylate.

SUMMARY OF THE INVENTION

Now, in accordance with the method of the present invention, a paraffinic raffinate recovered from a solvent extraction process and boiling in the gasoline range may be converted into a light naphtha having a high octane and into a C_3–C_4 hydrocarbon fraction comprising olefins and isoparaffins in a stoichiometric ratio suitable for charge to an alkylation reaction. A portion of the raffinate is hydrocracked to yield a light naphtha fraction boiling in the range of C_5 to 250°F. having a research clear octane rating of about 73, and into a C_4 hydrocarbon fraction rich in isobutane. The remainder of the raffinate is fluid catalytically cracked to yield a light naphtha fraction boiling in the range of C_5 to 250°F. having a research clear octane rating of about 60, and a C_3–C_4 fraction rich in olefin hydrocarbons. The ratio of isoparaffin to olefin hydrocarbons is controlled by adjusting the proportions of raffinate charged to the hydrocracking reaction and to the fluid catalytic cracking reaction.

One advantage to the method of the present invention is that the raffinate hydrocarbon, having an extremely low octane rating, is removed from the refinery gasoline pool. Removal of the raffinate increases the octane rating of the refinery pool and decreases the amount of octane improvers, such as tetraethyl lead, required to bring the refinery gasoline pool octane to a marketable level. Another advantage is that a substantial portion of the raffinate is converted to a high octane light naphtha suitable for addition to the refinery gasoline pool. A third advantage is that a substantial portion of the raffinate is converted into C_3–C_4 olefins and into isobutane which may be employed as reactants in an alkylation process to produce a high octane alkylate suitable for blending into the refinery gasoline pool. By adjusting the proportions of the raffinate charge to the hydrocracking process and to the fluid catalytic cracking process, the ratio of C_3–C_4 olefins to isobutane may be controlled to provide the proper ratio of olefin and isoparaffin reactants in an alkylation process. These and other advantages of the present invention will be more completely described in the detailed disclosure which follows.

BRIEF DESCRIPTION OF THE DRAWING

The attached drawing shows in schematic diagram one method for carrying out the process of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The raffinate hydrocarbons contemplated for use in the present invention include the non-aromatic raffinates from solvent extraction processes. Preferably the raffinate hydrocarbons are in the gasoline boiling range of from about 100°F. to 400°F.

Examples of solvent extraction processes yielding raffinate hydrocarbons suitable for use in the present invention include those processes in which a solvent selective for the absorption of aromatic hydrocarbon is employed. A hydrocarbon mixture, such as a catalytic

reformer effluent, containing both paraffinic and aromatic hydrocarbons is contacted with a solvent selective for the absorption of aromatic hydrocarbons in a contacting zone. The aromatic hydrocarbons dissolve into the solvent phase and the non-aromatic hydrocarbons separate into a raffinate phase. The raffinate phase is separated from the solvent phase by liquid-liquid separation techniques and the aromatic hydrocarbons are recovered from the solvent by such means as vaporization. Many solvents selective for the absorption of aromatic hydrocarbons from hydrocarbon mixtures are known. Examples of such selective solvents include sulfolane, diethylene glycol, and triethylene glycol. Such solvent extraction processes are well known in the prior art and need not be further described herein.

The raffinate phase recovered from the solvent extraction process comprises a high proportion of paraffinic hydrocarbons. Such raffinate phase has an extremely low octane rating. As an example, a catalytic reformer effluent boiling in the range of from about 264°F. to 338°F. was extracted with triethylene glycol to remove the aromatic hydrocarbons therefrom. The raffinate phase from the solvent extraction process comprising primarily paraffinic hydrocarbons boiling in the range of 264°F. to 338°F. had a clear research octane rating of 17.0. Such a raffinate phase is unsuitable for blending with the refinery gasoline pool as it reduces the octane rating of the entire pool. However, in the past it has often been necessary to blend such raffinate streams into the refinery gasoline pool in order to dispose of them.

According to the present invention, such a raffinate stream is divided into two portions. The first portion is hydrocracked and the second portion is fluid catalytically cracked.

In the hydrocracking reaction the raffinate is converted into a light hydrocarbon fraction, a C_4 hydrocarbon fraction, a light naphtha fraction boiling in the range of from about C_5 to about 250°F. and a heavy naphtha fraction boiling in the range of from about 250°F. to about 400°F. The boiling range of the heavy naphtha fraction will be affected by the boiling range of the raffinate stream subjected to hydrocracking. The C_4 hydrocarbon fraction recovered from the hydrocracking reaction is rich in isobutane and is substantially free of olefin hydrocarbons. Such a C_4 fraction is particularly suitable as isoparaffin charge stock to an alkylation reaction wherein C_3–C_4 olefins are alkylated with isobutane. The light naphtha fraction has a clear research octane rating of about 73 and is suitable for blending into the refinery gasoline pool. The hydrocracked heavy naphtha fraction has a clear research octane rating of only about 19. Although such hydrocracked heavy naphtha fraction may be blended into the refinery gasoline pool, it is preferable to subject such hydrocracked heavy naphtha fraction to additional treatment to improve its octane rating. The hydrocracked heavy naphtha fraction may be catalytically reformed and the reformates subjected to solvent extraction to recover aromatics therefrom and the solvent extraction raffinate may be returned to the hydrocracking and fluid catalytic cracking processes for further conversion. The hydrocracked heavy naphtha fraction may also be recycled to extinction in the hydrocracking process, thereby being converted into light naphtha, C_4 hydrocarbons, and light hydrocarbons.

The conversion of raffinate in the hydrocracking reaction depends upon the severity employed in the hydrocracking reaction. At increasing severities, the proportion of raffinate converted into lighter products increases. The raffinate may be charged to the hydrocracking process along with other hydrocracking charge stocks and the hydrocracking severities may be adjusted through a range in order to yield, overall, the highest proportion of desirable products. However, for simplicity, a hydrocracking reaction will be described herein as though only raffinate was being charged thereto. The presence of other charge stocks in the hydrocracking reaction will not substantially affect the conversion of raffinate provided the reaction conditions are maintained within the desired range.

The hydrocracking reaction may take place in one or a plurality of reaction zones and it may be preceded or followed by hydrotreating reactions for removal of contaminants such as sulfur, nitrogen and metals from the charge stock. Such hydrotreating reactions to remove contaminants are generally carried out under milder conditions than those employed in the hydrocracking reaction and the conversion of hydrocarbons into lower boiling fractions is generally very small. Therefore such hydrotreating processes, although they may be present in the process configuration, do not substantially affect the conversion of raffinate to desirable products and further discussion of such processes is not necessary herein.

In the hydrocracking reaction, the temperature is generally maintained between 600°F. and 850°F. and a pressure in the range of about 200 to 10,000 psig is employed. The liquid hourly space velocity is between about 0.2 and 10 volumes of oil per volume of catalyst per hour, and the hydrogen rate is between about 1,000 and 50,000 standard cubic feet of hydrogen per barrel of hydrocarbon charge. Preferably the pressure is between about 500 psig and 3,000 psig, the space velocity is between about 0.5 to 2 and the hydrogen rate is from about 3,000 to about 15,000 standard cubic feet per barrel. The preferred temperature range will vary somewhat with the type of catalyst employed; however temperatures in the range of from about 625°F. to about 750°F. may be used advantageously.

The hydrocracking zone catalyst may be any conventional hydrocracking catalyst which under the conditions in the hydrocracking zone will hydrocrack the raffinate to yield a light naphtha fraction boiling in the range from C_5 to 250°F. and a butane fraction comprising a substantial portion of isobutane. Such hydrocracking catalysts comprise a hydrogenation component and a cracking component.

Suitable hydrogenation components may be selected from Group VIII metals, their compounds, and mixtures thereof. Additionally, suitable hydrogenation components may be selected from Group XIII metals, their compounds, and mixtures thereof in combination with Group VI metals, their compounds and mixtures thereof. Metals of Group VIII of the periodic table and compounds thereof which are useful as hydrogenation components include nickel, cobalt, platinum, palladium, and compounds thereof. Metals of Group VI of the periodic table and compounds thereof which are suitable hydrogenation components include molybdenum, tungsten, chromium, and compounds thereof.

The cracking component of the hydrocracking catalyst is preferably a solid, acidic component having high

cracking activity. Suitable cracking components include silica-alumina, silica-alumina-zirconia, silica-alumina-titania, acid treated clays and zeolitic molecular sieves. An effective cracking component comprises a mixture of a modified crystalline silica-alumina zeolite and at least one amorphous inorganic oxide, with the modified zeolite being present in an amount between about 15 and 60 percent by weight of the cracking component. Suitable amorphous inorganic oxides are those having cracking activity such as silica, alumina, magnesia, zirconia, titania and beryllia which may have been treated with an acidic agent such as hydrochloric acid to impart cracking activity thereto. The modified zeolite portions of the cracking catalyst may be of the X or Y type having uniform pore openings of from about 4 to 14 angstroms and having a silica-alumina ratio of from about 2.5 to 10. Preferably the modified zeolite is in the hydrogen form or a divalent metal form with the major portion of monovalent metal cations removed therefrom by ion exchange. Monovalent metal cations such as sodium, may be present in the modified zeolite in amounts up to about 4 percent, however, the monovalent metal cation concentration is preferably below about 1 percent.

Hydrocracking catalysts comprise a hydrogenating component supported on a cracking component. The hydrogenation component may be combined with the cracking component by methods well known in the art such as by impregnation, cogellation, or combination of these procedures. When the hydrogenation component of the hydrocracking catalyst is a noble metal, such as platinum and palladium, it should be present in an amount between about 0.2 and 5.0 percent by weight based on the total catalyst composite. Preferably the noble metal is present in an amount between 0.5 and 2 percent. When the hydrogenation component comprises other members of Group VIII such as nickel, and cobalt in conjunction with Group VI metals, the Group VIII metals should be present in an amount between about 2 and 10 percent and the Group VI metals present in an amount between about 5 and 30 percent by weight of the total catalyst composite.

A specific hydrocracking catalyst suitable for use in this process is one containing about 0.75 weight percent palladium upon a support made up of about 22 percent modified zeolite Y, 58 percent silica and 20 percent alumina. Another suitable hydrocracking catalyst is one containing about 6 percent nickel and 20 percent tungsten on a support made up of about 22 percent modified zeolite Y, 58 percent silica and 20 percent alumina. When used in a sulfide form, the catalyst may be converted thereto by methods well known in the art such as by subjecting the catalyst at a temperature between about 400°F. and 600°F. to contact with a sulfiding agent, for example, hydrogen containing 10–20 percent hydrogen sulfide or a carbon disulfide-oil mixture.

The ratio of hydrogen to raffinate in the hydrocracking zone may be between 1,000 and 50,000 standard cubic feet of hydrogen per barrel of raffinate. Preferably, the hydrogen to hydrocarbon ratio is in the range of about 3,000 to 15,000 cubic feet per barrel. The hydrogen used in the hydrocracking process need not necessarily be pure. The hydrogen content of the hydrogenation gas should be at least about 60 percent and preferably 75 percent by volume. Hydrogen available from normal refinery sources, such as catalytic reformer by-product hydrogen, is suitable for use in this hydrocracking process.

The remaining portion of the raffinate stream is charged to a fluid catalytic cracking reaction under conditions to yield a fluid cracked light naphtha fraction boiling in the range of C_5 to 250°F. and a C_3–C_4 stream rich in propylene and butylenes. The raffinate may be charged to the fluid catalytic cracking reaction zone alone or in combination with other fluid catalytic cracking charge stocks. It is necessary only that the cracking conditions be of a severity sufficient to crack the raffinate charge stock of this invention into the desired product. Fluid catalytic cracking processes are well known in the prior art and a detailed description of the process configurations is not necessary herein.

Catalyst suitable for use in the fluid catalytic cracking process are solid, acidic, cracking catalysts having a high activity for cracking higher molecular weight hydrocarbons into lower molecular weight hydrocarbons.

A cracking catalyst particularly useful for converting naphtha hydrocarbons comprises an active metal oxide, as exemplified by a silica-alumina gel and clay, and a large pore crystalline alumino-silicate customarily referred to as zeolite. The zeolite employed as cracking catalyst herein possesses ordered rigid three-dimensional structure having uniform pore diameter within the range of from about 5 to about 15 angstroms. Such cracking catalyst may comprise from about 1 to 25 weight percent zeolite, about 10 to 50 weight percent alumina and the remainder silica. In general, the zeolite catalyst which forms the high activity component of the catalyst is an alkali metal crystalline alumino-silicate which has been treated to replace all or at least a substantial portion of the original alkali metal ions with other cations such as hydrogen and/or a metal or combination of metals, such as barium, calcium, magnesium, manganese, or rare earth metals such as cerium, lanthanum, neodymium, praseodymium, samarium and yttrium. The zeolites contemplated above may be represented by the formula:

$$M_{2/n}O:Al_2O_3:xSiO_2:yH_2O$$

where M represents hydrogen or a metal, n its valence, x has a value ranging from 2 to 10 and y ranges from 0 to 10. The preferred fresh zeolite is represented by zeolite X and zeolite Y where M is selected from the group consisting of hydrogen, calcium, manganese and rare earth metals, and where the zeolite content of the fresh catalyst varies from about 5 to 20 weight percent. Preferably, the equilibrium catalyst, consisting of fresh and regenerated catalyst, in the fluid cracking zone contains less than about 5 weight percent zeolite. The carbon deposited upon such equilibrium catalyst is preferably less than about 0.3 weight percent of the catalyst.

Conditions within the fluid catalytic cracking reaction zone must be maintained such that the raffinate will crack into the desired products. Temperatures in the range of from about 920°F. to 1,050°F. may be employed. Catalyst to oil weight ratios in the range of from about 5 to 1 to about 15 to 1 may be employed and are commonly adjusted, along with charge stock preheat temperature, to control the reaction zone temperature. Weight hourly space velocity, defined as pounds of oil per hour per pound of catalyst, in the range of from about 10 to about 100 are suitable for use in the present invention.

In the fluid catalytic cracking reaction it has been found that the yield of desirable products including light naphtha and C_3–C_4 range hydrocarbons may be improved by employing a relatively short period of good contact between the raffinate and the cracking catalyst. One reaction zone configuration which promotes the desirable contact between the hydrocarbon and the catalyst comprises a reaction vessel located adjacent to and above a regeneration zone and a riser conduit. The hydrocarbon charge enters near the bottom of the riser conduit and hot regenerated catalyst is admitted near the bottom of the riser wherein the hydrocarbon and catalyst mix. The vaporized hydrocarbon and catalyst flow upward through the riser conduit and discharge into the reaction vessel wherein the hydrocarbon disengages the catalyst. Catalyst is withdrawn from the bottom of the reaction vessel and passes into a regeneration zone wherein coke is burned from the catalyst with air. From the regeneration zone, the regenerated catalyst is returned to the riser conduit for contact with additional hydrocarbon charge stock. In the reaction vessel, the hydrocarbon vapor separated from the catalyst is recovered overhead and passed into a separation zone wherein the hydrocarbon vapor is separated into the desirable components. In such a reaction zone configuration, one or a plurality of riser conduits may be employed. For example, in co-pending application Ser. No. 183,905 filed Sept. 27, 1971, a fluid catalytic cracking process is described employing two riser conduits, one for fresh gas-oil feed and one for heavy recycle gas-oil. By means of employing a plurality of riser conduits, reaction conditions may be adjusted for each charge to the reaction zone to provide the most efficient cracking conditions. In this type of reaction zone configuration, the raffinate may be charged into a riser conduit along with other charge stocks to the fluid catalytic cracking process or it may be charged into a separate riser conduit. It is only necessary that the reaction conditions with the riser be maintained such that the raffinate will be cracked into the desired products.

When the reaction zone configuration employing a riser conduit or a plurality of riser conduits is employed, operating conditions suitable for cracking the raffinate include a temperature in the riser of from about 900°F. to about 1,050°F. and a catalyst to oil weight ratio in the range of from about 5/1 to about 15/1. The residence time of the raffinate in the riser may be from about 2 seconds to about 6 seconds and the average velocity, which must be sufficient to lift the catalyst through the riser, may be from about 15 feet per second to about 60 feet per second. The raffinate vapor and catalyst discharge from the riser into the reaction vessel wherein the vapor disengages the catalyst. Additional contact between the catalyst and vapor may be maintained in the reaction vessel. Suitable operating conditions within the reaction vessel include temperatures in the range of from about 920°F. to about 1,080°F., vapor velocities in the range of from about 1 foot per second to about 3 feet per second, and weight hourly space velocities of from about 2 to about 100 pounds of oil per hour per pound of catalyst. The cracked hydrocarbon vapor recovered from the reaction zone is separated into product fractions including a light naphtha fraction boiling in the range of C_5 to 250°F. and a C_3–C_4 fraction which is rich in propylene and butylene.

According to the method of the present invention the raffinate stream is split, with a portion being hydrocracked and a portion being fluid catalytically cracked. Light naphtha fractions boiling in the range of from about C_5 to 250°F. and having high octanes suitable for blending with a refinery gasoline pool are produced from both the hydrocracking reaction and a fluid catalytic cracking reaction. From the hydrocracking reaction a C_4 stream rich in isobutane is obtained and from the fluid catalytic cracking reaction a C_3–C_4 stream rich in propylene and butylene is obtained. These streams are suitable charge stocks to an alkylation reaction wherein the isobutane is alkylated with the propylene and butylene to yield a high octane alkylate suitable for use as a gasoline product. By adjusting the severity of operations in the hydrocracking reaction and in the fluid catalytic cracking reaction and by adjusting the proportion of raffinate charged to each of the reactions, the yield of isobutane from the hydrocracking reaction and the yield of propylene, butylene, and isobutane from the fluid catalytic cracking reaction may be balanced such that the isobutane, propylene, and butylene charged to the alkylation reaction are in stoichiometric balance.

The alkylation reaction contemplated in the present invention may be any alkylation reaction suitable for the alkylation of isobutane with propylene and butylenes, such as, for example, sulfuric acid alkylation and hydrofluoric acid alkylation. Such alkylation processes are well known in the prior art and need not be described in further detail herein.

In the hydrocracking reaction, the desired products are a light naphtha fraction and a C_4 fraction and in a fluid catalytic cracking process reaction the desired products are a light naphtha fraction and a C_3–C_4 fraction. However, in both cracking reactions in addition to the desired products, part of the raffinate is cracked into hydrocarbons boiling lower than the desired products and part of the raffinate is recovered as heavy naphtha boiling higher than the desired light naphtha. The heavy naphtha streams recovered both from the hydrocracking reaction and from the fluid catalytic cracking reaction, although boiling in the gasoline range, have a low octane rating and are undesirable for blending into the refinery gasoline pool. Therefore, it is within the contemplation of the present invention that such heavy naphtha streams be converted into the desired light naphthas, isobutane, propylene, and butylenes.

The heavy naphtha from the hydrocracking process boiling from about 250°F. to about the endpoint of the raffinate, may be recycled to the hydrocracking reaction zone for conversion into light naphtha and isobutane. Alternatively, the hydrocracked heavy naphtha may be charged to a catalytic reforming unit wherein cyclic paraffins are converted into aromatic hydrocarbons.

In the fluid catalytic cracking process the heavy naphtha fraction boiling from about 250°F. to about the end-point of the raffinate may be recycled to extinction in the fluid catalytic cracking reaction zone or, alternatively, may be charged to a catalytic reforming zone. Where one or more of the heavy naphtha streams from the hydrocracking process or from the fluid catalytic cracking process is returned to a catalytic reforming process, it is desirable that the reformer effluent be solvent extracted for the recovery of aromatics and that

the paraffinic raffinate from the solvent extraction step be employed as raffinate charge in the process of the present invention.

The method of the present invention may be better understood by reference to the appended drawing which is a schematic illustration of a group of interrelated process zones and flow paths suitable for use in practicing the present invention. For purposes of clarity, various pieces of conventional equipment such as heaters, pumps, instrumentation, valves, etc., have been omitted from the drawing. Such conventional equipment and its location and use will be readily apparent to those skilled in the art. The appended drawing and the detailed description which follows is intended to illustrate the present invention only and is not to be interpreted as a limitation on the scope of the present invention which is set out in the appended claims.

Referring now to the drawing, a hydrocarbon stream comprising aromatic hydrocarbons and paraffinic hydrocarbons boiling in the range of from about C_5 to about 450°F. and preferably in the range of from about 200°F. to about 400°F. is charged via line **1** into a solvent extraction zone **2** wherein the aromatic hydrocarbons are separated from the non-aromatic hydrocarbons. From solvent extraction zone **2** the aromatic hydrocarbons, suitable for use as chemicals or as blend stocks in a refinery gasoline pool are removed via line **3**. A raffinate stream comprising paraffinic hydrocarbons and containing less than about **5** percent aromatic hydrocarbons is removed from the solvent extraction zone **2** via line **4**. From line **4** a first portion of the raffinate stream passes via line **5** into hydrocracking zone **6** and a second portion of the raffinate stream passes via line **7** into fluid catalytic cracking zone **8**.

In the hydrocracking zone **6** the first raffinate portion is hydrocracked at a temperature of about 700°F., a pressure of about 1,500 psig, a liquid hourly space velocity of about 1.0 in the presence of about 7,000 standard cubic feet of hydrogen per barrel of raffinate. The hydrocracking reaction takes place in the presence of a hydrocracking catalyst comprising about 6 weight percent nickel and 20 weight percent tungsten, in their sulfide form, supported upon a base made up of about 22 weight percent modified zeolite Y, 58 percent silica and 20 percent alumina. Fresh hydrogen is supplied to the hydrocracking zone **6** via line **9**. From the hydrocracking zone **6**, a light hydrocarbon stream comprising hydrogen and methane through propane is vented via line **30**. A butane stream comprising about 67.2 percent isobutane and substantially free of butylene, and equivalent to about 6.4 percent of the first raffinate portion charged to the hydrocracking zone **6** is recovered via line **10** and passed as reactant charge to an alkylation zone **11**. A hydrocracked light naphtha fraction boiling in the range of C_5 to 250°F., representing about **17.6** percent of the first raffinate charge is recovered from the hydrocracking zone **6** and passed via line **12** to the refinery gasoline pool, not shown. A hydrocracked heavy naphtha fraction boiling above 250°F., representing about 70 percent of the first raffinate portion, is recovered from the hydrocracking zone **6** and passed via line **13** to a catalytic reforming zone **14**. Alternatively, the hydrocracked heavy naphtha fraction may be recycled to extinction within the hydrocracking zone **6** via line **15**. Also, fresh feed, such as gas-oil, in addition to the raffinate of the present invention may be charged to the hydrocracking zone **6** via line **16**. In such case where the hydrocracked heavy naphtha fraction is recycled or where the fresh feed in addition to the raffinate is charged to the hydrocracking zone the volume of light naphtha produced and butane produced will be increased. In the case where a gas-oil feed is supplied to the hydrocracking zone **6**, a distillate hydrocarbon stream boiling in the kerosine boiling range may be recovered from the hydrocracking zone **6** via line **17** and passed to storage, not shown.

In the fluid catalytic cracking zone **8** the second raffinate portion from line **7** is cracked in the presence of a synthetic cracking catalyst under cracking conditions including a reaction zone temperature of about 920°F., at a catalyst to oil weight ratio of about 5.6 to 1, a vapor velocity of about 40 feet per second in the fresh feed riser conduit, and a weight hourly space velocity of about 69.5 pounds of oil per hour per pound of catalyst in the riser conduit. In the reaction vessel, the cracked hydrocarbon vapors disengage from the catalyst and are subsequently separated into component fractions.

From the fluid catalytic cracking zone **8**, a dry gas stream comprising hydrogen through C_2 hydrocarbons is vented via line **18**. Such dry gas stream is equivalent to about **1.6** weight percent of the raffinate portion charged to the fluid catalytic cracking zone. A C_3–C_4 range fraction is recovered from the fluid catalytic cracking zone **8** via line **19** and is passed to the alkylation zone **11**. The C_3–C_4 range stream is equivalent to about 21.5 weight percent of the second raffinate portion and comprises propylene, butylene, and isobutane. The mole ratio of isobutane to olefins in the C_3–C_4 stream is lower than the stoichiometric requirements of a charge stock to the alkylation zone. However, the isobutane content of the C_4 stream recovered via line **10** from hydrocracking zone **6** is sufficient to provide the additional isobutane necessary for a stoichiometric balance of isobutane to olefins in alkylation zone **11**. In alkylation zone **11** the isobutane contained in the C_4 stream from the hydrocracking zone and in the C_3–C_4 stream from the fluid catalytic cracking zone **8** is reacted in the presence of sulfuric acid alkylation catalysts of about 93 percent concentration, at a temperature of about 46°F. From the alkylation zone **11**, an alkylated hydrocarbon product comprising C_7–C_8 hydrocarbons is recovered via line **20** in an amount equivalent to about 11.8 volume percent of the raffinate stream recovered from the solvent extraction zone **2**. Such alkylated hydrocarbons have a high octane rating and are passed via line **20** to the refinery gasoline pool.

A light naphtha fraction boiling in the range of C_5 to 250°F. equivalent to about 20.3 weight percent of the second raffinate portion is recovered from the fluid catalytic cracking zone **8** via line **21**. Such cracked light naphtha fraction has a high octane rating and is a suitable gasoline component. The cracked light naphtha fraction is passed via line **21** to the refinery gasoline pool.

A cracked heavy naphtha fraction equivalent to about **55** weight percent of the second raffinate portion is recovered from the fluid cracking zone **8** via line **22**. Such cracked heavy naphtha has a relatively low octane rating and is unsuitable for blending with the refinery gasoline pool. The cracked heavy naphtha fraction is passed via line **22** into a catalytic reforming zone **14**.

In the catalytic reforming zone **14** the hydrocracked heavy naphtha fraction from line **13** and the cracked heavy naphtha fraction from line **22** is reacted in the presence of a reforming catalyst comprising about 0.3 percent platinum and about 0.6 percent chlorine on an alumina base, at a temperature of about 920°F. to convert a major portion of the naphthene hydrocarbons contained in the heavy naphtha streams into aromatic hydrocarbons. From the catalytic reforming zone **14** a hydrogen stream is recovered via line **23** for use in refinery processes requiring hydrogen, such as the hydrocracking zone **6.** A light hydrocarbon stream comprising C_1 through C_4 hydrocarbons is recovered from the catalytic reforming zone **14** via line **24** and is passed to further processing, not shown. A gasoline range fraction comprising aromatic hydrocarbons and paraffinic hydrocarbons is recovered from the catalytic reforming zone **14** via line **1** and is passed to the solvent extraction unit **2** as hereinabove described. In order to provide sufficient raffinate to continue the process of the present invention, a reformer charge stock comprising naphthenic and paraffinic hydrocarbons is charged as fresh feed to the catalytic reforming zone **14** via line **25.**

By circulating the hydrocracked heavy naphtha fraction and fluid cracked heavy naphtha fraction to the catalytic reforming zone **14,** a substantial portion of the naphthene hydrocarbon content of these cracked heavy naphthas is converted to aromatic hydrocarbons. Such aromatic hydrocarbons are subsequently recovered in the solvent extraction zone **2** and the nonaromatic hydrocarbons are recycled to extinction as components of the solvent extraction zone raffinate stream which is charged to hydrocracking zone **6** and fluid catalytic cracking zone **8.** The recycled components of the heavy naphtha streams are cracked in hydrocracking zone **6** and fluid catalytic cracking zone **8** into the desired lower boiling C_3–C_4 fractions and light naphtha fractions.

In the fluid catalytic cracking zone **8,** an alternate to circulating the cracked heavy naphtha fraction to the catalytic reforming zone **14** is to recycle such cracked heavy naphtha to extinction within the fluid catalytic cracking zone via line **26.** When the cracked heavy naphtha fraction is recycled in this manner, the yield of cracked light naphtha and C_3–C_4 hydrocarbons, based upon the second raffinate portion increases over the yields of such products as described above.

In fluid catalytic cracking zone **8** it may be desirable to charge a fresh feed gas-oil as well as the second portion of the raffinate. In such case, gas-oil is charged via line **27** to fluid catalytic cracking zone **8** and a light cycle gas-oil product suitable for furnace oil is recovered via line **28.** Additionally, a residual stream suitable for fuel oil is recovered from the fluid catalytic cracking zone **8** via line **29.**

By following the process as described hereinabove, a raffinate stream having an extremely low octane rating is converted into light naphtha fractions boiling in the C_5 to 250°F. range and into alkylated hydrocarbons having high octane ratings suitable for blending into a refinery gasoline pool. Advantages of this process include removing raffinate having an extremely low octane rating from the refinery gasoline pool, and adding high octane light naphthas and alkylated hydrocarbons to the refinery octane gasoline pool. By so doing, the octane rating of the gasoline pool is increased and the requirement for octane improvers such as tetraethyl lead is decreased.

EXAMPLE I

A solvent extraction unit raffinate is separated into two portions, the first portion being hydrocracked and the second portion being fluid catalytically cracked. The ratio of the hydrocracked portion to the fluid catalytically cracked portion is selected such that under the reaction conditions employed in this example, the yield of isobutane, propylene, and butylenes from the hydrocracking reaction and the fluid catalytic cracking reaction are in stoichiometric balance for charge to an alkylation reaction. In order to obtain the desired ratio of isobutane to propylene and butylene under the reaction conditions employed in this example, 40 percent of the raffinate is charged to the hydrocracking reaction and 60 percent is charged to the fluid catalytic cracking reaction.

In the hydrocracking reaction, the reaction conditions include a temperature of 700°F., a pressure of 1,500 psig, a liquid hourly space velocity of 1.0 volumes of raffinate per hour per volume of catalyst and a hydrogen rate of 7,000 standard cubic feet of hydrogen per barrel of raffinate. The hydrocracking catalyst employed comprises about 6 percent nickel and 20 percent tungsten, both in the sulfide form supported upon a cracking base comprising 22 weight percent hydrogen exchanged Y type silica-alumina zeolite, 58 weight percent amorphous silica, and 20 weight percent amorphous alumina.

The fluid catalytic cracking reactor employed for the catalytic cracking reaction comprises a riser conduit and a reactor vessel. Raffinate is charged into the lower end of the riser conduit and is contacted with hot regenerated synthetic mordenite zeolite cracking catalyst. Oil vapor and cracking catalyst pass upward through the riser conduit and are discharged into the reactor vessel wherein the oil vapor disengages the cracking catalyst in a fluidized bed. The reaction conditions in the riser conduit include a temperature of 920°F., a catalyst to hydrocarbon weight ratio of 5.6, a vapor velocity in the riser conduit of 40 feet per second and a residence time in the conduit of 4 seconds. In the reactor vessel, wherein the catalyst is maintained in a fluidized bed, the hydrocarbon vapors disengage the catalyst bed and are recovered overhead. Reaction conditions in the reactor vessel include a temperature of 940°F., a weight hourly space velocity of 12.8 pounds of oil per hour per pound of catalyst and a pressure of 23 psig.

The raffinate employed in the present example has the following properties:

ASTM Distillation
IBP — 264°F.
5 percent — 271
10 percent — 272
50 percent — 281
90 percent — 305
95 percent — 318
EP — 338
API gravity — 63.4°
Research Octane — Clear — 17.0
Research Octane plus 3 cc. tetraethyl lead — 55.0
Total paraffins — 86.5 weight percent
Cycle paraffins — 10.3 weight percent
Aromatics — 3.2 weight percent

Effluent from the hydrocracking zone is fractionated into a C_3 and lighter fraction, a light naphtha fraction boiling in the range of C_5 to 250°F., and a fraction boiling above 250°F.

The hydrocracked light naphtha fraction comprises about 18.6 volume percent yield based on the raffinate portion charged to the hydrocracking reaction. This hydrocracked light naphtha is a high octane gasoline blending stock, having an octane number of 90, research method, plus 3 cc. tetraethyl lead.

The hydrocracked heavy naphtha boiling above 250°F. is recovered in a yield of about 70 percent based upon raffinate charged to the hydrocracking zone. The hydrocracked heavy naphtha has a low octane rating of about 19 research clear and about 54 research method plus 3 cc. tetraethyl lead per gallon. The hydrocracked heavy naphtha is suitable for a catalytic reformer charge stock.

The C_4 fraction recovered from the hydrocracking reaction is equivalent to about 8.3 volume percent of the raffinate portion charged thereto. Isobutane comprises about 67.2 percent of the hydrocracked C_4 stream recovered. The hydrocracked C_4 stream is substantially free of butylenes and other olefins.

Effluent from the fluid catalytic cracking reaction is fractionated into a dry gas fraction comprising hydrogen through ethane, a C_3–C_4 fraction, a cracked light naphtha fraction boiling in the range C_5 to 250°F. and a heavy naphtha fraction boiling above 250°F. About 44 volume percent of the raffinate charged to the fluid catalytic cracking reaction is converted to products boiling below about 250°F. per pass to the reaction zone. About 1.6 weight percent of the raffinate is converted to coke in the reaction zone.

The C_3–C_4 cracked fraction has a volume equal to about 28.2 percent of the volume of the raffinate portion charged to the fluid catalytic cracking reaction zone. The cracked C_3–C_4 fraction comprises about 23.2 volume percent propylene, 17.0 volume percent butylene, and 35.5 volume percent isobutane. This C_3–C_4 fraction is suitable as charge stock for an alkylation process wherein isobutane is alkylated with propylene and butylenes to yield C_7–C_8 range alkylated hydrocarbons having a high octane number.

The cracked light naphtha fraction, equivalent to about 21.7 volume percent of the raffinate charged to the catalytic cracking unit is an acceptable gasoline blend stock, having an octane number of 60 research method clear, and 80 research method plus 3 cc. tetraethyl lead.

The cracked heavy naphtha fraction boiling above 250°F. is equivalent to about 55.7 volume percent of the raffinate charged to the catalytic cracking zone. This cracked heavy naphtha has a low octane number; 19 research clear and 54 research method plus 3 cc. tetraethyl lead. The cracked heavy naphtha is not suitable for gasoline blending but is suitable for a catalytic reformer charge stock.

The C_3–C_4 fraction from the fluid catalytic cracking zone and the C_4 fraction from the hydrocracking zone comprise propylenes, butylenes and isobutane. Under the reaction conditions employed in this experiment, the moles of propylene plus butylene contained in the C_3–C_4 fraction is equal to the moles of isobutane contained in the C_3–C_4 fraction and the hydrocracked C_4 fraction when about 60 percent of the raffinate is charged to the fluid catalytic cracking zone and about 40 percent of the raffinate is charged to the hydrocracking zone. The cracked C_3–C_4 fractions and the hydrocracked C_4 fraction may be combined to provide a balanced charge stock for an alkylation zone. When such C_3–C_4 fraction and C_4 fraction are combined and charged to an alkylation zone the yield of C_7–C_8 range alkylated hydrocarbons has a high octane number and is suitable for use as gasoline. The yield of alkylated hydrocarbons from the propylene, butylene, and isobutane content of the cracked C_3–C_4 fraction and the hydrocracked C_4 fraction amounts to about 11.8 volume percent of the total raffinate charged in this process.

Many variations may be made in the process of the present invention as disclosed herein without departing from the spirit and scope thereof. All such variations are intended to be included which are within the spirit and scope of the appended claims.

We claim:

1. A process for manufacturing high octane gasoline from a low octane raffinate, which comprises:
   A. Hydrocracking a first portion of the raffinate to yield a hydrocracked C_4 fraction comprising isobutane and a hydrocracked light naphtha fraction;
   B. Fluid catalytically cracking a second portion of the raffinate to yield a cracked C_3–C_4 fraction comprising propylene, butylenes and isobutane and a cracked light naphtha fraction;
   C. Recovering the hydrocracked light naphtha fraction and the cracked light naphtha fraction as gasoline blend stocks; and
   D. Charging the hydrocracked C_4 fraction and cracked C_3–C_4 fraction to an alkylation zone.

2. The process of claim 1 wherein the hydrocracked C_4 fraction and the cracked C_3–C_4 fraction charged to an alkylation process yield high octane C_7–C_8 alkylated hydrocarbons suitable for use as gasoline blend stocks.

3. The process of claim 2 wherein the ratio of raffinate charged to the hydrocracking process and raffinate charged to the fluid catalytic cracking process is maintained such that the combined hydrocracked C_4 fraction and cracked C_3–C_4 fraction contains isobutane in about an equal molar ratio to propylene and butylenes.

4. The method of claim 1 wherein the raffinate boils in the range of about C_5 to about 400°F., wherein a hydrocracked heavy naphtha fraction boiling above 250°F. is recovered from the hydrocracking reaction, and wherein a cracked heavy naphtha fraction boiling above 250°F. is recovered from the fluid catalytic cracking reaction.

5. The method of claim 4 wherein the hydrocracked heavy naphtha fraction and the cracked heavy naphtha fraction are charged as feed stock to a catalytic reforming reaction, wherein a reformed hydrocarbon fraction boiling in the range of from about C_5 to about 400°F. comprising aromatic hydrocarbons and paraffinic hydrocarbons recovered from the catalytic reforming reaction, is solvent extracted to yield a raffinate fraction comprising paraffinic hydrocarbons and an aromatic fraction, wherein the raffinate fraction is employed as charge stock to the hydrocracking and fluid catalytic cracking reactions, and wherein the aromatic hydrocarbon fraction is recovered from the solvent extraction zone.

6. The method of claim 4 wherein the hydrocracked heavy naphtha fraction is recycled to extinction within the hydrocracking reaction zone, and wherein the cracked heavy naphtha fraction is recycled to extinction within the fluid catalytic cracking reaction zone.

7. The method of claim 5 wherein fresh feed in addition to raffinate is charged to the hydrocracking zone and wherein fresh feed in addition to the raffinate is charged to the fluid catalytic cracking zone.

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