This invention relates to an improvement in processes for producing fuels for internal combustion engines. It relates more particularly to processes for the conversion of naphthas in the gasoline boiling range, including conversion of low octane number components therein to high octane number components.

It is an object of the present invention to provide a process for producing a high octane number fuel from a gasoline boiling range naphtha. It is a further object of the invention to provide processes in which fuels of improved octane number are produced from naphthas containing normal and slightly branched aliphatic hydrocarbons. It is a specific object of the invention to provide a process for producing a balanced fuel of high octane number from a straight run naphtha. Other objects of the present invention will appear from the following description thereof.

The processes according to the present invention include the step of treating a naphtha boiling in the range between 100° and 450° F. and preferably not higher than about 300° F. or 350° F. with a reactive proportion of iodine at an elevated temperature in excess of 300° C. to produce a gasoline of high octane number. In one modification the present invention is directed to a process for producing a gasoline from a gasoline boiling range naphtha by subjecting the naphtha to a first hydrocarbon conversion process in which a substantial proportion of the hydrocarbons are converted to a form having a high octane number while a substantial proportion of iodine aromatizable compounds, such as normal and slightly branched paraffins of poor octane number remain unconverted, and subjecting at least a portion of the first reaction product, containing said iodine aromatizable compounds, to treatment with a reactive proportion of iodine at an elevated temperature in excess of 300° C. to further improve its octane number by converting the normal and slightly branched paraffins to aromatic hydrocarbons. In a preferred modification said first hydrocarbon conversion process serves to condition the naphtha for the iodine conversion step by removing cycloparaffins having five carbon atoms in the ring and/or by converting aliphatics having more than 6 carbon atoms in a chain to those having less than the original number but no less than 6 carbon atoms in a chain and/or by converting paraffins to monoolefins.

The present invention is concerned with the improvement of naphthas to produce superior fuels for spark ignition internal combustion engines. In the present specification and claims the terms “fuel” and “motor fuel” refer to fuels for both automobile and aviation engines of this type, commonly referred to as “motor gasoline” and “aviation gasoline,” respectively, as well as to major blending stocks employed in such gasolines. A complete motor fuel consists mainly of normally liquid hydrocarbons having from 6 to 12 carbon atoms per molecule and boiling in the range between 100° and 450° F., but not necessarily throughout that range. Vapor pressure characteristics of such fuels are adjusted, i.e., by adding lower molecular weight hydrocarbons such as normal butane and isopentane. Other materials are added in small quantities to improve other characteristics of the fuels, e.g., tetraethyl lead to improve the anti-knock characteristics.

Four major hydrocarbon types, namely paraffins, olefins, naphthenes, and aromatics, may be present in the naphthas from which motor fuels are prepared and in the final gasoline.

It is well known that hexane and heavier normal paraffins have very low octane numbers and are therefore undesirable components of fuels. Similarly, the slightly branched paraffins, especially the monomethyl and dimethyl paraffins having six or more carbon atoms in a chain, have poor octane numbers and are not desirable fuel constituents. The octane number of paraffins improves with the degree of branching, and such compounds as 2,2,4-trimethylpentane (iso-octane) are very suitable fuel components of high octane number. The octane number of any given skeletal type of paraffin increases as the total number of carbon atoms per molecule decreases.

The octane number of aliphatic olefins is generally superior to that of paraffins having a corresponding carbon skeleton. Certain olefins, however, tend to be unstable on storage and produce gum in gasoline; olefins are, therefore, substantially excluded, for example, from aviation gasoline, but they are generally included in motor gasoline.

The naphthenes which occur to a substantial extent in the gasoline boiling range are cyclopentane, cyclohexane and their alkyl substituted derivatives. The cyclopentane derivatives generally have a higher octane number than the cyclohexane derivatives of the same number and type of alkyl substituents.

Aromatics are desirable constituents in motor fuels. They have high octane numbers and good fuel characteristics. They are desirable in aviation gasoline to provide good rich mixture ratings but are employed only in a limited concentration, in part because their heat content, i.e., available energy per unit weight, is lower than that of the other hydrocarbon types. They are desirable in motor gasoline because of their high octane numbers but are often employed in limited amounts, inter alia because it is necessary to balance the volatility and clean burning characteristics of the fuel and for other reasons. Often, however, the use of aromatic motor gasolines is limited only by aromatics availability.

The stocks to be upgraded in accordance with the present invention are naphthas boiling in the range between 100 and 450° F. The preferred naphthas contain substantially no components boiling above about 300° F., or at most, about 350° F.; i.e., the naphthas contain preferably no components heavier than C_9 or, at most, C_10 hydrocarbons. The stocks to be processed include broad boiling range naphthas covering substantially the entire range as well as narrow cuts, e.g., those including substantially only hydrocarbons of a single carbon number.

The naphthas which may be processed according to the present invention include virgin naphthas; cracked naphthas, i.e., those produced by thermal or catalytic cracking processes or by hydrocracking; and synthetic naphthas, i.e., those produced by hydrocarbon synthesis processes such as the Fischer-Tropsch hydrogenation of carbon monoxide or other processes for hydrogenation of carbon oxides.

Naphthas are generally described as paraffinic, naphthenic, and, occasionally, aromatic in accordance with the type of hydrocarbon which predominates. The chemical composition of some typical straight run gasolines is shown in Table I. The paraffin content of these
typical stocks varies from a low of 26% to a high of 75%, the naphthene content from a low of 18% to a high of 71% and the aromatics content from a low of 3% to a high of 22%. So far as is known, the paraffins occurring in these virgin naphthas invariably contain a high percent of normal and slightly branched compounds and the naphthenes are relatively evenly divided into those having 5 and 6 carbon atoms in the ring.

**TABLE I.—CHEMICAL COMPOSITION OF STRAIGHT RUN GASOLINES**

<table>
<thead>
<tr>
<th>Crude Oil</th>
<th>End Point (°F)</th>
<th>Aromatic</th>
<th>Naphthenes</th>
<th>Paraffinic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pennsylvania</td>
<td>425</td>
<td>7</td>
<td>18</td>
<td>75</td>
</tr>
<tr>
<td>Rodessa, La.</td>
<td>470</td>
<td>10</td>
<td>29</td>
<td>45</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>477</td>
<td>3</td>
<td>71</td>
<td>29</td>
</tr>
<tr>
<td>Bakers (Burnsberry)</td>
<td>304</td>
<td>10</td>
<td>69</td>
<td>40</td>
</tr>
<tr>
<td>Santa Fe Springs, Calif.</td>
<td>302</td>
<td>12</td>
<td>21</td>
<td>57</td>
</tr>
<tr>
<td>Aromatic</td>
<td>302</td>
<td>10</td>
<td>38</td>
<td>54</td>
</tr>
<tr>
<td>Midland, Texas</td>
<td>302</td>
<td>10</td>
<td>38</td>
<td>54</td>
</tr>
<tr>
<td>Matlock</td>
<td>302</td>
<td>10</td>
<td>38</td>
<td>54</td>
</tr>
</tbody>
</table>

1 From "Reces of Petroleum," vol. V, part 1, 1900, page 87.

For purposes of the present specification and claims, a "naphtha conversion process" is defined as a process in which the hydrocarbons in a naphtha are, at least in part, converted to different hydrocarbons of the same or approximately the same molecular weight. The term, therefore, excludes such processes as polymerization and alkylation of light hydrocarbons or cracking of gas oils or heavier stocks to produce gasoline.

Commercial hydrocarbon conversion processes for the improvement of naphthas generally include at least one of the following reactions:

1. Isomerization of paraffins to more highly branched paraffins.
2. Isomerization of naphthenes, in which alkylicyclopentanes are converted to cyclohexanes of the same number of carbon atoms, or vice versa.
3. Dehydrogenation of saturated hydrocarbons to the corresponding olefins.
4. Dehydrogenation of aromatic hydrocarbons to olefins.
5. Dehydrocyclization (aromatization) processes of paraffinic hydrocarbons having at least 6 carbon atoms in a straight chain to aromatic hydrocarbons.
7. Cleavage in an acyclic chain, resulting in an olefinic and paraffinic fragment, known as cracking.
8. Cleavage resulting in the removal of an alkyl substituent in an acyclic or cyclic hydrocarbon, known as dealkylation.
9. Cleavage in the presence of hydrogen, generally resulting in two paraffinic fragments, known as hydrogen-cracking.

The commercial processes available for carrying out the above reactions often involve several of the reactions simultaneously.

A great variety of commercial naphtha conversion processes are in existence. The major processes in current use are described, for example, in "Petroleum Refiner," vol. 23, No. 9, pp. 115-276 (September 1954). If a single reaction predominates greatly, the conversion process is generally named by reference to that reaction, as isomerization, hydrogenation, dehydrogenation, aromatization, or the like. Almost any conversion process for the improvement of the motor fuel qualities of a naphtha may be called "refining." The catalytic reforming processes in use today generally include several of the reactions listed above.

Many attempts have been made to provide a process for converting naphthas having substantial proportions of normal and slightly branched paraffins into motor fuels substantially devoid of such compounds. Isomerization of paraffins at relatively low temperatures, i.e., below about 200° C., has not been found practical for heptanes and heavier stocks. Isomerization at elevated temperatures, i.e., above 300° C., even when carried to the theoretical dynamic equilibrium, does not permit the conversion of more than a minor percentage of normal and slightly branched paraffins present to highly branched paraffins of good octane number.

Dehydrogenation of the paraffins to the corresponding olefins permits octane number improvement; the resultant products, however, still include some low octane number components. Besides, as pointed out above, olefins are undesirable constituents in some fuels, e.g., in aviation gasoline. Dehydrogenation processes, both thermal and catalytic, tend to involve great losses by cracking and polymerization.

Hydrocarbon type separation, e.g., solvent extraction, may be employed, but it is often difficult and expensive and it leaves the low octane stocks segregated but unconverted.

Conversion of the low octane number paraffins in the naphtha to aromatics is generally considered a desirable solution. Dehydrocyclization (aromatization) processes available to the prior art employ heterogeneous catalysts, such as certain metals or metal compounds, which may be supported on a porous solid. Chromium oxide is generally considered the best known dehydrocyclization catalyst. In some cases commercial reforming catalysts, such as molybdenum-on-alumina hydroforming catalyst and platinum-on-silica-alumina or halogen-containing platinum-on-alumina have some dehydrocyclizing activity at relatively severe reaction conditions. Aromatization of paraffins over heterogeneous catalysts is favored by high temperatures, low pressures and short contact times. Each of these conditions also favors the loss of naphtha constituents by cracking to produce light gaseous products and coke. The coke decreases the activity of the catalyst, thus requiring still more severe conditions to maintain conversion; ultimately the catalyst must be regenerated. Hydrogen is often added to suppress some extent the undesired cracking and coking reactions. However, to obtain any substantial conversion of paraffins to aromatics over heterogeneous catalysts of the prior art requires conditions that are so severe that a large amount of the naphtha constituents is lost to gas and coke.

Both in dehydrocyclizing and reforming processes the conventional way of expressing the results obtainable is in terms of a "yield-octane number" relationship. In the conversion of naphthas containing hydroaromatic naphthenes and paraffins over heterogeneous catalysts, substantial octane number improvement is obtainable without severe loss in yield up to a limit set by the amount of aromatics producible from the hydroaromatic naphthenes and the improvement obtainable by isomerization of the paraffins. In order to obtain further octane number improvement by dehydrocyclization of the normal and slightly branched paraffins of low octane number, a substantial sacrifice in yield of light gaseous products is usually required. In severe reforming, part of the octane number improvement may be obtained by aromatization of such paraffins, but a great part of the octane number improvement is due to the removal of normal paraffins from the gasoline boiling range by cracking to gaseous products and by formation of heavier material, in particular coke.

The present invention provides a novel and superior solution to the problem of converting a naphtha boiling in the gasoline boiling range, at high yield of gasoline boiling range product, into a fuel of good octane number and particularly into a balanced mixture of normal and slightly branched paraffins, aromatic hydrocarbons, and a greatly reduced concentration of normal and slightly branched paraffins having six or more carbon atoms in a chain.
According to the present invention there are provided novel and useful processes for the conversion of naphthas in the gasoline boiling range to motor fuels of improved octane number. These processes include the step of converting iodine-aromatizable hydrocarbons (as defined below) to aromatics by subjecting a naphtha containing iodine-aromatizable hydrocarbons and a reactive proportion of iodine to an elevated temperature sufficient to effect a C-to-H bond cleavage in the iodine-aromatizable molecules. Thus, according to the present invention, superior motor fuels are produced by processes including the conversion of iodine-aromatizable compounds of low octane number, especially normal and slightly branched paraffins, to compounds of high octane number, especially aromatics, in a homogeneous reaction with iodine which is highly selective at very high conversion levels. By virtue of employing the iodine reaction step according to the present invention, yield-octane number relationships of the resulting motor fuels are generally superior to those obtainable with the commercial naphtha improvement processes known to date.

It has been found that production of improved motor fuels by conversion of naphthas with iodine at an elevated temperature may be further improved by including in the process one or more of the following steps prior to the iodine conversion:  
(1) The removal of naphthenes having 5 carbon atoms in the ring;  
(2) The conversion of aliphatic hydrocarbons having more than 6 carbon atoms in a chain to aliphatics having less than the original number but no less than 6 non-quaternary carbon atoms in a chain;  
(3) The conversion of paraffins having 6 or more contiguous non-quaternary carbon atoms in a chain to the corresponding olefins.

The conditions suitable for use in the naphtha conversion processes which may be employed in conjunction with the iodine process according to the present invention are generally well known to the art. For the sake of illustration, suitable conditions are set out below. In all cases, conditions are varied within suitable ranges depending on the particular charge naphtha and catalyst employed, and are correlated to provide the particular desired results. It is known to carry out isomerization of saturated hydrocarbons at temperatures below 200° C., referred to herein as isomerization at low temperatures, and above 300° C., referred to as isomerization at elevated temperatures.

Isomerization at low temperatures is suitable for converting naphthenes having five carbon atoms in the ring to hydroaromatic naphthenes. It is, in general, not satisfactory for converting paraffins in the gasoline boiling range to more highly branched paraffins because, with known catalysts, conditions suitable for isomerization of paraffins are so severe that a great amount of degradation of the naphtha is caused. Naphthene isomerization at low temperatures is effected, e.g., by contact with acid-generating metal halide isomerization catalysts, employing a hydrogen halide activator and hydrogen, if desired. Of the acid-generating metal halide catalysts, aluminium chloride is the most efficient and is preferred. Other acid-generating metal halide catalysts such as aluminium bromide or the halides of Zr, Ta, Ga, Be, Nb, Sb, In, Sn, Cd, Co, Ti, Zn, B and Cu may also be employed, if desired in conjunction with AlCl₃ or AlBr₃.

Aluminium chloride catalyst may be employed as powdered anhydrous AlCl₃ suspended in the naphtha; or supported on an adsorptive carrier, such as alumina, in the form of a fixed catalyst bed; or in the form of a hydrocarbon complex addition compound, such as a gustavson complex.

Suitable temperatures are between −20° and 200° C. and preferably between 40° and 130° C. Suitable pressures range from 1 to 50 atmospheres or more; it is preferable, to avoid degradation, to supply a substantial hydrogen pressure on the reaction mixture, thus permitting operation at the relatively higher temperatures. The low temperature isomerization is most suitable for naphthas containing very low concentrations of olefins and aromatics since both of these compounds tend to be degraded by reaction with aluminum chloride. When some olefins or aromatics are present, the reaction temperature should be in the lower part of the range.

Isomerization of saturated hydrocarbons at an elevated temperature above 300° C. is carried out, e.g., by contact with heterogeneous catalysts containing metals or metal salts including oxides and sulfides which have hydrogen-generating activity. Nickel, palladium, cobalt, molybdenum and tungsten have been demonstrated as isomerization catalysts. Nickel salts including the phosphate, tetrafluoroborate, tungstate, chromate and molybdate are suitable. The catalyst may be supported on a porous adsorbent, such as alumina or activated carbon, but the preferred support is an acidic solid, e.g., silica-alumina composites such as cracking catalysts. It is preferable to reduce the cracking activity of the support such as by partially deactivating it, e.g., by steaming, to reduce its surface area to no more than about 80 sq. m. per gram.

The conditions under which isomerization at elevated temperatures is suitably carried out are temperatures in the range between 300° and 550° C. and preferably between 375° and 450° C. and pressures from 1 to 50 atmospheres or more, preferably in the presence of hydrogen. Hydrogen to hydrocarbon ratios of 0.5:1 and 5:1 have been found equally satisfactory.

The lower temperatures within the above range are suitable for feeds containing substantial amounts of hydrocarbons of higher molecular weights. In isomerization at elevated temperatures, alkyl cycloparaffins are not converted to a substantial extent to cyclohexanes, due to an unfavorable equilibrium, unless conditions are chosen such that the resulting cyclohexanes are further dehydrogenated to aromatic hydrocarbons, thus continually upsetting the equilibrium.

The dehydrogenation of aliphatic hydrocarbons may be carried out thermally or catalytically. In either case, the conditions required are quite severe and dehydrogenation is generally accompanied by substantial cracking.

Thermal dehydrogenation may be carried out by means of the thermal reforming process which, in effect, is a thermal cracking and polymerization operation at temperatures between 500 and 600° C. and at pressures up to 75 atmospheres, charging gasoline boiling range naphthas, sometimes in the presence of lighter hydrocarbons.

Catalytic dehydrogenation of saturated aliphatic hydrocarbons in the gasoline boiling range is carried out, e.g., at temperatures between 450 and 700° C. and pressures between 1 and 20 atmospheres, with catalysts comprising the metal, oxides or sulfides, of Cu, Cr, Mo, V, Ti, Ce, W, Fe, Co, Ni, Pt, Pd and other metals. The oxides of transition metals of groups IV, V and VI of the periodic table are generally suitable catalysts. Dehydrogenation is favored by operation at low pressures and in the absence of substantial amounts of hydrogen, but hydrogen is often added to suppress undesired reactions such as coke formation.

The dehydrogenation of hydroaromatic napthenes can be carried out quite selectively in the presence of mixed sulfides of nickel and tungsten, e.g., a catalyst containing two parts of nickel sulfide and one part of tungsten sulfide, either unsupported or on porous adsorbent. Suitable temperatures are between 450° and 500° C. at presen...
sures between 1 and 20 atmospheres. Hydroaromatic naphthenes are also readily dehydrogenated in commercial naphtha reforming processes.

The catalytic reforming processes may be divided into those employing noble metal catalysts and those employing other metals and metal compounds. The processes employing noble metal catalysts may be further classified into non-regenerative and regenerative processes. The non-regenerative operation is of necessity relatively mild and requires relatively high pressures, including a substantial hydrogen pressure.

Noble metal catalysts suitable for reforming comprise platinum or palladium on a support such as activated alumina or silica-alumina. Excess halide may be present, especially if the support is aluminum oxide. Such catalysts and the processes for employing them are described, for example, in U.S. 2,479,110 to Haensel, and in U.S. 2,550,531 to Capetta.

Reforming over a noble metal catalyst can be carried out at temperatures between 315° and 600° C., pressures between 3 and 80 atmospheres, hydrogen-to-hydrocarbon mole ratios between 1 and 20 and weight hourly space velocities between 0.5 and 10 w.w./hr. Preferred temperatures are between 460° and 510° C. Pressures for the regenerative operation are generally between 13 and 25 atmospheres and for non-regenerative operation between 25 and 50 atmospheres.

Reforming over catalysts other than noble metal catalyst includes hydroforming and other similar processes. Suitable catalysts are molybdenum oxide-on-alumina, chromium oxide-on-alumina, and the like. The compounds of group 6 metals are preferred hydroforming catalysts. Temperatures in the hydroforming and similar processes are between 425 and 540° C. and preferably between 460° and 510° C. Pressures are between 10 and 85 atmospheres and preferably between 13 and 40 atmospheres. Hydrogen-to-hydrocarbon mole ratios are between 1 and 20 and liquid hourly space velocities between 0.5 and 2 w.w./hr.

To facilitate description of the present invention, hydrocarbons are classified into three "groups" in the manner shown in Table II. Group I consists of those compounds which are "iodine-aromatizable," i.e., which are converted into aromatics by reaction with iodine at elevated temperatures in accordance with the present invention. Group II consists of compounds which are "iodine-resistant" in the presence of compounds of group I, although in the absence of group I compounds they are convertible by reaction with iodine in the manner set out. Group III is limited to aromatic hydrocarbons which are "iodine-resistant" regardless of the presence of other compounds in the mixture.

The reaction of individual hydrocarbons with iodine is described in detail in co-pending U.S. patent application Serial No. 489,301 of J. H. Raley, filed February 18, 1955, now abandoned. The dehydrocyclization of such compounds as group I-B(1) of Table II by reaction with iodine is described in co-pending U.S. patent application Serial No. 489,302 of J. H. Raley, filed February 18, 1955. Reactions of compounds such as Group II-B(1) of Table II are described in co-pending U.S. patent application Serial No. 489,303 of J. H. Raley and R. D. Mullineaux, filed February 18, 1955, now U.S. Patent 2,880,252.

TABLE II—IODINE REACTIVITY OF C₆ TO C₁₂ HYDROCARBONS

<table>
<thead>
<tr>
<th>Group</th>
<th>Iodine-aromatizable:</th>
<th>Hydroaromatic all-cyclics</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>By dehydrogenation</td>
<td>(1) Hydroaromatic all-cyclics</td>
</tr>
<tr>
<td></td>
<td>By dehydrocyclization</td>
<td>(1) Compounds containing an aliphatic chain of at least six non-quaternary carbon atoms</td>
</tr>
</tbody>
</table>

Group II—Iodine-resistant in presence of group I compounds:

A—Dehydrogenatable in absence of group I compounds—(1) Compounds having an aliphatic chain of two to five non-quaternary carbon atoms.

B—Dehydrogenatable in absence of group I compounds—(1) Compounds having an aliphatic chain of at least five, not on indenone atoms including, respectively, one or two quaternary carbon atoms, and having no chain of six non-quaternary carbon atoms.

C—Subject to coupling as predominant reaction—

(1) Aromatic having methyl nuclear substituents.

(2) Compounds having a non-dehydrogenatable 5-carbon ring.

Group III—Iodine-resistant regardless of presence of other compounds: (1) Aromatic having no ring substituents.

In the groupings set out above it must be understood that each less reactive group includes only those compounds which do not contain a more reactive arrangement.

For example, group II-C(1) includes only those methyl substituted aromatics which do not fall into group I-A(1) by virtue of being bridged in some way to a hydroaromatic naphthenic ring, nor into group I-B(2) by virtue of containing as nuclear substituents other alkyl groups capable of closing a six-carbon ring. The order of arrangement within groups, however, is not an indication of relative reactivity. Thus, a compound may fall into more than one subgroup; e.g., ethylcyclohexane belongs to group II-A(1) by virtue of its ethyl group and group II-A(2) by virtue of its dehydrogenatable 5-carbon ring.

Since the ultimate reaction products obtainable from saturated and from olefinic hydrocarbons of identical carbon skeleton structure are the same, Table II has not been subdivided to list the saturated and olefinic compounds separately. Thus, group I-A includes naphthenes and cycloolefins, group I-B(1) includes paraffinic hydrocarbons having a chain of at least six non-quaternary carbon atoms as well as olefins and diolefins of that structure, and so forth.

The reaction of hydrocarbons in the gasoline boiling range with iodine at elevated temperatures at the conditions set out in more detail below is highly selective. As long as aromatizable hydrocarbons (group I) are present in substantial concentration the reaction proceeds almost exclusively to convert these compounds to aromatics, to the substantially entire exclusion of conversion of iodine resistant compounds of group II. Thus, by charging a hydrocarbon mixture containing both group I and group II compounds with elemental iodine into a reaction zone maintained at an elevated temperature, the conversion of group I compounds to the substantially entire exclusion of conversion of group II compounds can be obtained by limiting the amount of iodine charged to no more than the stoichiometric equivalent of one atom of iodine for each atom of hydrocarbon removed from an aromatizable hydrocarbin.

The following examples illustrate the individual hydrocarbons, occurring in the gasoline boiling range, which fall into the various subdivisions on Table II. It will be noted that Table II is concerned only with those hydrocarbons having from six to twelve carbon atoms per molecule.

Group I-A(1) includes those allicyclic hydrocarbons
having six carbon atoms in the ring, e.g., cyclohexane, methylcyclohexane and poly(methylcyclohexanes) through hexamethylcyclohexane. Ethylcyclohexane, for example, is also included in group I-A(1), being convertible to ethylbenzene. Ethylbenzene, in turn, is a compound of the type of group II-A(1), having an aliphatic chain of two non-quaternary carbon atoms. This compound, though more resistant to conversion, is ethylcyclohexene or other aromatizable hydrocarbons, is further converted to styrene if iodine is present in the absence of any group I compounds in the mixture. Group I-A(1) includes other alkyl naphthenes having various alkyl substituents from methyl to hexyl, so long as the total number of carbon atoms per molecule is no more than twelve. Group I-A(1) further includes the cycloolefins and cycloolefines corresponding to the just described naphthenes, i.e., cyclohexene, cyclohexadiene, methylcyclohexene, poly(methylcyclohexenes), ethylcyclohexene and other alkyl and poly(methylocyclc)olefines and cyclohydrocarbons.

Group I-B(1) includes all normal paraffins, olefins and diolefins having from six to twelve carbon atoms, i.e. n-hexane, n-heptane, n-octane etc. through n-dodecane. It also includes branched chain paraffins having at least six non-quaternary carbon atoms in the chain, i.e., all monomethylhexanes (2-methylhexane, 3-methylhexane, all monomethylheptanes (2-, 3-, and 4-methylheptane), all the monomethyloctanes, monononyl-nane, etc. through monomethylundecanes. Group I-B(1) further includes the non-quaternary dimethyl paraffins from the octanes (2,3-dimethylhexane, 2,4-dimethylhexane, 2,5-dimethylhexane, and 3,4-dimethylhexane) through the dodecanes (2,3-dimethyldecane, 2,4-dimethyldecane, etc.). Also included in group I-B(1) are the trimethyl paraffins from the nonanes (2,3,4-trimethylheptane, 2,3,5-trimethylhexane) through the dodecanes (2,3,4-trimethyldecane, 2,3,5-trimethyldecane, etc.). Similar compounds to the above, but including longer alkyl side chains, are also included in group I-B(1). For example, the group includes ethyl substituted paraffins such as 2-ethylhexane, 2-methyl-3-ethylhexane, 3,4-dieethylhexane and similar compounds up to monomethyldecanes. Compounds with longer alkyl chains are also included, e.g. 4-n-propylheptane, 2,3-dimethyl,4-n-propyl-heptane.

In those compounds in group I-B(1) having a chain of at least 8 carbon atoms or having an alkyl substituent other than methyl, the resulting aromatic hydrocarbon may contain an alkyl chain of two to five non-quaternary carbon atoms and such product is an iodine resistant compound of group II-A(1), which will react with iodine in the absence of group I compounds in the mixture, or it is a member of group I-B(2).

The compounds of group I-B(1) have been described in terms of the aromatic hydrocarbons. The same reactions are also undergone by the olefins, including monoolefins and diolefins having the identical carbon skeletons; i.e., hexene-1, hexene-2, and hexene-3 undergo the same reaction as n-hexane, and so forth.

Group I-B(2) consists of cyclic compounds which have one or two alkyl chains capable of meeting to close a ring of six carbon atoms, producing such substances as naphthalene, can react to form naphtalene, as can ortho-methyl, n-propylbenzene. 1,2-diethylcyclopentane can react to form indane. Other such compounds are cyclics having one carbon chain of at least four carbon atoms attached to the ring carbon, e.g., n-butylbenzene, n-pentylbenzene, etc. The aliphatic chains in these compounds may be saturated or olefinic, i.e., they may be alkyl or alkenyl or alkyldienyl chains. The cyclic rings may also be unsaturated.

Group II consists of compounds which do not react with iodine as long as an appreciable proportion of group I compounds is present in the reaction mixture. This is thought to be due to the fact that the reaction products or intermediates of group II compounds are present in a reversible equilibrium with the remainder of the reaction mixture. The products or intermediates are reverible to the initial hydrocarbon by reaction with hydrogen iodide which is present in the reaction mixture. Hence, although the compounds of group II may actually be at any given moment partly reacted with iodine, there is no appreciable amount of reaction product recovered from the reactor effluent as long as group I compounds are present in appreciable amount and no more iodine is present in the original feed to the reactor than is required to convert the group I compounds. Group II, in effect, includes all those hydrocarbons which are not capable of reaction with iodine and which are not themselves aromatics of group III.

Group II-A(1) includes those compounds having aliphatic chains of two to five non-quaternary carbon atoms. It includes, among the paraffins, the monomethylnaphtalenes (2-methylpentane and 3-methylpentane) the dimethylnaphtalenes (2,3- and 2,4-dimethylpentane), 3-ethylpentane, 2,6-ethylpentane and 2,3,4-trimethylbutane. Group II-A(1) further includes cyclic hydrocarbons having alkyl chain substituents, i.e., ethylbenzene, propylbenzene, ethylmethylbenzenes, diethylbenzenes except ortho-diethylbenzene, etc., as well as the similarly substituted non-hydroaromatic naphthenes, e.g., cyclopropyl-cyclopentane, propylcyclopentane, etc., as long as the substituent groups are not capable of closing a ring of six carbon atoms. Unsaturated compounds corresponding to the above saturated ones are also included.

Group II-A(2) includes all compounds having a dehydrogenatable five carbon atom ring, as long as the ring does not contain such substituents as would make them fall into a more reactive group. The group includes cyclopentane, methylcyclopentane and polymethylcyclopentanes, and corresponding cycloentanes. In the absence of compounds of group I, these compounds are converted by reaction with iodine to the corresponding more unsaturated compounds, i.e. monoolefins and diolefins. Cycloolefins are not further dehydrogenatable in an orderly reaction. They are subject to further reaction to form carbonaceous material under reaction conditions including prolonged residence times at the higher temperatures in the ranges set out hereinafter.

Group II-B(1) is limited to those compounds having an aliphatic chain of at least five carbon atoms including one quaternary, or at least four carbon atoms including two quaternary carbon atoms. Such compounds are 2,2-dimethylpentane, 3,3-dimethylpentane, 2,2,3-trimethylpentane and 2,2,3,3-tetramethylbutane. This subgroup also includes compounds having longer carbon chains, e.g., 5,5-dimethylhexane which contains a chain of five carbon atoms including a quaternary carbon atom and which does not have a chain of six non-quaternary carbon atoms. Compounds of group II-B(1), in the absence of iodine aromatizable hydrocarbons, are convertible to the corresponding isomers in which one of the methyl substituents has been moved from the quaternary to a non-quaternary carbon atom. These compounds, in turn, react in accordance with their new structure.

Group II-C(1) consists of aromatics having methyl substituted substituents, e.g., toluene, ortho-, meta- and para-xylene, and the tri-, tetra-, penta- and hexamethylbenzenes. Compounds containing other alkyl substituents,
Compounds of this subgroup are convertible to bicyclic compounds, e.g., toluene yields dibenzyl and/or stilbene, and so forth.

Group III consists of aromatics without substituent groups. These aromatics, i.e., benzene and naphthalene, are substantially completely unreactive with iodine under any of the reaction conditions of the iodine step of the present invention.

Although the reaction of hydrocarbons with iodine is highly selective, differences are observed between various hydrocarbons, both in rate of reaction and selectively to a particular compound.

Thus, olefins of group I are converted to aromatics more rapidly than the corresponding paraffins, often by a factor of 10 or more, when reacted under otherwise identical conditions. For this reason, subjecting a naphtha to a first dehydrogenation process in which olefins are produced from corresponding saturated hydrocarbons not only permits a saving in the amount of iodine required for removal of hydrogen in the subsequent iodine step but also permits carrying out the iodine reaction with a shorter residence time. This has the advantage that it requires less reaction space and also cuts down the time available for undesired side reactions.

It has also been found that the ideal length of the open chain of contiguous non-quaternary carbon atoms of aliphatic Group I-B(1) for conversion to aromatics is from 6 to 7 carbon atoms. When longer chains are aromatized the product contains not only the aromatic of the same number of carbon atoms but also appreciable amounts of lower aromatics, formed by splitting off of short fragments. This involves an undesirable loss of gasoline boiling range material to gas. For this reason, a greater ultimate yield of gasoline is obtainable from a naphtha containing aliphatic with chains of 8 or more carbon atoms by subjecting it, prior to the iodine reaction, to an isomerization step in which the carbon chain lengths are reduced and the degree of branching increased.

It has also been observed that, when compounds having a 5-carbon atom ring (e.g. group II-A(2)) are reacted with iodine in the absence of iodine- aromatizable compounds they not only undergo dehydrogenation to form cycloolefins and cycloolefin, but they tend to form coke to a much greater extent than other hydrocarbons. Hence, at least in those cases where it is desired to react a naphtha containing 5-carbon ring naphthenes with more than the amount of iodine stoichiometrically required to convert iodine-aromatizable compounds, it is advantageous to remove such 5-carbon ring naphthenes when less than the stoichiometric equivalent amount of iodine, based on aromatizable compounds, is to be employed, because some coke formation can occur even under these conditions.

The above classification and description of the iodine reactivity of hydrocarbons includes numerous compounds which are ordinarily found to a very limited extent or not at all in gasoline boiling range naphthas. For example, straight run naphthas usually contain substantial no olefins. Also, highly branched paraffins, e.g. trimethylpentanes, tetramethylpentanes, etc., generally encountered only in trace amounts or not at all. The above classifications and description, however, permits ready determination of whether any particular compound is or is not iodine-aromatizable and whether it is or is not iodine reactive in the absence of iodine-aromatizable compounds. With this information and with an analysis of the naphtha to be converted in the iodine step one can readily determine the stoichiometric amount of iodine required for the conversion of the aromatizable compounds and also whether the naphtha will undergo further substantial reaction if more than the stoichiometric amount of iodine required for conversion of aromatizable compounds is charged.

The ratio of iodine to iodine reactive hydrocarbons in the charge is a very important variable in the iodine conversion step of the present invention. The stoichiometric amount of iodine required for complete conversion of an iodine-reactive compound is two atomic proportions of iodine per new C-C linkage; for example, in the case of n-hexane being converted to benzene, eight C-H bonds are cleaved and four new C-C bonds are formed, thus requiring eight atomic or four molecular proportions of iodine (I₂). For convenience, a theoretical (stoichiometric) equivalent of iodine is referred to as one "theory" of iodine.

By contacting the naphtha to be converted at the proper reaction conditions with one stoichiometric equivalent of iodine, based on iodine-aromatizable hydrocarbons in the naphtha, it is possible to carry the conversion of these compounds to aromatics substantially to completion without appreciably converting iodine-resistant compounds present. In the production of motor fuels in accordance with the present invention there is generally no advantage in maintaining a very low degree of conversion. The total amount of elemental iodine which contacts the hydrocarbons in the conversion step is, therefore, ordinarily at least 0.3 stoichiometric equivalents, based on iodine-aromatizable hydrocarbons, and not usually in excess of 1.2 stoichiometric equivalents. It is preferred to contact the naphtha in the iodine reaction step with a total amount of elemental iodine in the range between 0.5 and 1.2 stoichiometric equivalents, based on iodine-aromatizable compounds in the naphtha, so as to obtain a high conversion of group I compounds without appreciable conversion of group II compounds.

In one mode of operation, the total amount of elemental iodine used in the reaction step is charged as elemental iodine, admixed with the hydrocarbon feed. In that case the total mixture passes through the reaction zone and the amount of reaction obtained under proper reaction conditions is approximately equivalent to the amount of reaction theoretically obtainable at the iodine-to-hydrocarbon ratio employed.

It has been found by the present inventors and coworkers that the effective ratio of iodine to hydrocarbon can be increased over the ratio in which elemental iodine is charged with the hydrocarbon feed to the reaction zone, by employing what may be designated an "iodine extender." The principle of such iodine extenders is that HI, formed by the reaction of iodine and hydrocarbon, is reconverted to elemental iodine while present in the partially reacted mixture, e.g. within the reaction zone or between sequential reaction zones, so that the iodine charged to the reaction will serve to remove more than its atomic equivalent of hydrogen from the hydrocarbon.

For convenience of reference, the amount of elemental iodine present in the mixture entering the reaction zone is called the "actual amount of iodine charged," while the "effective total amount" of elemental iodine includes iodine regenerated from HI in the reaction mixture and elemental iodine injected into the reaction zone at locations other than the inlet, if any. The ratio of iodine-to-hydrocarbons which corresponds to the effective total amount of iodine is called the "effective ratio."

In the mode of operation described in detail in copending U.S. patent application Serial No. 563,660 of J. H. Riley et al., filed February 6, 1936, now U.S. Patent 2,898,386, a catalyst suitable for converting HI to elemental iodine and hydrogen is present in at least 1% of the reaction zone or between reaction zones to reconvert HI back to elemental iodine as well as hydrogen. Effective catalysts are, for example, platinum metal as such, platinum supported on a porous solid absorbent (preferably one of relatively non-acidic character to avoid cracking reactions) and other metal catalysts and metal iodides, as well as some relatively non-acidic porous solids including...
ing alumina and activated carbon. When employing such catalysts the actual amount of elemental iodine charged with the feed is suitably reduced so that the effective total amount of elemental iodine which contacts the hydrocarbon feed is in the range between 0.3 and 1.2 stoichiometric equivalents based on iodine- aromatizable hydrocarbons present.

Another material suitable as iodine extender is a hydrogen accepting olefin, which may boil below the gasoline boiling range, e.g., ethylene or propylene. This method of iodine extension is described in detail in copending U.S. patent application Serial No. 554,733 of J. H. Raley et al., filed December 22, 1955, now U.S. Patent 2,880,249. When employing a hydrogen accepting olefin the actual amount of elemental iodine charged to the reaction zone is reduced so that the sum of the moles of iodine charged and the moles of hydrogen accepting olefin which are convertible to paraffin in the reaction is in the range of the stoichiometric equivalent stated above e.g., between 0.3 and 1.2 stoichiometric equivalents based on iodine-aromatizable hydrocarbons in the feed.

Other iodine extenders may be employed, and it will be understood that the amount of iodine in the range between 0.3 and 1.2 stoichiometric equivalents, based on the iodine-aromatizable hydrocarbons in the feed, refers to the effective total amount of elemental iodine which contacts the hydrocarbon feed from the time that it enters the reaction zone to the time that it leaves the reaction zone.

The conversion of iodine-reactive hydrocarbons with elemental iodine, under the conditions to be described, is peculiar in that the selectivity of the reaction to the favored compound is greatly increased as the amount of iodine present in the initial reaction mixture increases from a very small value up to about 0.1 to 0.2 mole of iodine per mole of iodine-reactive hydrocarbon. Therefore, even when an iodine extender is employed, the ratio of the actual amount of iodine charged with the feed to the reaction zone to iodine-reactive hydrocarbon must be at least 0.1 mole, and is preferably at least 0.2 mole of iodine per mole of iodine-reactive hydrocarbon.

The amount of iodine used in this invention represents a very substantial proportion, when expressed in weight percent of the hydrocarbon charge. To illustrate, the following tabulation shows the weight percentage of iodine at different iodine-to-hydrocarbon levels for a naphtha in which both iodine-aromatizable and iodine-resistant compounds have an average molecular weight of 128 and are present in equal mole percentage.

<table>
<thead>
<tr>
<th>Column</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometric equivalents of 1/16 mole iodine aromatic-</td>
<td>0.025</td>
<td>0.05</td>
<td>0.3</td>
<td>0.3</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>Mole iodine aromatizable</td>
<td>0.1</td>
<td>0.2</td>
<td>1.2</td>
<td>2.0</td>
<td>4.0</td>
<td>4.8</td>
</tr>
<tr>
<td>Percent by weight, based on</td>
<td>6.9</td>
<td>19.8</td>
<td>119</td>
<td>198</td>
<td>297</td>
<td>476</td>
</tr>
<tr>
<td>Percent by weight, based on</td>
<td>18.7</td>
<td>36.0</td>
<td>258</td>
<td>297</td>
<td>794</td>
<td>603</td>
</tr>
<tr>
<td>iodine-aromatizable</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Column 1 is the minimum actual amount of iodine which must be charged at the reactor inlet (0.1 mole/mole); column 2 is the desired minimum actual amount of iodine to be charged (0.2 mole/mole). Columns 3 to 6 are values from 0.3 to 1.2 stoichiometric equivalents of iodine, based on iodine-aromatizable compounds present. Such amounts may be actually charged, and may represent effective total amounts, in case iodine extenders or iodine injection into the reaction zone are employed.

The iodine takes part in the present reaction as free iodine. In the absence of iodine extenders the iodine is preferably supplied as elemental iodine, although it may also be supplied in the form of an iodine compound which yields free iodine, either molecular or atomic, under the reaction conditions. Hence, iodine may be supplied in the form of organic iodides which shall be stable under the conditions of the reaction and liberate elemental iodine.

When an iodine extender is employed, but only in that case, iodine may also be charged to the reaction zone in the form of hydroiodide, since the iodine extender will convert hydroiodide to iodine in the reaction zone.

In the course of the reaction free iodine is converted to hydroiodide. In the absence of an iodine extender, iodine charged to the reaction zone and converted therein is present in the reactor effluent in the form of hydroiodide. Upon completion of the conversion reaction it is generally desirable to separate the hydroiodide as well as unconverted iodine rapidly and completely from the organic reaction products. The separated hydroiodide may be recovered and reconverted to free iodine, for reuse, by thermal or catalytic decomposition with simultaneous liberation of hydrogen, or by oxidation. If free iodine is present in the product stream it can be recovered in admixture with the hydrocarbons and then separated from them in a subsequent operation, or it can be recovered in admixture with hydrogen iodide.

In a suitable method of recovering the gasoline product from the iodine reaction step a total reactor effluent is cooled without condensation and is charged directly to a fractional distillation column in which only the hydrogen iodide and light gaseous product is taken overhead and the total gasoline boiling range and heavier material is taken as bottoms. This bottoms stream is then charged to another fractional distillation column to make a separation between the gasoline boiling range material, which is taken overhead, and a bottoms stream containing a small amount of heavier material which may be formed in the reaction plus the elemental iodine, which will be in liquid form. The gasoline boiling range material may be caustic- and water-washed and is then a suitable gasoline blending stock of high octane number and substantial aromatics content. The hydroiodide taken overhead in the first column may be reconverted to iodine and returned to the reaction zone. Elemental iodine recovered from the bottoms of the second column is also returned to the reaction zone.

The temperature required in the iodine reaction is at least about 300° C., generally being at least about 350° C. and preferably being in the order of about 425° to 575° C. Higher temperatures, up to 650° C. may be employed but it is usually preferred not to go above about 600° C. Higher temperatures are not objectionable so long as other undesirable changes, e.g. thermal cracking, are not affected.

The reaction with iodine is suitably carried out at various pressures, from subatmospheric to superatmospheric pressures, either in liquid or vapor phase, generally preferably in vapor phase. Although atmospheric pressure is suitable and is advantageous in most cases, other considerations, such as factors which are involved in the separation and recovery of the hydrogen iodide from the product stream in some cases make a superatmospheric pressure more desirable. Thus, in the case of vapor phase processes, the pressure can be at any value at which the reactants are sufficiently vaporized at a temperature at which the hydrocarbon is substantially thermally stable. The pressure can be, for example, as high as from 500 to 1000 pounds per square inch, and even higher in some cases.

Residence time of the reactants at the selected reaction conditions should in general be at least about 0.01 second and usually at least about 0.1 second; while usually it should not be over about 1 minute, it may be as much as 3 to 5 minutes but no more. Generally, times in the range from 1 second to 1 minute and particularly from 1 to 30 seconds are preferred.
The following operations illustrate the use of the present invention:

A naphtha boiling between 100° and 300° F. is charged directly to an iodine conversion step by vaporizing the naphtha, adding to it from 0.3 to 1.2 stoichiometric equivalents and preferably from 0.5 to one stoichiometric equivalent of iodine based on iodine-aromatizable compounds therein to produce a vapor mixture, and maintaining the vapor mixture at a temperature between 300° and 650° C. and preferably between 425° and 575° C. for from 0.1 second to 5 minutes and preferably for from 1 to 60 seconds. Hydrocarbon product boiling between 100° and 300° F. or up to 350° F. is recovered from the reactor effluent. This is a motor fuel blending stock of greatly improved octane number. This method of operation is particularly suitable for straight run paraffinic naphthas, but may also be employed with aromatic naphthas and with cracked naphthas. Although highly naphthenic naphthas may also be treated in this manner, they are preferably first subjected to another conversion step.

In determining the amount of iodine required to be charged in the above reaction, reasonably satisfactory results may be obtained by assuming that approximately 50% of the naphtha consists of iodine-aromatizable compounds and that 4 moles of iodine per mole of hydrocarbon represents the stoichiometric equivalent. However, in ordinary refinery operations the actual analysis of a naphtha charged to a conversion process for fuel production is almost invariably available or obtainable and, consequently, the stoichiometric requirement of iodine for conversion of the iodine-aromatizable compounds in the naphtha is readily calculated.

In a generally preferred mode of operation in accordance with the present invention, a gasoline boiling range naphtha is charged to a hydrocarbon conversion process suitable for converting the naphtha to an improved motor fuel blend stock which still contains a substantial proportion of iodine-aromatizable compounds. The gasoline boiling range fraction of the product of said conversion process is then charged in vapor form, with from 0.3 to 1.2 stoichiometric equivalents of iodine and preferably from 0.5 to 1 stoichiometric equivalent based on the iodine-aromatizable compounds therein, to a reaction zone maintained at a temperature in the range between 300° and 650° C. and preferably between 425° and 575° C. for from 0.1 second to 5 minutes and preferably for from 1 to 60 seconds. The gasoline boiling range fraction recovered from the effluent of the reaction zone is a superior motor fuel.

The conversion process employed in the first step of the above operation is selected for best results depending on the composition of the naphtha charged thereto and also on processing equipment available in a given refinery situation.

When the naphtha to be converted is a straight run naphthenic naphtha, particularly when it is desired to use iodine in excess of 1 stoichiometric, based on aromatizable compounds, the first conversion process may be a low temperature isomerization employing a Friedel-Crafts catalyst, operated under the conditions known to the art, and briefly described supra, to produce a naphtha having a substantially reduced concentration of non-hydroaromatic naphthenes. This naphtha is then charged to the iodine reaction.

In another modification for treatment of a naphthenic naphtha, the conversion process employed in the first step is a dehydrogenation process in which the hydroaromatic naphtha is catalytically reforming hydrocarbons to aromatic hydrocarbons. Such a process may be carried out with a nickel-tungsten-sulfide catalyst or a non-isomerizing platinum reforming catalyst, in accordance with methods known to the art. These processes are preferably operated in the presence of hydrogen, and cause relatively little conversion of paraffins to olefinic compounds and virtually no conversion of paraffins to aromatics. The resulting naphtha is charged to the iodine reaction.

If desired, catalytic dehydrogenation may be carried out under slightly more severe conditions with low concentrations of hydrogen to convert not only hydroaromatics to aromatics but also a substantial proportion of the paraffins present in the naphtha to olefins. The latter are substantially more easily converted in the subsequent iodine reaction step than the corresponding paraffins and consequently the olefin-creating process is suitably converted at relatively lower contact times. Suitable conditions include from 0.3 to 1.2 stoichiometric equivalents of iodine (based on conversion of iodine-aromatizable compounds) and preferably amount 0.5 to 1 stoichiometric equivalent of I₂, temperatures of 460°–550° C. and contact times of 0.1 to 30 seconds and preferably about 0.5 to 15 seconds. In this modification, substantially less iodine is required since 1 theory for conversion of an olefin to an aromatic is only 3 moles per mole of hydrocarbon as compared to 4 moles per mole for conversion of a paraffin. The iodine requirement is further reduced by the amount which would have been required to dehydrogenate the hydroaromatic naphthenes.

In a further suitable combination of processes for treating a straight run naphthenic gasoline boiling range naphtha, the naphtha is first subjected to low temperature isomerization to remove a substantial proportion of non-hydroaromatic naphthenes, the product from the isomerization is subjected to dehydrogenation to convert the hydroaromatic naphthenes to aromatic hydrocarbons and, if desired, to convert some of the paraffins to olefins, and the product from the dehydrogenation is then treated with from 0.3 to 1.2 stoichiometric equivalents of iodine based on the iodine-aromatizable compounds therein, to produce a highly aromatic gasoline blending stock of very high octane number.

In another modification of the present invention, suitable for treating a gasoline boiling range naphtha of a straight-run paraffinic type, the naphtha is first subjected to a high-temperature isomerization process i.e., isomerization at a temperature in excess of 300° C., for example, over a nickel or platinum catalyst supported on silica-alumina of approximately 80 m²/g. surface area, as described above, to convert normal and slightly branched paraffins to more highly branched paraffins having a lower number of carbon atoms contiguous in the chain. The gasoline boiling range product recovered from the isomerization process, which still contains a high proportion of iodine-aromatizable normal and slightly branched paraffins, is then charged with from 0.3 to 1.2 stoichiometric equivalents and preferably from 0.5 to about 1 stoichiometric equivalent iodine, based on the iodine-aromatizable compounds therein, to iodine conversion at a temperature between 300° and 650° C. and preferably between 425° and 575° C. for a time between 0.1 second and 5 minutes and preferably from 1 to 60 seconds to convert selectively the iodine-reactive low octane number paraffins into aromatics. The resulting gasoline boiling range hydrocarbon product comprises a valuable motor fuel having both highly branched paraffins and aromatic hydrocarbons of high octane number and containing few or no low octane number components such as normal or very slightly branched paraffins.

A preferred mode of practicing the present invention, suitable for use with a variety of straight-run naphthas, whether of paraffinic, naphthenic, or aromatic type, consists in subjecting the gasoline boiling range naphtha to catalytic reforming operation in the presence of hydrogen, either by hydroforming over a group VI metal catalyst or by reforming over a noble metal catalyst in the conditions known to the art and briefly set out above, followed by recovering the total gasoline boiling range reformate and charging it with from 0.3 to 1.2 stoichiometric equivalents and preferably from 0.5 to 1 stoichio-
metric equivalent of iodine to an iodine conversion step at a temperature between 300° and 650° C. and preferably between 425° and 575° C. for a time between 0.1 second and 5 minutes, preferably between 1 and 5 seconds. The reforming step serves to substantially convert the hydroaromatic naphthenes to aromatic hydrocarbons and also converts a part of the non-hydroaromatic naphthenes by isomerization to hydroaromatic naphthenes followed by continuous removal of the resulting hydroaromatic naphthenes by dehydrogenation to aromatics. If the reforming catalyst has sufficient isomerization activity some conversion of paraffinic compounds similar to that mentioned in the above high-temperature isomerization process will also take place.

An especially preferred processing sequence in accordance with the process invention comprises converting virgin naphtha in a first catalytic reforming step, carried out at relatively mild conditions such that a high liquid yield is obtained without substantial conversion or loss of normal and slightly branched paraffins in the naphtha due to dehydrocyclization or hydrocracking. Such mild reforming is sufficient to convert hydroaromatic naphthenes in the charge stock to aromatics and preferably also reduces the concentration of non-hydroaromatic naphthenes by isomerization and subsequent conversion to aromatics. Such mild reforming is not conventionally employed in the production of motor fuels because the high temperature of relatively low octane number normal and slightly branched paraffins makes the resulting reformate unsuitable as a fuel or, if the low octane number materials are segregated by hydrocarbon type, leaves the reformed with a large volume of low octane number fractions. The mild reforming operation has the advantage that it involves little loss of hydrocarbon material to non-gasoline boiling range materials such as gas or coke. Further, it has the advantage that the catalytic life in such a process is extended by virtue of the reduced coke formation. The product from the mild reforming operation is then passed to the iodine reaction step under the conditions set out above to convert the normal and slightly branched paraffins therein by reaction with iodine into aromatics of high octane number. The resulting gasoline boiling range fraction is obtained in much greater volume and with a higher octane number than is obtainable in the conventional reforming processes. In processes above in which the first conversion process is carried out at an elevated temperature e.g., the high-temperature isomerization process, the dehydrogenation process and the catalytic reforming process, a particularly suitable modification comprises adding iodine in the desired amount, e.g., from 0.3 to 1.2 stoichiometric equivalents, based on iodine-aromatizable compounds, directly to the vaporized effluent from the first conversion step at a temperature between 300° and 650° C. and charging the total mixture directly to a further reaction zone in which it is contacted for a time not exceeding 5 minutes, and preferably for a time not exceeding 1 minute, at temperatures in the range between 400° and 600° C. to produce the desired conversion of iodine reactive compounds to compounds of higher octane number. Not only are substantial heat economies realized by operating in this manner, but other advantages are realized as well; e.g., it becomes unnecessary to provide separation equipment following the first conversion step to segregate the gasoline boiling range naphtha from lower and higher boiling products. In many cases, the total effluent from the first conversion step is unstable or contaminated and requires chemical treatment before storage. Such treatment can be avoided by charging the effluent directly to the iodine conversion step.

A further modification suitable in operations in accordance with the present invention involves the separation of the product of a first naphtha conversion process into a converted fraction of high octane number, generally consisting essentially of iodine resistant compounds (i.e. compounds of "group II" and "group III"), and into a fraction of iodine reactive components of iodine number, and subsequently charging only the latter fraction to the iodine conversion step. For example, a naphthenic naphtha is charged to a platinum reforming process in which some non-hydroaromatic naphthenes are converted to aromatics by isomerization and dehydrogenation, substantially all hydroaromatic naphthenes are converted to aromatics by dehydrogenation and, depending upon the catalyst and conditions employed, some paraffins may be converted to more highly branched paraffins having less carbon atoms contiguous in the chain. The reformed naphtha is then subjected to a separation process to recover a high octane number product and a low octane number fraction which is charged to the iodine conversion process. The separation may comprise a solvent extraction or extractive distillation, e.g., employing phenol, furfural, liquid SO2 or other solvents selective for aromatics, or a solid adsorptive separation process, e.g., employing silica gel. Such processes are well known. The raffinate from the extraction or adsorption process comprises essentially paraffins and non-hydroaromatic naphthenes, the latter in reduced quantity, compared to the original naphtha. This raffinate is then charged to the iodine conversion process to convert the normal and slightly branched paraffins therein to good yield and high selectivity to aromatic hydrocarbons of high octane number. Highly branched, i.e. non-iodine-aromatizable paraffins present are retained essentially in unconverted form. The gasoline boiling range product of high octane number recovered from the first conversion step and the gasoline boiling range product recovered from the iodine conversion step are suitably blended to form a major portion of a balanced motor fuel of high octane number.

All of the above-illustrated processes are suitable for use with a total gasoline boiling range naphtha, i.e., which boils from about 100° F. to about 450° F., but are equally useful in processing naphthas of narrower boiling ranges. For example, it is advantageous to employ naphthas having an initial boiling point above 130° F., since in this manner cyclopentane and neohexane, both of which are non-iodine-aromatizable but subject to carbon formation in the iodine reaction step, are excluded.

It is also often preferred not to charge to conversion processes the higher boiling range portion of the naphtha. Thus, naphthas charged to the conversion processes may boil from 130° to 200° F., from 100° to 250° F. from 150° to 300° F., and so forth. An endpoint no higher than 300° to 320° F. is particularly preferred.

It is sometimes preferable to produce by fractional distillation narrow boiling range fractions in the naphtha boiling range in which either high octane number components or low octane number components are selectively concentrated. For instance, fractions boiling between 150° and 160° F. generally contain substantially all the normal hexane present in the naphtha, those boiling between 205° and 215° F. the normal heptane, those between 250° and 270° F. the normal octane, and those between 290° and 310° F. the normal nonane. Similarly, the fractions boiling between 155° and 180° F. generally contain most of the benzene present in the naphtha, those boiling between 205° and 235° F. most of the toluene and those boiling between 250° and 290° F. most of the xylenes and ethylbenzene. It is sometimes desirable to separate from a straight run naphtha either the former fractions containing iodine-aromatizable low octane number components and charge them to the iodine conversion step or, conversely, to separate the fractions containing the concentrated aromatics and charge the total remaining naphtha to iodine conversion. It is also often possible to select similar concentrates from a naphtha which has previously undergone a hydrocarbon conversion proc-
ess, e.g. from a naphtha which has been selectively dehydrogenated or reformed or isomerized. In the above discussion, the cut points indicated are to be considered merely as guides. For any available naphtha, the proper cuts may be wider or narrower depending on its composition and octane number characteristics.

Example I

In an operation in accordance with the present invention, a naphthenic virgin naphtha boiling between about 160° and 230° F. was reformed in a commercial non-re- generative platinum reforming unit of the "Platforming" type, operating with reactor inlet temperatures of about 477° C., at pressures from 340 to 275 p.s.i.g., a liquid hourly space velocity of about 2 v/v/hr. and a hydrogen to feed mole ratio of about 5.2 over a commercial platinum-on-alumina catalyst suitable for non-regenerative operation. The toluene fraction of the reformed naphtha, boiling essentially between about 200° and 228° F., was recovered by fractional distillation and separated into an aromatic extract and a non-aromatic raffinate fraction by extractive distillation with phenol. The raffinate, representing slightly over 50 volume percent of the toluene fraction, had an initial boiling point of 196° F., 10% point of 200° F., 50% point of 208° F. and end point of 244° F.

The raffinate admixed with iodine in a ratio of 2.74 moles of iodine to one mole of the total feed hydrocarbon (approximately 0.839 stoichiometric equivalent, based on 81.7 mole percent of iodine reactive compounds; 1 stoichiometric equivalent = 4 moles I₂ per mole reactive compound) was passed in vapor phase through a reaction zone maintained at 505°±5° C. at a pressure of 1 atmosphere (absolute) with a nominal residence time, based on feed to reactor, of 6.4 seconds. The reactor effluent was contacted with excess aqueous sodium hydrosulfide (3% concentration) to remove the hydrogen iodide and iodine. Shown in Table III are the composition of the naphtha feed to the iodine conversion step, of the part of the feed which did not convert, of the part recovered, and of the total recovered product. The content of iodine-aromatizable and iodine-resistant compounds in the feed is shown. The former amounted to approximately 82% of the feed, having a calculated octane number (RM, blending) of about 33, while the latter amounted to about 18% with a calculated octane number (RM, blending) of about 93.5. These calculated octane numbers, though only approximate, clearly indicate the high fuel quality of the iodine resistant fraction and the low fuel quality of the iodine-aromatizable one. The feed charged to the iodine step had an actual F-1-0 octane number (50% blend in catalytically cracked gasoline) of 58. It was found that six-sevenths of the iodine-aromatizable C₈ and C₉ paraffins were converted, while the iodine-resistant compounds showed no loss due to conversion, except for the C₈ naphthenes of which about 2.8 moles disappeared per 100 moles of feed. The total liquid product recovered had a F-1-0 blending octane number of 100.

### TABLE III

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed (Moles)</th>
<th>Feed Dis-</th>
<th>Feed Recovered</th>
<th>Total Product Recovered (Moles per 100 moles feed)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>I-Aromatic</td>
<td>Unconverted</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Resistant</td>
<td>(Moles)</td>
<td></td>
</tr>
<tr>
<td>o-xylene</td>
<td>1.8</td>
<td>0.7</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>m-xylene</td>
<td>1.4</td>
<td>0.7</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>p-xylene</td>
<td>1.1</td>
<td>0.7</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>C₈ paraffin</td>
<td>10.7</td>
<td>7.7</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>C₉ paraffin</td>
<td>11.8</td>
<td>8.7</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>C₈ naphtene</td>
<td>1.8</td>
<td>1.0</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>C₉ naphtene</td>
<td>1.4</td>
<td>1.0</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>C₈ olefin</td>
<td>1.0</td>
<td>1.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>C₉ olefin</td>
<td>1.4</td>
<td>1.0</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>C₈ gas (C₈ equivalents)</td>
<td>1.6</td>
<td>1.0</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>C₉ gas (C₉ equivalents)</td>
<td>1.8</td>
<td>1.0</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>C₈ aromatics</td>
<td>1.4</td>
<td>1.0</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>C₉ aromatics</td>
<td>1.8</td>
<td>1.0</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>81.7</td>
<td>18.3</td>
<td>72.1</td>
</tr>
<tr>
<td>Blending Octane Number</td>
<td>100.0</td>
<td>58</td>
<td>42</td>
<td>72.1</td>
</tr>
</tbody>
</table>

* Actual (F-1-0).
* Calculated (Research method).

Example II

For the sake of illustration, the same feed as shown in Table III was converted by aromatization over a conventional chloria-alumina catalyst under favorable conditions. The results of this run (identified as run B) are compared with the results of the run described in Example I (run A) in Tables IV and V.

### TABLE IV

<table>
<thead>
<tr>
<th>Run</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst or Reagent</td>
<td>Iodine 50% Cr₂O₃-AI₂O₃</td>
<td></td>
</tr>
<tr>
<td>Reactor Temperature, °C</td>
<td>~286</td>
<td>~60</td>
</tr>
<tr>
<td>Reactor Pressure, p.s.i.</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td>Reactor-Oil Ratio (WL)</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Iodine-Feed Ratio (WL)</td>
<td>6.8</td>
<td>6.8</td>
</tr>
<tr>
<td>Iodine Oil Mol Fraction</td>
<td>0.77</td>
<td>0.77</td>
</tr>
<tr>
<td>Iodine Oil Partial Pressure, p.s.i.a.</td>
<td>1800</td>
<td>1800</td>
</tr>
<tr>
<td>Contact Time, sec.</td>
<td>6.4</td>
<td>6.4</td>
</tr>
<tr>
<td>Yields, Percent wt.:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen (or H as H₂)</td>
<td>6.5</td>
<td>2.6</td>
</tr>
<tr>
<td>C₆-C₉ Hydrocarbons</td>
<td>93.1</td>
<td>93.1</td>
</tr>
<tr>
<td>C₁₀+(excluding residue and coke)</td>
<td>93.5</td>
<td>93.5</td>
</tr>
<tr>
<td>Coke</td>
<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Loss</td>
<td>6.9</td>
<td>2.2</td>
</tr>
</tbody>
</table>

* Residue from distillation.

### TABLE V

<table>
<thead>
<tr>
<th>Run</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition, percent vol.:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aromatics</td>
<td>66</td>
<td>37</td>
</tr>
<tr>
<td>Olefins</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>20</td>
<td>39</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Number</td>
<td>F-1-0</td>
<td>93.5</td>
</tr>
<tr>
<td>F-1-3</td>
<td>93.5</td>
<td>93.5</td>
</tr>
<tr>
<td>arom/D.</td>
<td>1.4600</td>
<td>1.4102</td>
</tr>
</tbody>
</table>

* Octane numbers on 50% blend in catalytically cracked gasoline.

It will be seen that losses to gas and coke were drastically lower, the liquid recovery was higher and the octane number of the liquid product was much higher in run A than in run B. The loss of 6.9 weight percent in run A was due to shortcomings of the experimental setup used and will be much lower in commercial operation. The "residue" in run A can also be reduced to a much lower value. The liquid yield in accordance with the
present invention can thus be increased to 90% by weight or even higher while the very low gas and coke formation and high product octane number are retained.

**Example III**

The following data compare the results obtained by converting the normal paraffinic components of a straight run naphtha (1) in accordance with the present invention and (2) by platinum reforming. n-Octane was converted with iodine in run G. In runs C through F, n-octane was passed at increasingly severe reforming conditions over a platinum-on-alumina ("Platforming") catalyst. The conditions used and results obtained are shown in Table VI.

**TABLE VI**

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>Temp., °C</th>
<th>Pressure, psig</th>
<th>Octane Number</th>
<th>Vol. % Mole Ratio</th>
<th>Conversion of n-C8 percent</th>
<th>Product Distribution, Percent</th>
<th>Aromatics, Percent</th>
<th>Blending Octane No. of C8+ Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>POCUP/AO</td>
<td>450</td>
<td>700</td>
<td>2.0</td>
<td>7.2</td>
<td>0.9</td>
<td>4.0</td>
<td>6.7</td>
<td>90</td>
</tr>
<tr>
<td>D</td>
<td>POCUP/AlOH</td>
<td>450</td>
<td>700</td>
<td>3.0</td>
<td>6.0</td>
<td>0.4</td>
<td>3.0</td>
<td>5.5</td>
<td>95</td>
</tr>
<tr>
<td>E</td>
<td>POCUP/AlOH</td>
<td>650</td>
<td>700</td>
<td>4.0</td>
<td>5.6</td>
<td>0.6</td>
<td>3.0</td>
<td>4.5</td>
<td>100</td>
</tr>
<tr>
<td>F</td>
<td>POCUP/AlOH</td>
<td>350</td>
<td>800</td>
<td>5.0</td>
<td>4.0</td>
<td>0.6</td>
<td>3.0</td>
<td>4.5</td>
<td>100</td>
</tr>
<tr>
<td>G</td>
<td>None</td>
<td>450</td>
<td>700</td>
<td>6.0</td>
<td>1.0</td>
<td>0.3</td>
<td>3.0</td>
<td>4.5</td>
<td>100</td>
</tr>
</tbody>
</table>

It is shown in reforming at relatively mild conditions (runs C and D) there is no useful increase in octane number for the total product. Aromatics formation is very low. Even the octane number of the converted fraction (ex n-octane) is probably quite low, as indicated by the low octane numbers of the converted fraction in runs E and F. At progressively more severe reforming conditions (runs E and F) greater and greater amounts of the charge are lost from the gasoline boiling range (C9+). In run F, 98% wt. of the n-octane feed was recovered, but only 37% wt. (based on feed) was recovered as C9+ product. The total recovered gasoline boiling range liquid had an octane number of 65; the converted part (ex n-octane) had an octane number of 68.

By contrast, in run G only 64% of the n-octane was converted (because only 0.58 stoichiometric equivalent of iodine had been added) and only 8.2% wt. of the feed was lost from the gasoline boiling range. The converted C8+ fraction represented 59.5% by weight of the total recovered C8+ fraction (or about 54% by weight based on octane feed) and had a calculated blending research octane number of about 119. Because of the large amount of unconverted n-octane remaining, the total C8+ fraction had an octane number of 56.2. By increasing the iodine ratio to about one stoichiometric equivalent, an essentially theoretical yield of liquid product with a blending octane number well over 100 is readily obtainable. It will be seen that such results are physical impossibilities with the platinum reforming process of this example and the chromina-alumina aromatization process of Example II.

It should be noted that a 100% yield of liquid product is not theoretically possible in aromatization. For example, in converting n-octane to ethylene the theoretical yield is about 95% by weight and about 77% by volume.

It is also illustrated by the above data that superior results are obtainable by converting a gasoline boiling range naphtha in a platinum reforming process under relatively mild conditions, e.g., those of C5 or C6, at which, as is known, hydroaromatic naphthenes are converted to aromatics but n-paraffins are only slightly isomerized and even more slightly dehydrocyclized to aromatics, and then converting at least the paraffinic component of the reformate in an iodine reaction as illustrated.

We claim as our invention:

1. A process for preparing a motor fuel of improved octane number from a naphtha boiling in the range between 100° F. and 450° F., containing a substantial proportion of iodine-aromatizable compounds which comprises subjecting said naphtha to a hydrocarbon conversion process in which a substantial proportion of hydrocarbons is converted to iodine-resistant hydrocarbons having a higher octane number to produce a product containing iodine-resistant hydrocarbons of high octane number and iodine-aromatizable hydrocarbons of low octane number and then contacting at least a portion of said product containing iodine-aromatizable hydrocarbons and an effective total amount of iodine in the range from 0.3 to 1.2 stoichiometric equivalents, based on said iodine, aromatizable hydrocarbons, at a temperature of at least about 300° C. for a time in the range between 0.01 second and 5 minutes whereby iodine-aromatizable hydrocarbons and elemental iodine react to form aromatic hydrocarbons and hydrogen iodide, and recovering from the reaction product a naphtha of increased octane number.

2. A process according to claim 7 in which said iodine-aromatizable compounds comprise a substantial proportion of aliphatic hydrocarbons.

3. A process according to claim 7 in which said iodine-aromatizable compounds comprise essentially saturated hydrocarbons.

4. A process according to claim 7 in which said naphtha is a straight run naphtha.

5. A process according to claim 7 in which said naphtha is a cracked naphtha.

6. A process according to claim 7 in which said naphtha is the product of the hydrogenation of an oxide of carbon.

7. A process according to claim 1 in which said conversion process effects the removal of a substantial proportion of alkycyclic hydrocarbons having 5 carbon atoms in the ring.

8. A process according to claim 1 in which said conversion process comprises contact with a heterogeneous dehydrogenation catalyst at dehydrogenating conditions.

9. A process according to claim 1 in which said conversion process comprises contact with an isomerization catalyst at isomerizing conditions.

10. A process according to claim 11 in which said isomerization conditions include an elevated temperature in excess of 300° C.

11. A process according to claim 1 in which said conversion process comprises contact with a heterogeneous reforming catalyst at reforming conditions.

12. A process according to claim 11 in which said reforming conditions are relatively mild, such that aliphatic compounds in the naphtha are not substantially converted in the reforming step.

13. A process according to claim 11 in which said
catalyst includes platinum as the catalytically active component.

14. A process for preparing a motor fuel of improved octane number from a naphtha boiling in the range between 100° F. and 450° F. containing a substantial proportion of iodine- aromatizable compounds which comprises subjecting said naphtha to a hydrocarbon conversion process at a temperature in excess of 500° C. in vapor phase in which a substantial proportion of hydrocarbons are converted to iodine-resistant hydrocarbons having a higher octane number to produce a product containing iodine-resistant hydrocarbons of high octane number and iodine-aromatizable hydrocarbons of low octane number, withdrawing the total product effluent from said conversion process at an elevated temperature, admixing therewith a reactive proportion of iodine, in the range from 0.3 to 1.2 stoichiometric equivalents, based on iodine-aromatizable hydrocarbons, and heating the resulting mixture at an elevated temperature of at least 300° C., sufficient to effect C-to-H bond cleavages in the iodine-aromatizable molecules, for a time in the range from 0.01 second to 5 minutes, whereby iodine-aromatizable hydrocarbons and elemental iodine react to form aromatic hydrocarbons and hydrogen iodide, and recovering from the reaction product a naphtha of increased octane number.

15. A process for preparing a motor fuel of improved octane number from a naphtha boiling in the range between 100° F. and 450° F. containing a substantial proportion of iodine-aromatizable compounds which comprises subjecting said naphtha to a hydrocarbon conversion process in which a substantial proportion of hydrocarbons are converted to a form having a higher octane number including aromatic hydrocarbons to produce a first product, subjecting at least a portion of said first product to a separation process to separate at least one fraction comprising a substantial amount of aromatic hydrocarbons and at least one fraction comprising essentially non-aromatic hydrocarbons, contacting said non-aromatic fraction and an effective total amount of iodine in the range from 0.3 to 1.2 stoichiometric equivalents, based on iodine-aromatizable compounds present in said non-aromatic fraction, at an elevated temperature of at least about 300° C. for a time in the range between 0.01 second and 5 minutes sufficient to effect C-to-H bond cleavages in iodine-aromatizable molecules whereby iodine-aromatizable hydrocarbons and elemental iodine react to form aromatic hydrocarbons and hydrogen iodide, recovering the resulting mixture as a second product and recovering from said second product a naphtha having a substantially higher octane number than said non-aromatic fraction.

16. A process according to claim 15 in which the portion of the first product subjected to said separation process is a C4 cut boiling between 205 and 235° F.

17. A process according to claim 15 in which the portion of the first product subjected to said separation process is a C3 cut boiling between 250° and 290° F.

18. A process for preparing a motor fuel of improved octane number from a naphtha boiling in the range between 100° F. and 450° F. containing a substantial proportion of iodine-aromatizable compounds which comprises subjecting said naphtha to a hydrocarbon conversion process in which a substantial proportion of hydrocarbons are converted to a form having a higher octane number including aromatic hydrocarbons to produce a first product, subjecting at least a portion of said first product to a separation process to produce at least one fraction comprising a substantial amount of aromatic hydrocarbons and at least one fraction comprising essentially non-aromatic hydrocarbons, contacting said non-aromatic fraction and an effective total amount of iodine in the range from 0.3 to 1.2 stoichiometric equivalents, based on iodine-aromatizable compounds present in said non-aromatic fraction, at an elevated temperature of at least about 300° C. for a time in the range between 0.01 second and 5 minutes sufficient to effect C-to-H bond cleavages in iodine-aromatizable molecules whereby iodine-aromatizable hydrocarbons and elemental iodine react to form aromatic hydrocarbons and hydrogen iodide, recovering the resulting mixture as a second product, recovering from said second product a naphtha having a substantially higher octane number than said non-aromatic fraction and combining it with said aromatic fraction to produce an improved motor fuel.

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