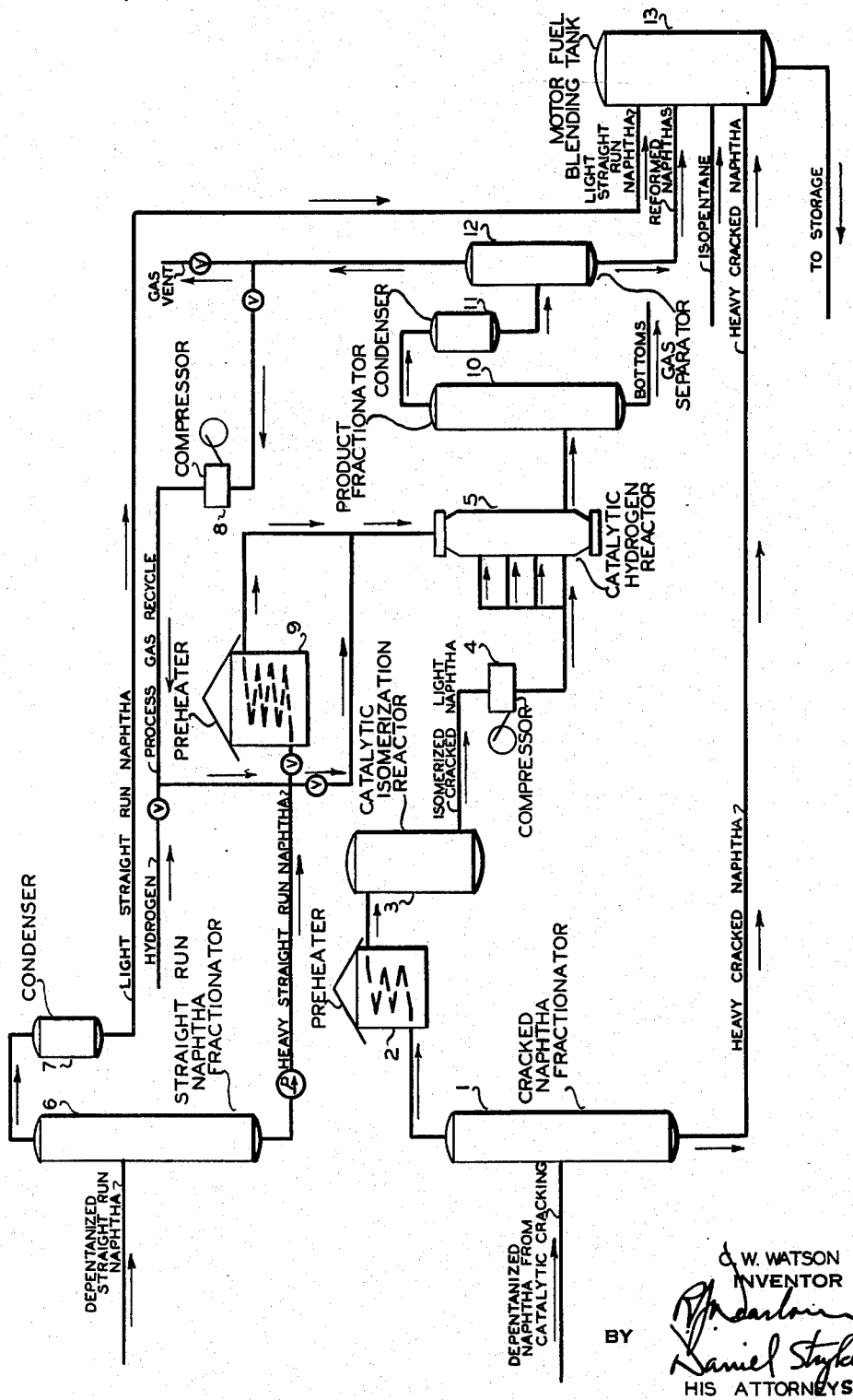
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HYDROCARBON CONVERSION PROCESS

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C. W. WATSON
INVENTOR

BY Daniel Styker
HIS ATTORNEYS

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HYDROCARBON CONVERSION PROCESS

Claude W. Watson, Tuckahoe, N. Y., assignor to The Texas Company, New York, N. Y., a corporation of Delaware

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My invention relates to the conversion of hydrocarbons into other hydrocarbons of more desirable characteristics, and particularly to a process for the conversion of olefinic hydrocarbons of motor fuel range into hydrocarbons of improved stability and high anti-knock value.

Although olefins are produced in large quantities in petroleum refinery cracking operations, only the gaseous olefins have been commercially utilized to any substantial extent for conversion to more valuable compounds. No practical means have been found for recovering normally liquid olefins from petroleum fractions, and the processes which have been proposed for treating entire fractions for the conversion of their olefin content have not afforded sufficient improvements to be economical. Thus, the liquid olefins of motor fuel range are undesirable fuel constituents in view of their potential gum-forming characteristics, but such olefins have been separated from motor fuel fractions only by destructive methods such as acid treating. On the other hand, treatment of motor fuel fractions to effect hydrogenation of the olefinic components results in a substantial loss of anti-knock characteristics, since the octane numbers of most of the olefins are substantially higher than those of the corresponding paraffins.

An object of my present invention is to provide a process for the conversion of liquid olefinic hydrocarbons into hydrocarbons of improved motor fuel characteristics.

Another object of my invention is to provide a method for the conversion of olefinic petroleum hydrocarbons of motor fuel range into motor fuel components of low potential gum content, high anti-knock value, and excellent lead susceptibility, especially suited for use in aviation fuels or other motor fuels for high compression engines.

A further object of my invention is to provide a process for the production of motor fuel of aviation grade from a relatively unsaturated cracked naphtha and a relatively saturated naphthenic hydrocarbon fraction.

Other objects and advantages of my invention will be apparent from the following description:

In accordance with my present invention, liquid olefinic hydrocarbons are subjected to catalytic isomerization and the resulting isomerizate is reacted, under hydrogen transfer conditions, with cyclic hydrocarbons containing alicyclic methylene groups. The hydrogen transfer reaction effects hydrogenation of the olefins and dehydrogenation of the cyclic hydrocarbons. By this combination of reactions, a petroleum hydrocarbon fraction of high olefin content, such as a catalytically cracked naphtha, may be converted to a paraffinic blending stock of high anti-knock value. If a naphthenic fraction of motor fuel range is employed in the hydrogen transfer reaction with the cracked naphtha isomerizate, the naphthenes are dehydrogenated, and the resulting aromatic hydrocarbons further improve the anti-knock characteristics of the reaction product. By this means it is possible to obtain a product having an octane number at least as high as that of the original cracked naphtha, and having a low bromine number and ability to meet the most stringent specifications as to accelerated gum formation.

My process is applicable to the treatment of any normally liquid olefins which are capable of conversion to paraffins of increased chain branching. Relatively pure compounds may be treated by my process, if desired, but this procedure is especially adapted for the treatment of olefinic hydrocarbon mixtures such as cracked petroleum fractions. My process is of most value for improving the motor fuel characteristics of hydrocarbon fractions of motor fuel range containing olefins which are predominantly of relatively low chain branching, such as naphthas obtained by catalytic cracking or by high temperature thermal cracking. Full range naphthas may be treated, or the naphtha may be fractionated to obtain relatively saturated and unsaturated fractions, in which case the more saturated fraction may be directly incorporated in the final motor fuel, and the more unsaturated fraction may be isomerized and reacted with cyclic hydrocarbons before incorporation in the motor fuel.

The isomerization of the olefins is effected at elevated temperatures in the presence of an isomerization catalyst which has substantially no polymerization activity under the conditions employed. Since high pressures tend to favor polymerization, it is generally desirable to effect the isomerization in the vapor phase at relatively low pressures. I prefer to operate at pressures such that the total partial pressure of the olefins in the charge is substantially below one atmosphere. When employing hydrocarbon mixtures such as cracked naphthas, the other types of hydrocarbons in the charge serve as diluents, so that operation at atmospheric pressure results in the partial pressure of the olefins being below one atmosphere. The use of additional inert diluents, such as steam, will enable satisfactory operation at pressures substantially above atmospheric pressure.

The isomerization catalyst may be any catalyst which has hydrocarbon converting activity, but which is free from polymerization activity, at the temperature and pressure employed. Any of the solid, extensive surface hydrocarbon conversion catalysts, such as cracking catalysts and reforming catalysts, may be used at relatively high temperatures and low pressures. Difficultly reducible metal oxides, silicates, clays, and the like, are suitable catalysts of this general type. I prefer to use the metal oxide catalysts such as alumina or thoria.

The space velocity for the isomerization may vary over a considerable range, depending upon the temperature and the activity of the catalyst employed. With the metal oxide catalysts at relatively high temperatures, space velocity of 50 to 1500 volumes of vapor charge per volume of catalyst per hour will usually be satisfactory (vapor volumes calculated to 32° F. and 760 mm. pressure). With alumina or thoria catalysts, at atmospheric pressure and temperatures of 700 to 800° F., I generally prefer to use space velocities of 100 to 750, or contact times of 1 to 5 seconds.

The isomerization temperature should be considerably below the temperature at which any substantial cracking occurs, and is preferably the lowest temperature which permits practical conversion with the catalyst employed. When treating cracked petroleum fractions, the isomerization temperature is preferably substantially below the temperature which had been employed in the cracking process from which the isomerization charge stock was obtained. In general, the isomerization temperature should be as much as possible below the temperature reached by the charge stock in a previous conversion process, in order that the isomerization equilibrium will favor increased chain branching.

The isomerization may be carried out in any suitable apparatus of the type usually employed for high temperature catalytic hydrocarbon conversion processes. The usual operating expedients for such processes may be employed, and the catalysts may be regenerated in the usual manner when they become deactivated from protracted use.

The isomerized olefins may be converted to paraffins by reaction, under hydrogen transfer conditions, with any cyclic hydrocarbon which contains alicyclic methylene groups which can serve as hydrogen donors. As examples of this type of hydrocarbon there may be mentioned cycloparaffins, cyclo-olefins, terpenes, and polycyclic hydrocarbons of alicyclic or mixed alicyclic-aromatic character. The hydro-aromatic hydrocarbons are preferred as hydrogen donors for the hydrogenation of the olefins, since they will be simultaneously dehydrogenated to aromatics. The monocyclic and dicyclic 6-carbon ring compounds and their alkylated derivatives are especially desirable for this purpose. These hydrocarbons are contained in naphthenic petroleum fractions of motor fuel range, such as naphthenic straight-run naphthas and light naphtha cuts of condensates from distillate fields. I prefer to use naphthenic fractions containing at least 25 per cent by volume of naphthenes. Certain Gulf Coast and California straight-run naphthas, and condensates from certain distillate fields, are particularly high in naphthene content and are thus desirable charge stocks for this reaction. If available petroleum fractions have an undesirably low naphthene content, a suitable naphthenic charge stock can be prepared by solvent extraction or other known methods for obtaining naphthene concentrates.

The ratio of cyclic hydrocarbons to olefins for the hydrogen transfer reaction will depend upon the degree of unsaturation of the olefinic charge stock and the available hydrogen in the cyclic hydrocarbons. It is usually desirable to employ an excess of the cyclic hydrocarbons over that theoretically required to supply all of the hydrogen necessary for saturation of the olefins. However, lower ratios may be used if gaseous hydrogen is employed to make up for the hydrogen deficiency of the cyclic charge stock. In the latter case the cyclic hydrocarbons will serve partially as hydrogen carriers, in addition to serving as hydrogen donors. I prefer, however, to use an excess of cyclic hydrocarbons, even when the reaction is effected under superatmospheric hydrogen pressure. Ratios of cyclic hydrocarbons to olefins in the charge may suitably range from 1.1 to 1.5 times the theoretical ratio.

The hydrogen transfer reaction is effected at elevated temperatures using known hydrogenation-dehydrogenation catalysts. The hydrogen transfer is favored in most cases by the presence of an atmosphere of hydrogen, and usually by superatmospheric pressure. In many cases it is desirable to operate at pressures above the vapor pressure of the reaction mixture at the reaction temperature. In such cases the pressure may be obtained by the use of an external source of high pressure gas, or by recycling the gaseous constituents of the reaction product. The initial pressure for a continuous process is suitably obtained by the use of hydrogen, after which recycling of the process gas under pressure will serve to maintain a hydrogen atmosphere during the reaction.

Any hydrogenation-dehydrogenation catalyst may be used for the hydrogen transfer reaction in my process. The metallic catalysts which are commonly used for hydrogenation reactions are effective for hydrogen transfer under less drastic reaction conditions than the catalysts which are commonly employed for dehydrogenation reactions. Thus, complete hydrogen transfer between methylcyclohexane and di-isobutylene is obtained at 600° F. in an atmosphere of hydrogen at a pressure of 760 mm. when employing a catalyst comprising platinum black supported on pumice. On the other hand, alumina-chromia catalysts or alumina-molybdena catalysts generally require temperatures above 750° F. and pressures ranging from 100 to 600 pounds per square inch for hydrogen transfer between olefins and naphthenes. Any of the catalysts which are suitable for use in the hydrocarbon conversion process known as "hydroforming" may be used in the present reaction under substantially the same conditions employed for hydroforming. The difficultly reducible metal oxides are hydrogen transfer catalysts having general applicability to naphthenic charge stocks containing alkylated cyclopentanes of cyclopentenes as well as to charge stocks containing compounds of six carbon atom rings. Catalysts having more specific action may be employed with appropriate charge stocks; thus, a tungsten nickel sulfide catalyst may be used when employing a charge stock containing cyclohexane or its alkylated derivatives.

The reaction conditions for the hydrogen transfer will depend upon the particular catalyst employed, as indicated above. With the oxide

or sulfide type catalysts the temperature will usually range from 750 to 950° F., and the pressure from 50 to 1500 pounds per square inch. With such catalyst I prefer temperatures of 800 to 900° F. and pressures of 100 to 600 pounds per square inch. With more active hydrogenation-dehydrogenation catalysts, such as the metallic catalysts, lower temperatures or lower pressures or both may be employed, depending upon the activity of the particular catalyst. The hydrogen transfer reaction will thus be effected in either wholly vapor phase or under liquid-vapor phase conditions, depending upon the temperature and pressure necessary for use with the particular catalyst employed.

The contact time for the hydrogen transfer reaction will likewise vary with the activity of the particular catalyst employed, but will usually range from 0.1 second to 10 seconds. Charge rates corresponding to 0.1 to 2.0 volumes of liquid charge stock per volume of catalyst per hour will usually be satisfactory when employing oxide or sulfide type catalysts with recycle of process gas. I prefer to use charge rates of 0.5 to 1.5 volumes per hour with such catalysts at reaction temperatures of 800 to 900° F. and gas recycle rates of 1000 to 10,000 cubic feet per hour per barrel of liquid charge.

The hydrogen transfer reaction may be effected in any suitable type of apparatus commonly employed for high temperature catalytic reactions. The reactor may suitably be provided with multiple charge ports for the olefinic charge in order to obtain improved heat balance through the reactor between the exothermic hydrogenation reaction of relatively high reaction velocity and the endothermic dehydrogenation reaction of relatively lower reaction velocity. Various other modifications of apparatus and operating procedure may also be employed without departing from the scope of my invention.

One embodiment of my invention is illustrated diagrammatically in the accompanying drawing. Referring to this flow diagram, a dependanized catalytically cracked naphtha is charged to fractionator 1, and a light naphtha of about 220° F. end point is taken overhead. The overhead vapors from the fractionator 1 are charged through preheater 2 to the isomerization reactor 3 which is packed with an alumina catalyst, or other suitable extensive surface isomerization catalyst.

The isomerizate leaving reactor 3 is charged through compressor 4 to the hydrogen transfer reactor 5, which is packed with an alumina-molybdena catalyst or other suitable hydrogenation-dehydrogenation catalyst. By means of the compressor 4 and suitable coolers or heat exchangers, not shown, the isomerizate is brought to the desired temperature and pressure for charging to the hydrogen transfer reaction. Alternatively, the isomerizate may be fractionated to remove any polymer or other heavy ends, and the condensed distillate may then be pumped to the hydrogen transfer reactor through a suitable preheater. The isomerizate is suitably charged to the reactor 5 through multiple charge ports, as illustrated in the drawing, in order to maintain the desired reactor heat balance.

A dependanized straight-run naphtha is charged to fractionator 6, and a heavy naphtha bottoms fraction of about 250° F. initial boiling point is obtained for charging to the hydrogen transfer reaction. The light overhead fraction is condensed in the condenser 7, and is suitably blended with the hydrogen transfer reaction product to produce motor fuels.

The heavy naphtha from the bottom of the fractionator 6, together with recycle gas from the compressor 8, is charged to the preheater 9, or directly to the hydrogen transfer reactor 5, depending on the temperature requirements for the catalyst employed and the amount of heat supplied by the hot isomerizate vapors from compressor 4.

The product leaving the hydrogen transfer reactor 5 is charged to a fractionator 10, where any polymer or other high boiling material may be removed as fractionator bottoms. The fractionator 10 may also serve to separate the reaction product into fractions of desired boiling ranges for aviation grade fuels, automotive grade fuels, and the like. In the modification shown in the drawing the full range reaction product is taken overhead from the fractionator 10 through condenser 11 and gas separator 12 to the fuel blending tank 13. The hydrogen-containing gas, taken from the top of the gas separator 12, is recycled in the desired volume through compressor 8 to the hydrogen transfer reactor 5.

The light straight-run condensate from condenser 7, and the heavy cracked naphtha bottoms fraction from fractionator 1 may also suitably be charged to the fuel blending tank 13, together with sufficient isopentane to impart the required volatility characteristics to the resulting blend.

It may be seen that in the modification illustrated, a fuel of the desired gum stability and anti-knock characteristics is obtained, utilizing all of the two charge stocks, but requiring treatment of only a portion of each. It is to be understood, however, that the various fractions need not be recombined but can be used separately in different types of motor fuels, or for other purposes, as desired. Alternatively, charge stocks comprising full range or dependanized naphthas may be charged directly to the reactors without prefractionation, or only one of the charge stocks may be prefractionated, as desired. It should also be understood that the drawing discussed above is merely diagrammatic, and that numerous elements such as valves, pumps, heat exchangers, and the like have been omitted for the sake of simplicity.

My invention will be further illustrated by the following specific example:

Example

A dependanized catalytically cracked naphtha of about 150 to 400° F. boiling range is distilled to obtain a light overhead fraction of about 69° A. P. I. gravity and about 220° F. end point, containing the major proportion of the olefin content of the charge. The more saturated bottoms fraction is used directly in the product fuel blends, but the overhead fraction is first subjected to isomerization and reaction with naphthenes.

The isomerization is effected at about 750° F. and atmospheric pressure, using alumina as the isomerization catalyst. The light naphtha overhead stream from the fractionator, amounting to approximately 20 barrels per hour, is charged through a preheater to a reactor packed with 50 cubic feet of alumina. The resulting contact time in the reactor is approximately 2 seconds. The vapors leaving the isomerization reactor are then compressed to 300 pounds per square inch and 850° F., and charged to the hydrogen transfer reactor.

A dependanized straight-run naphtha of about

150 to 400° F. boiling range is distilled to obtain a heavy bottoms fraction of about 49° A. P. I. gravity, and 250 to 400° F. boiling range. This fraction contains about 26% of naphthenes, constituting the bulk of the hydro-aromatics in the charge naphtha. The light overhead fraction is used directly in the product fuel blends, but the heavy fraction is first reacted with the light cracked naphtha isomerizate.

The heavy straight-run bottoms stream from the fractionator, amounting to approximately 30 barrels per hour, is charged to a preheater together with about 17,500 cubic feet per hour of recycle process gas. The mixture is heated to about 850° F. at 300 pounds per square inch pressure, and is charged to the hydrogen transfer reactor together with the light cracked naphtha isomerizate. The reactor is packed with about 280 cubic feet of an alumina-molybdena catalyst containing about 10 per cent by weight of molybdena. The contact time at these charge rates and reaction conditions is between 1 and 2 minutes.

The product leaving the hydrogen transfer reactor is distilled to separate any polymer or other high boiling reaction products. The distillate is then blended with the untreated fractions of the charge stocks, and sufficient isopentane is added to meet volatility requirements. The resulting blend is an excellent automotive grade fuel, which may safely be leaded to an octane number of 85 or higher.

A base stock for the production of aviation grade fuel is obtained by fractionating the product from the hydrogen transfer reactor to obtain a 340° F. end point overhead fraction. The heavier bottoms fraction is then blended with the untreated fractions of the charge stocks for the production of automotive grade fuel. The 340° F. end point fraction is blended with a minor proportion of isobutane-isobutene alkylate and sufficient isopentane for volatility requirements. The resulting blend meets all specifications for aviation fuels with respect to storage stability and gum formation. Anti-knock specifications considerably in excess of 100 octane are easily met by the use of 4 cc. of tetraethyl lead per gallon, and adjustment of the alkylate content of the blend.

It is to be understood, of course, that the above example is merely illustrative, and does not limit the scope of my invention. Other olefinic and cyclic charge stocks may be used in place of the cracked and straight-run fractions employed in this example. Similarly other isomerization catalysts and hydrogen transfer catalysts may be used, and the reaction conditions may be modified in numerous respects in accordance with the foregoing discussion. In general, it may be said that the use of any equivalents or modifications of procedure which would naturally occur to those skilled in the art is included in the scope of this invention. Only such limitations should be imposed on the scope of my invention as are indicated in the appended claims.

I claim:

1. A process for the production of aviation grade fuel base from cracked and straight run naphthas which comprises obtaining a cracked naphtha comprising hydrocarbons boiling in the range of 150 to 400° F. by conversion of hydrocarbons at a predetermined cracking temperature, separating from said cracked naphtha a light fraction consisting of hydrocarbons boiling below about 220° F. and containing olefins which are predominantly of relatively low branched chain character, subjecting said light fraction in vapor phase to separate contact with a solid isomerizing catalyst comprising alumina for not in excess of about 5 seconds, effecting said contact under substantially non-polymerizing conditions at a temperature below said cracking temperature and in the range about 700 to 800° F., such that substantial conversion of olefins into olefins of increased branched chain character occurs, separating from the straight-run naphtha a fraction boiling in the range about 250 to 400° F. rich in cyclic hydrocarbons containing alicyclic methylene groups, subjecting the catalytically treated cracked fraction to reaction with said straight-run fraction by contact with an alumina-molybdena dehydrogenation-hydrogenation catalyst containing about 10% by weight of molybdena at a temperature in the range about 800 to 900° F., effecting this latter contact under a pressure in the range about 100 to 600 pounds and employing a time of contact between catalyst and hydrocarbons of about 0.1 to 10 seconds such that hydrogen transfer from cyclic straight-run hydrocarbons to olefins occurs, and fractionating the effluent hydrocarbons from said hydrogen transfer reaction to separate therefrom a distillate product consisting of hydrocarbons boiling below about 340° F.

2. A process for the production of an aviation grade fuel base and an automotive fuel base from cracked and straight-run naphthas which comprises obtaining a cracked naphtha comprising hydrocarbons boiling in the range of about 150 to 400° F. by conversion of hydrocarbons at a predetermined cracking temperature, separating said cracked naphtha into a light fraction consisting of hydrocarbons boiling below about 220° F. and a heavier fraction, said light fraction containing olefins predominantly of relatively low branched chain character, separating straight-run naphtha of about 150 to 400° F. boiling range into a light fraction and a heavier fraction boiling in the range about 250 to 400° F., said heavier fraction containing naphthenes, subjecting said light fraction of cracked naphtha in the vapor phase to separate contact with a solid isomerizing catalyst comprising alumina for not in excess of about five seconds, effecting said contact under substantially non-polymerizing conditions at a temperature below said cracking temperature and in the range about 700 to 800° F. such that isomerization of olefins occurs, subjecting the resulting isomerized hydrocarbons to reaction with said straight-run heavy fraction by contact with an alumina-molybdena dehydrogenation-hydrogenation catalyst containing about 10% by weight of molybdena at a temperature in the range 800 to 900° F., effecting said latter contact under a pressure in the range about 100 to 600 pounds and with a time of contact between catalyst and hydrocarbons of about 0.1 to 10 seconds such that hydrogen transfer from naphthenes to olefins occurs, fractionating the effluent hydrocarbons from said hydrogen transfer reaction into a light fraction boiling below about 340° F. suitable as an aviation grade fuel base and a heavier fraction, and blending said last mentioned heavier fraction with said heavy cracked fraction and said light straight-run fraction to produce automotive-grade fuel.

3. A process for the production of aviation grade fuel base from cracked and straight-run naphtha which comprises obtaining a cracked naphtha comprising hydrocarbons boiling in the

range of about 150 to 400° F. by conversion of hydrocarbons at a predetermined cracking temperature, separating from said cracked naphtha a light fraction consisting of hydrocarbons boiling below about 220° F. and containing olefins which are predominantly of relatively low branched chain character, subjecting said light fraction in vapor phase to separate contact with a solid isomerizing catalyst comprising alumina for not in excess of about five seconds, effecting said contact under substantially non-polymerizing conditions at a temperature in the range about 700 to 800° F. such that substantial conversion of olefins into olefins of increased branched chain character occurs, subjecting the catalytically treated cracked naphtha fraction to reaction with straight-run naphtha containing naphthenic hydrocarbons in substantial amount by contact with a dehydrogenation-hydrogenation catalyst at a temperature in the range about 800 to 900° F., effecting this latter contact under a pressure in the range about 100 to 600 pounds and employing a time of contact between catalyst and hydrocarbons of about 0.1 to 10 seconds such that hydrogen transfer from cyclic straight-run hydrocarbons to olefins occurs, and fractionating the effluent hydrocarbons from said hydrogen transfer reaction to separate therefrom a distillate product consisting of hydrocarbons boiling below about 340° F.

4. The method according to claim 3 in which the dehydrogenation-hydrogenation catalyst comprises alumina-molybdena containing about 10% by weight of molybdena.

5. A continuous method of preparing gasoline rich in aromatic hydrocarbons and saturated aliphatic hydrocarbons from virgin naphtha and cracked naphtha involving dehydrogenation of hydrocarbon constituents of the straight-run naphtha and hydrogenation of hydrocarbon constituents of the cracked naphtha concurrently in the same reaction zone which comprises maintaining an elongated reaction zone containing a solid stationary mass of dehydrogenation-hydrogenation catalyst through which hydrocarbons undergoing treatment flow from inlet to outlet, continuously introducing to the inlet of said zone straight-run naphtha containing naphthene hydrocarbons in substantial amount at a temperature of about 800 to 900° F., effecting dehydrogenation of naphthenic constituents of said straight-run naphtha such that substantial hydrogen is liberated, subjecting cracked naphtha boiling in the range of about 150° F. to 220° F. to brief contact with an alumina isomerizing catalyst at a temperature in the range of about 700 to 800° F. under substantially non-polymerizing conditions to effect isomerization of olefins to olefins of increased branched character, continuously introducing the resultant isomerized product to the reaction zone at a plurality of succeeding points intermediate the inlet and outlet of the reaction zone, effecting hydrogenation of cracked naphtha during flow through the contact mass, continuously withdrawing from the outlet of said reaction zone an effluent stream of naphtha hydrocarbons rich in aromatic and saturated aliphatic hydrocarbons and containing hydrogen gas, separating said hydrogen gas, and recycling the separated gas to the reaction zone in amount sufficient to maintain therein an atmosphere of hydrogen.

CLAUDE W. WATSON.