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3,193,490

**COMBINED JET FUEL-GASOLINE PRODUCTION**  
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This invention relates to a process for separating a hydrocarbon fraction such as a petroleum distillate into two products, one of which consists of the straight chain paraffinic components of the fraction which is an excellent jet fuel and the other fraction of which is the cyclic and branched chain hydrocarbons which are thereafter converted into an effective gasoline product of high octane number and desirable burning characteristics. More specifically, this invention concerns a process for recovering the normal paraffinic components of a jet fuel hydrocarbon fraction having an end boiling point not in excess of about 600° F. utilizing a molecular sieve sorbent as the separating agent to recover the normal paraffinic components which are desirable jet fuel constituents and thereafter reforming the raffinate stream from the separation stage of the process at mild reaction conditions to thereby produce a gasoline product having a high octane number and desirable burning characteristics.

One object of this invention is to provide a process for recovering the normal paraffinic components of a jet fuel boiling range fraction to thereby produce a product having optimum properties for use as a jet fuel. Another object of this invention is to provide a method for pre-treating a gasoline boiling range fraction to remove the components of the fraction which are difficult to reform and thereby provide a feed stock to a reforming reaction which is capable of being reformed to produce a high octane gasoline product at low-severity reaction conditions, at which conditions the yield and octane number of the resulting reformat are maximized. Still another object of this invention is to enhance the economic value of a gasoline boiling range fraction by separating the fraction into component cuts, each having optimum properties for a particular use.

In one of its embodiments this invention relates to a combination process which yields a fraction having optimum properties for jet fuel use and another fraction having optimum properties for use as a gasoline motor fuel which comprises contacting a jet fuel boiling range hydrocarbon fraction with a molecular sieve selective for normal hydrocarbons, separating a raffinate stream consisting of branched chain and cyclic hydrocarbons, recovering the normal hydrocarbons from the molecular sieve as said product having optimum properties for jet fuel use, reforming said raffinate stream in the presence of hydrogen and a reforming catalyst at low-severity reforming conditions and recovering a gasoline boiling range fraction from the reforming reaction product as said fraction having optimum properties for gasoline motor fuel use.

One of the important characteristics required for petroleum fractions boiling in the gasoline and lower kerosene boiling ranges for use as fuels in jet engines is that the fuel burns with a non-luminous flame. The achievement of this characteristic in a jet fuel permits a jet engine to operate at a higher combustion temperature for a given temperature of the metal parts of the jet engine itself. That is, when a fuel capable of burning with a non-luminous flame is utilized in a jet plane, the temperature differential between the combustion gas and the metallic components of the jet engine may be substantially greater and as a consequence, the fuel may be burned in a jet engine with a higher rate of efficiency of fuel utilization and a greater thrust output from the engine can be ob-

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tained at the permissible temperature limit of the metal components of the jet engine. Although most liquid, combustible hydrocarbons, can be employed as a source of fuel in jet engines, certain fractions of petroleum boiling in the gasoline range and lower kerosene boiling range are particularly suitable because of their high energy yield (thrust) per pound of fuel. Another desirable characteristic of a fuel for jet engine use is the absence of luminosity when the fuel combustion products are exhausted from the exhaust port of the engine. Of the hydrocarbons which are liquid at ground temperatures and pressure and which do not solidify at the subzero temperatures of the upper atmosphere in which jet engines customarily cruise on long range flights, the fractions boiling in the gasoline and lower kerosene boiling ranges, preferably up to about 500° F. and not in excess of about 600° F. at normal pressures, are especially suitable for jet engine use. Of these normally liquid hydrocarbons it has been found that the most desirable species within this range of boiling points are the normal paraffins which, upon combustion, have the least degree of luminosity and the highest thrust per pound of the various structural classes of hydrocarbons. On the other hand, the olefins, naphthenes, aromatics and branched chain hydrocarbons occurring within the foregoing boiling range materials burn with the highest degree of luminosity and yield the lowest thrust per pound of fuel. Accordingly, the higher the normal paraffin content of the hydrocarbon fractions utilizable as a jet fuel, generally within the range of carbon atom content of from C<sub>6</sub> to about C<sub>12</sub>, the more desirable is the fuel for jet engine use. Ideally, hydrocarbon fractions in the C<sub>7</sub> to C<sub>11</sub> range and composed of normal paraffinic hydrocarbons are the preferred fuels for jet engine use.

Branched chain and cyclic hydrocarbons, including particularly, aromatic hydrocarbons, such as benzene and toluene, are, on the other hand, particularly suitable and especially preferred for gasoline fuels for use in internal combustion engines. Thus, it is well-known that of the gasoline boiling range hydrocarbons the isoparaffins are much more desirable for use in internal combustion engines than normal hydrocarbons, because of their more desirable antiknock ratings (knock resistance in internal combustion engines operated at high compression ratios) and the antiknock rating increases as the degree of branching of the aliphatic chain increases. Of the cyclic hydrocarbons boiling within the gasoline range, aromatic hydrocarbons have a substantially higher octane number and more desirable burning characteristics in high compression internal combustion engines than the corresponding naphthenic hydrocarbons. Accordingly, for gasoline use in an internal combustion engine, it is desirable to reform the hydrocarbon components boiling within the gasoline boiling range in order to increase the proportion of isoparaffinic hydrocarbons in the fraction and also to dehydrogenate and isomerize the naphthenic components into aromatic hydrocarbons, both of which classes have more desirable properties for use in high compression internal combustion engines.

The process of this invention provides a means of segregating the components present within a gasoline boiling range fraction of hydrocarbons into (1) a fraction having optimum properties for jet fuel engine use and (2) a separate fraction, the components of which may be reformed into a product especially suitable for gasoline use in an internal combustion engine. By segregating the normal paraffinic components from the gasoline boiling range feed stock in the present pretreatment operation, a product is recovered from the pretreatment stage consisting essentially of normal paraffins which are particularly suitable and preferred for jet fuel engine use, leaving a raffinate stream or fraction which is particularly suitable

and desirable as a feed stock to a reforming conversion from which a high quality gasoline product may be recovered having optimum properties for use in an internal combustion engine operated at high compression ratios. An additional advantage of the pretreatment stage of the present process is that by removing the normal paraffinic components from the feed stock prior to the reforming conversion, the latter stage of the process may be operated at less severe reforming conditions to produce the same octane number of product than when the reforming conversion is attempted on the same fraction prior to the removal of the normal paraffins. The advantages of operating at the less severe reforming reaction conditions is particularly apparent in the substantially greater yield of the desired product being obtained at the less severe reforming conditions in that less of the product is converted to the undesired light gaseous hydrocarbons and coke. It is well-known that the reforming process is a vigorous reaction which causes deep-seated changes in the structure of the hydrocarbons undergoing the reforming conversion. Hydrocracking, dearomatization, dehydrogenation and isomerization are the typical conversions which take place during a typical reforming process. In general, the degree of dehydrogenation, isomerization and aromatization increases with an increase in the severity of the reaction conditions; that is, as the pressure and temperature conditions, the time of contact of the feed stock with the catalyst are increased and as such other factors as the amount of acidic component in the catalyst composition are increased, the octane number of the product is increased; but accompanying such increased conversion is a marked, simultaneous increase in the deposition of carbonaceous deposits on the catalyst and the conversion of feed stock to low molecular weight, normally gaseous hydrocarbons having little use when the desired end product is a normally liquid gasoline boiling range product.

The preferred source of the hydrocarbon fractions utilized as feed stocks in the present process are the gasoline and light gas oil fractions of straight-run petroleum distillates which contain only small concentrations, if any, of olefinic hydrocarbons which, if present, may interfere in the processing steps involved in the present invention. The most desired fractions are separated as straight-run petroleum distillates boiling up to about 600° F. and more preferably, up to about 500° F., the gasoline boiling range fraction of 400° F. end point being separated from the reformate product. Although straight-run distillates constitute one of the most desirable petroleum fractions for use in the present process as feed stock and for the production of a jet fuel product, fractions having similar boiling ranges may also be utilized herein as charge stock, such as a fraction boiling up to 500° F. separated from the products of a catalytic cracking reaction (generally containing, however, higher concentrations of olefinic components than the corresponding boiling range fraction of a straight-run distillate), gasoline boiling range stocks prepared by the polymerization of lower olefinic hydrocarbons, such as propylene, butylene or mixed polymerization products of butylenes and propylene, gasoline boiling range fractions of petroleum reformates (which, however, generally contain higher proportions of aromatic components) and the generally paraffinic products recovered from the Fischer-Tropsch synthesis, as well as a variety of other sources which provide gasoline boiling range hydrocarbon fractions. Those charge stocks hereinabove specified which contain an appreciable proportion of olefinic components are preferably subjected to a prehydrogenation treatment in the presence of a suitable hydrogenation catalyst to convert these olefins to the corresponding paraffins prior to the separation treatment provided herein.

In the separation step of the present process wherein the normal paraffinic components of the feed stock are selectively recovered from the branched chain paraffinic and cyclic components, which may also be present in

the gasoline boiling range fraction utilized as feed stock, the hydrocarbon fraction is contacted with a so-called "molecular sieve" type of solid sorbent containing pores into which the normal paraffin components of the feed stock are selectively sorbed, but into which the branched chain and cyclic components present within the feed stock do not enter because the pore openings in the sorbent are not of sufficient size to accommodate the branched chain and cyclic hydrocarbon components having diameters greater than the pore openings in the molecular sieve sorbent. The pores present in the structure of such molecular sieve sorbents must have a cross-sectional diameter of about 5 Angstrom units but not greater than about 6 Angstrom units in order to exhibit the required selectivity to permit the entry of the normal paraffin isomers of the feed stock, while rejecting the branched chain and cyclic hydrocarbons having cross-sectional diameters greater than about 5 Angstrom units and are thus incapable of entering the pore openings of the solid sorbent. The term "sorbate," referred to herein is intended to designate those components of the hydrocarbon feed stock capable of entering the pores of the sorbent and of being selectively retained thereby; the term "raffinate" is intended to refer to the branched chain and cyclic components of the feed stock which have molecular diameters greater than will permit their entry into the pores of the sorbent. It is the former sorbate component which constitutes the select fraction of the feed stock utilizable as the premium jet fuel product hereof and the raffinate fraction of the feed stock is the material utilized herein as feed stock to the subsequent reforming stage of the process from which a premium grade gasoline product is recovered.

Suitable molecular sieve sorbents of the type hereinabove described, capable of sorbing and selectively retaining normal paraffin hydrocarbons within their porous structure include, particularly, certain metal aluminosilicates formed by the dehydration of the corresponding zeolitic hydrated metal aluminosilicates, which by virtue of such dehydration contain pores of about 5 Angstrom units in cross-sectional diameter. Of these, the zeolitic calcium aluminosilicates, especially dehydrated to develop porous structures of about 5 Angstrom units, constitute one of the most desirable and effective sorbents contemplated herein, although other metal aluminosilicates in which the metal is selected from other alkaline earth metals such as barium, magnesium and cesium, or from such metals as zinc, copper, iron, nickel, cobalt, etc., may also be prepared and utilized as sorbents herein. The material known by its trade name as "Linde 5A molecular sieves" and Davison Chemical Company "Microtraps" are generally available commercial sources of sorbents for use in the present process. The sorbents are generally prepared by mixing a suitable source of silica sol or a silicic acid ester such as an alkali metal silicate (sodium silicate or "water-glass" is a generally available source) or an alcohol ester of silicic acid such as ethyl orthosilicate with a source of an ionizable aluminum salt capable of yielding alumina or aluminum hydroxide by reaction with the silicate or with alkali. By maintaining certain ratios of alkali metal to silica, alumina to silica and water to silica in the reaction mixture and by maintaining the temperature of the aqueous mixture at crystallization conditions, a hydrated alkali metal aluminosilicate forms in a zeolitic crystalline modification which may thereafter be filtered, dried and calcined at temperatures not in excess of about 500° C. to dehydrate the water of crystallization from the alkali metal aluminosilicate, leaving pores within the resulting crystals having pore diameters of about 4 Angstrom units. The sorbents containing sieve pores of about 5 Angstrom units are prepared by ion-exchange of the alkali metal aluminosilicate with an aqueous solution of a salt of the metal to be placed in the chemical composition of the ultimately desired molecular sieve sorbent. Thus, in

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order to form a calcium aluminosilicate having pores of about 5 Angstrom units, constituting one of the most desirable sorbents for use in the separation step of the present process, an aqueous slurry of sodium aluminosilicate crystals in hydrated form is mixed with an aqueous solution of a calcium salt, such as calcium chloride, which, by ion-exchange, exchanges the sodium present in the aluminosilicate crystals with calcium. When the latter crystals, recovered from the resulting aqueous slurry, are dehydrated and calcined, molecular sieve sorbent crystals having pore diameters of about 5 Angstrom units are produced; these crystals are capable of being utilized directly in the sorption step of the present process or they may be composited with a binder clay, extruded into larger particles and thereafter utilized as the present sorbent.

Other selective sorbents of the molecular sieve type, capable of selectively retaining the normal paraffin constituents of the present feed stock include, among others, certain activated carbons formed by carbonization of acid-hydrocarbon sludges produced as by-products in certain acid-catalyzed hydrocarbon conversion processes, subsequently calcined at a temperature sufficient to carbonize the sludge hydrocarbons, and thereafter washed with water to free the carbonization residue of any acidic material. Other sorbents of the molecular sieve type are prepared from certain activated aluminas formed by high temperature calcination of aluminum oxide or aluminum hydroxide and containing pores having cross-sectional diameters of about 5 Angstrom units. Still another class of material utilizable herein as a molecular sieve sorbent for separating the normal paraffinic component from the feed stock is urea in aqueous or alcoholic solution or, if utilized in a fixed-bed type of process, the urea crystals themselves, which also selectively combine with the normal or straight chain components of the feed stock to form molecular complexes or adducts capable of existing in crystalline form at certain temperatures, generally below about 40° C. After contact with the feed stock, the resulting adduct crystals are separated, for example, by filtration, and the normal paraffin components separated from the crystals by heating the latter to a temperature above about 30° C. whereby the normal paraffin hydrocarbons complexed with the urea separate out as an insoluble upper phase from the lower layer of molten urea crystals. In an alternative type of separation process, thiourea may be utilized as the adduct-forming reagent, combining selectively with isoparaffinic and cyclic hydrocarbons to form a crystalline adduct thereof. The normal paraffins remain free and may be recovered from the adduct.

Processes for the utilization of molecular sieve sorbents and the process conditions required for their use are well-known in the prior art and reference is made herein to such art for the specific details involved in the use of such materials.

In carrying out the separation stage of the present combined process, the hydrocarbon feed stock is contacted with the molecular sieve sorbent at the particular temperature and pressure conditions and in either liquid or vapor state suitable for the particular molecular sieve sorbent utilized in the separation stage. Thus, in the use of urea or thiourea as the separating agent, relatively low temperatures at which the feed stock exists in the liquid phase must be employed. When utilizing the refractory metal aluminosilicate molecular sieves, on the other hand, either liquid or vapor phase operation may be utilized, although even in the use of the latter sorbents, relatively low temperatures and pressures sufficient to maintain the feed stock in substantially liquid phase are preferred.

Upon contact with the particles of sorbent, the straight chain components present in the feed stock selectively enter the pore openings in the structure of the sorbent and are thereafter retained within the pores by physical

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forces. The non-sorbed effluent, or raffinate, comprising the branched chain or cyclic hydrocarbon components of the feed stock continues its flow through the bed of molecular sieve sorbent and is ultimately withdrawn from the separation step as the raffinate fraction of the feed stock, hereinafter charged into the reforming stage of the process as feed stock thereto. The normal or straight chain components retained by the sorbent within the porous structure of the molecular sieve are recovered from the "spent" sorbent by desorption with a suitable displacing material or by a change of the physical conditions which result in the displacement or desorption of the retained normal paraffins from the molecular sieve sorbent. A preferred method of desorption which enables the sorbent to be utilized in a swing cycle process arrangement involves the use of one bed of sorbent in the sorption stage to accept feed stock while simultaneously another bed of sorbent undergoes desorption which regenerates the sorbent for further contact with the feed stock when the fluid streams entering the two beds of sorbent are subsequently shifted. This method of desorption depends upon the displacement of the sorbed normal component of the feed stock by surrounding the particle of sorbent containing the sorbed normal component with a stream of another normal hydrocarbon compound boiling above or below the boiling point of the sorbed normal component of the feed stock to enable the mixture subsequently recovered to be readily separated by fractional distillation means. In this method of desorption, it is essential that the molar ratio of desorbent supplied to the sorbent particle is sufficient to cause the displacement by the mass action effect.

One of the preferred desorbents for use in the present process is a normal paraffin of lower molecular weight than the sorbed normal component of the feed stock, although a paraffin of higher molecular weight may also be used as desorbent and in some instances may be preferred. The desorbent is supplied to the "spent" sorbent in a quantity sufficient to provide a mass action effect which displaces the sorbed normal paraffin from the molecular sieve sorbent and which may be subsequently fractionated from the desorption effluent as an overhead, if a lower molecular weight paraffin is used as desorbent or as a distillation bottoms if a higher molecular weight paraffin is utilized as desorbent. Thus, normal paraffins from normal butane to about normal hexane constitute suitable desorbents for use in the present process when the desorbent is to be fractionated from the desorption effluent as an overhead.

Desorption of the sorbed normal paraffin may also be effected by heating the "spent" sorbent and/or reducing the pressure thereon, preferably while passing through the "spent" sorbent a gas which is inert to both the sorbent and the sorbate component displaced from the "spent" sorbent. Thus, as a perfluent stream of an inert stripping gas such as nitrogen, isobutane, normal butane, carbon monoxide, methane, etc., is passed through the mass of spent sorbent, the mass of sorbent is heated by raising the temperature of the stripping gas and recovering the sorbate component from the desorption effluent by cooling and condensing the sorbate therefrom. Desorption is also promoted by reducing the ambient pressure on the spent sorbent while passing an inert gas through the mass of sorbent. Stripping the sorbate component from the sorbent in this manner thereby regenerates and reactivates the sorbent for repeated reuse in the system.

The normal paraffin components recovered from the feed stock by the molecular sieve separation technique are especially desirable jet fuels because of their high luminosity index rating and their desirable burning characteristics in that they produce a large thrust per pound of fuel, being in this regard, much more effective for jet fuel purposes than their corresponding branched chain and cyclic isomers.

In accordance with the combination process of this invention, the raffinate stream recovered from the normal paraffin separation stage of the present process, consisting of branched chain and cyclic hydrocarbons initially present in the feed stock to the process is subjected to a reforming conversion in the presence of hydrogen at reforming conditions which are relatively less severe than would be required to obtain a product having the same octane number when reforming the feed stock without removing the normal paraffins therefrom in a preceding separation procedure.

It is well-known that the degree of conversion or severity of the reforming conversion is influenced directly by several reaction variables, including the temperature, the pressure, the space velocity of the feed stock relative to the catalyst, and the catalyst composition (mostly by the quantity of acidic component in the catalyst) and any one or more of these factors may be varied independently of the other to affect the severity of the reaction. At the more severe reaction conditions, the proportion of feed stock converted to light, non-condensable gases such as hydrogen, methane, ethane and other normally gaseous hydrocarbons is increased and inversely the amount of liquid product constituting the desired end product of the process decreases directly as the severity of the reaction conditions increases. It is also known that the octane number of the desired liquid product increases in direct proportion to the severity of the process conditions, caused by more deep-seated isomerization and dehydrogenation reactions occurring during the reforming conversion. However, it has now been found that when the normal paraffin components are removed from the charge stock prior to the reforming conversion, for example, by the first stage of the process of this invention, the same or higher octane number may be obtained in the desired liquid portion of the product without increasing the severity of the reaction condition to those levels at which conversion of the normal components must be effected.

Although generally, conversion temperatures within the range of from about 800° to about 1000° F. or even higher are required to produce a product having an octane number in the range set for premium gasolines, generally above about 90 octane number, the present process may, on the other hand, be operated at temperatures in the range of from about 650° to about 850° F. when utilizing the raffinate feed stock provided herein. The pressure maintained within the reforming conversion reactor is superatmospheric, up to about 3000 pounds per square inch, although this reaction condition may be varied considerably without substantially changing the character of the product. Preferred pressures are from about 500 to about 1500 pounds per square inch gauge, the depth of conversion generally increasing as the pressure maintained during the process is increased.

The reforming stage of the present process is preferably effected in the presence of a catalyst which is not only capable of effecting dehydrogenation of the naphthenes present in the feed stock to form aromatic hydrocarbons thereby, but is also capable of effecting hydrogenation and isomerization of the paraffinic and olefinic hydrocarbons to form more highly branched chain components. Satisfactory reforming catalysts for this purpose generally contain a metal oxide or sulfide of a metal selected from the elements of Group VIII of the Periodic Table supported on a refractory oxide, such as alumina. One of the preferred catalysts for this purpose is platinum supported on alumina containing an acidic component combined with the platinum and/or alumina, the catalyst being described in U.S. Patent No. 2,478,916, issued August 16, 1949. A particularly preferred catalyst composition useful in the reforming stage of the process comprises alumina composited with platinum and a combined halogen, of the type described in U.S. Patent No. 2,479,109, issued August 16, 1949. The preferred platinum-

alumina-combined halogen type of reforming catalyst contains from about 0.01 percent to about 1 percent by weight of a Group VIII noble metal, such as platinum, palladium or rhodium and from 0.1 percent to about 5 percent by weight of a combined halogen such as chlorine, or a portion of the chlorine may be replaced by fluorine in an amount of from about 0.1 percent to about 3 percent by weight of the total composite. The lower levels of halogen content are particularly suitable if the severity of the reforming reaction is not reduced by reaction temperature reduction. Other reforming type catalysts may also be effectively utilized in the present process, including such catalyst compositions as molybdena-alumina composites containing from about 1 percent up to about 20 percent by weight of molybdena, chromia-alumina composites containing from 1 percent up to about 25 percent by weight of chromia, nickel and/or cobalt oxide or sulfide composited with alumina or combined with a preformed molybdena-alumina composite, as well as others recognized in the petroleum refining art for their reforming capacity.

The reforming reaction is preferably effected in the presence of hydrogen charged to the process in an amount sufficient to provide from about 1:1 to about 15:1 molar proportions of hydrogen per mol of hydrocarbon feed stock, the excess hydrogen usually being recycled in the process until its concentration in the recycle gas stream is reduced to less than about 50 mol percent. The reforming process is an equilibrium reaction, the formation of aromatic hydrocarbons by dehydrocyclization and isomerization being favored by high pressures up to about 3000 pounds per square inch gauge.

Depending upon whether the severity of the reforming reaction has been reduced by a prior reduction in temperature and/or acidic component in the catalyst composition, the rate of charging the feed stock relative to the catalyst may also be increased in order to reduce the severity of the conversion. Thus, space velocities may be increased from about 0.5 volume of feed stock in the liquid state per volume of catalyst per hour to liquid hourly space velocities in the range of from about 0.8 to 3.0, depending, as indicated, on the modification of other reaction variables to reduce the severity.

The products of the reforming conversion comprising generally a non-condensable gaseous fraction made up in large part of hydrogen may be recycled to the reforming conversion until the mol percent of hydrogen in the gas stream is reduced to less than about 50 mol percent. A normally liquid fraction containing C<sub>4</sub> to about C<sub>12</sub> hydrocarbons, generally a large proportion of which are of isoparaffinic and aromatic structure is separated as a distinct cut, comprising the desired high antiknock gasoline product. Its lead-free antiknock rating may be well above 100 and is readily classified as a premium gasoline for use in internal combustion engines of high compression ratios.

This invention is further described with respect to several of its specific embodiments in the following examples, which, however, are not introduced herein for the purpose of limiting the broad scope of the invention but merely for illustrating working embodiments of the invention.

#### Example I

A straight-run petroleum distillate separated from a Pennsylvania crude oil and having an end boiling point of about 500° C. is utilized as feed stock in a combination process involving separation of the normal paraffin components of the fraction with a calcium aluminosilicate molecular sieve (Linde Products Co. 5A sieves), followed by reforming the raffinate to produce a gasoline motor fuel product of high octane number.

The feed stock is a mixture of saturated (i.e., paraffinic and cycloparaffinic) hydrocarbons containing from 4 to 12 carbon atoms. Analysis of the fraction indicates that

the hydrocarbon components are of the following types in the indicated proportions:

	Percent by weight	
n-Paraffins -----	38	5
Branched chain paraffins -----	46	
Cycloparaffins -----	12	
Aromatics -----	4	

The above fraction at a temperature of 30° C. (i.e., in liquid phase) is permitted to flow downwardly through a vertical column of the 5A molecular sieves until n-paraffins began to appear in the effluent from the bottom of the column, as indicated by infra-red analysis of timed samples of the effluent raffinate, the raffinate being separately reserved for subsequent conversion in the reforming stage of the present combination process. Approximately 1 ft.<sup>3</sup> of molecular sieves for each 0.8 gallon of feed stock is required to complete the recovery of n-paraffins from the feed stock. The residual feed stock remaining in the column is thereafter flushed from the molecular sieve particles with liquid isobutane charged at a pressure of 20 lbs./in.<sup>2</sup>, the flush effluent being separately recovered to determine the volume of feed stock thereby recovered after distilling overhead the isobutane. The sorbed n-paraffins retained within the pores of the sieves are then recovered by passing a liquid stream of n-butane at 20 lbs./in.<sup>2</sup> through the column of "spent" sieves and collecting the desorbent effluent in a separate container. After distillation of the n-butane from the desorbent effluent, the residue is analyzed for n-paraffin content, the analysis indicating that 98.6 percent of the sorbate product consists of n-paraffins of C<sub>5</sub>-C<sub>12</sub> chain length and 95 percent of the n-paraffin content of the feed stock is recovered, the remainder consisting of n-butane which is distilled overhead from the desorption effluent. When a sufficient quantity of the n-paraffin product had been accumulated to provide a test of these paraffins as fuel for a jet engine, the product was compared from the standpoint of luminosity, smoke production and thrust output with the initial feed stock mixture. These tests establish the superiority of n-paraffins as jet fuel, the n-paraffin product burning with a clean, blue-white exhaust compared to a more highly luminous yellowish-red, smoky exhaust of the initial feed stock. The n-paraffin product yields a thrust output some 8 percent greater than the initial feed stock mixture under similar test conditions.

The raffinate effluent of the initial separation stage of the process utilizing the 5A molecular sieves and representing approximately 62 percent by weight of the feed stock is composed for the most part of cycloparaffins and slightly branched chain isoparaffins and has a Research Method octane number (without added TEL) of 62.

The above raffinate effluent is subjected to a reforming conversion by charging the raffinate at a pressure of 700 lbs./in.<sup>2</sup> and in the presence of 1.5 mol percent hydrogen through a catalyst-packed tubular reactor maintained at a temperature of 700° F., the catalyst being a composite of alumina with 0.375 percent by weight of platinum, 0.35 percent by weight of combined chlorine and 0.35 percent by weight of combined fluorine, in the form of pellets 1/8-inch by 1/8-inch size. The reformat product is cooled and the normally gaseous portion of the product at the process pressure is cooled to 60° F. to separate a non-condensable gas fraction (consisting of 89 percent H<sub>2</sub> and small quantities of methane and ethane) from the condensable gases consisting of C<sub>3</sub> and C<sub>4</sub> paraffins. The normally liquid product (gasoline fraction) is distilled from the product to an end-point of 400° F. A yield of gasoline product of 96 weight percent is obtained, the product having a Research Method octane number (without added TEL) of 96. Analysis of the gasoline product indicates that it contains 24 percent by weight of aromatics formed by dehydrogenation and aromatization of the cycloparaffinic components and 69 percent by weight

of isoparaffinic components of highly branched chain structure.

The overall yield of useful, liquid products is 96.5 percent by weight of the initial feed stock.

#### Example II

In a second run utilizing the process flow of Example I, above, as well as the molecular sieve sorbent and the reforming catalyst specified in the foregoing example, except that the feed stock is a fraction having an end boiling point of about 600° F. of a catalytically cracked naphtha, lightly prehydrogenated to eliminate olefinic components. Analysis of the charge stock indicates the following composition in the indicated proportions:

	Percent by weight	
n-Paraffins -----	46	15
Isoparaffins -----	25	
Cycloparaffins -----	3	
Aromatics -----	26	20

Separation of the above fraction into an n-paraffin sorbate product utilizing 5A molecular sieves, in accordance with the procedure described in Example I, yields a premium jet fuel containing 97.5 percent n-paraffins in a yield representing 44 percent of the naphtha charged.

The raffinate effluent of the foregoing separation, consisting of the branched chain and cyclic paraffins, as well as the aromatics contained in the initial charge stock are subjected to reforming at the reaction conditions and with the catalyst specified in Example I, above. The octane number (Research Method, without added lead) of the charge stock (400° F. end point fraction) compared to the gasoline boiling range cut of the reformat product is 54 vs. 91.

In a similar reforming conversion in which the initial 600° F. end point charge stock is utilized as feed stock to the reforming reaction, but the catalyst temperature is raised in 25° F. increments during the passage of feed stock into the reaction zone until the reformat product (400° F. end point) has an octane number of 91, the catalyst temperature must be increased to 900° F. to obtain a gasoline boiling range product of the same octane number as the product obtained by conversion of the raffinate effluent at 700° F. and the yield of gasoline boiling range product is 84 percent by weight of the feed stock compared to 94 percent by weight of the feed stock based on utilizing the raffinate effluent as feed.

I claim as my invention:

1. A combination process for producing a fraction having optimum properties for jet fuel use and another fraction having optimum properties for use as a gasoline motor fuel which comprises contacting a hydrocarbon fraction predominating in saturated hydrocarbons of from 4 to 12 carbon atoms and having an end boiling point of from about 500° to about 600° F. with a molecular sieve selective for normal paraffinic hydrocarbons, separating a raffinate stream consisting essentially of branched chain and cyclic hydrocarbons, recovering the normal paraffinic hydrocarbons from the molecular sieve and removing the same, without any further conversion thereof, from the process as said product having optimum properties for jet fuel use, reforming said raffinate stream in the presence of hydrogen and a reforming catalyst at low-severity reforming conditions and recovering a gasoline boiling range fraction from the reforming reaction product as said fraction having optimum properties for gasoline motor fuel use.

2. The process of claim 1 further characterized in that said hydrocarbon fraction is a straight-run petroleum distillate.

3. The process of claim 1 further characterized in that said hydrocarbon fraction has an end boiling point of about 500° F.

4. The process of claim 1 further characterized in that

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said molecular sieve is a dehydrated calcium aluminosilicate containing pores of about 5 Angstrom units in cross-sectional diameter.

5 5. The process of claim 1 further characterized in that said reforming catalyst is a composite of alumina, platinum and a halogen selected from the group consisting of chlorine and fluorine.

10 6. The process of claim 1 further characterized in that said low-severity reforming conditions comprise a reforming reaction temperature up to about 850° F.

7. The process of claim 1 further characterized in that

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said hydrocarbon fraction is a non-olefinic, catalytically cracked hydrocarbon fraction.

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