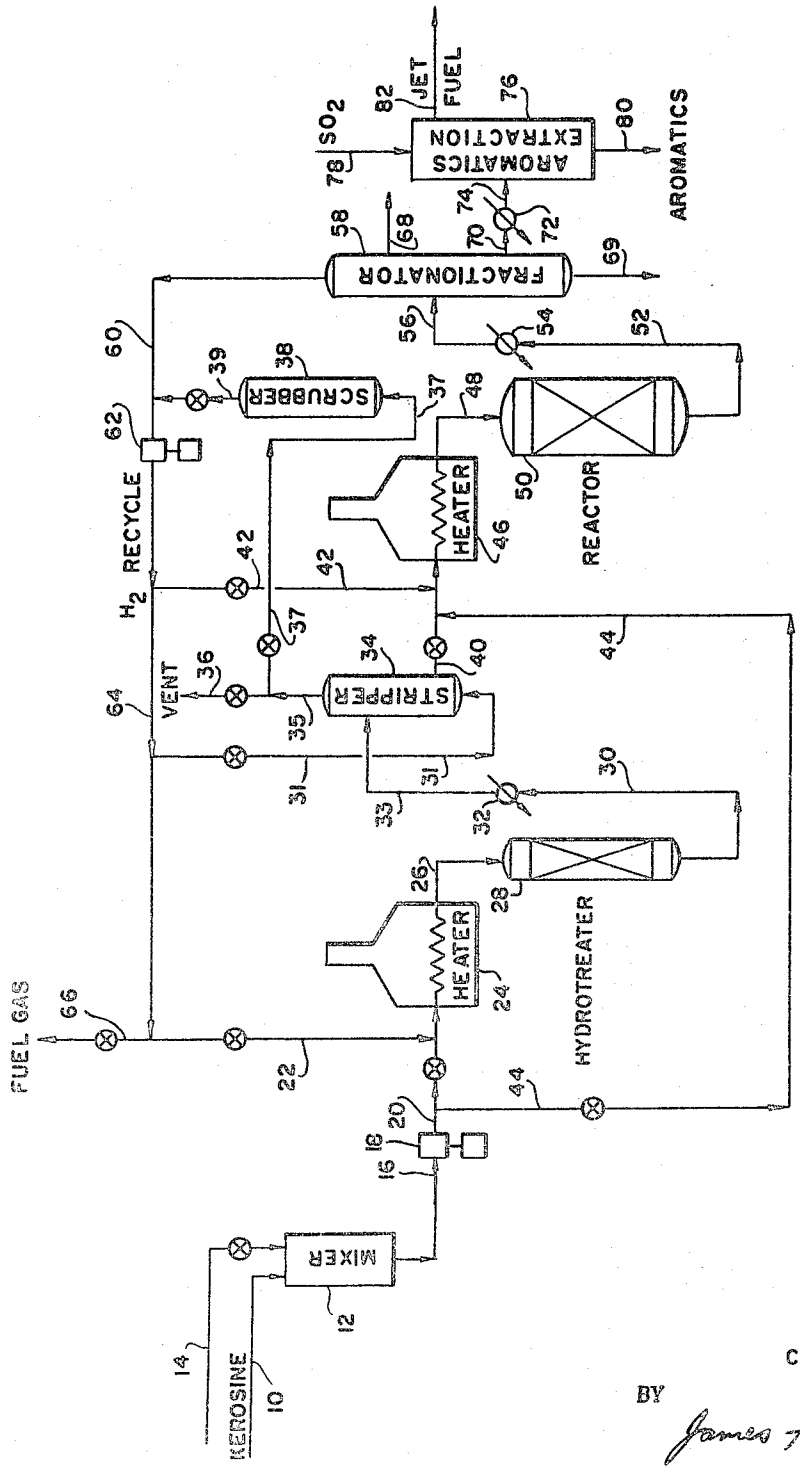
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JET FUEL PRODUCTION

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JET FUEL PRODUCTION

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The present invention relates to a process for the manufacture of hydrocarbon fuels for jet engines in general, including those of the turboprop type. In a particular embodiment, it is concerned with the production of fuels for jet engines of aircraft operating in supersonic speed ranges.

Although turbojet and turboprop engines may be operated with a variety of hydrocarbon fuels, specially refined kerosines are preferred for the purpose and suitable specifications for aviation kerosine jet fuels JP–4 and JP–5 are set forth in United States military specifications MIL–J–5624E.

In the case of supersonic jet planes operating under more severe conditions, especially in regard to extremes of temperature, more severe specifications are desirable for optimum performance than those established for the slower planes. In general, fuels boiling within the range between 300 and 600° F., and preferably between 350 and 550°, of high paraffinic contents (including isoparaffins) are desired; and they should not contain more than small amounts of aromatic hydrocarbons (for example, 5% or less). In view of the intense cold at the high operating altitudes of such aircraft, such fuel should have freezing points below about —20° F., and preferably below about —30° F. The supersonic fuels desirably comprise relatively high proportions of isoparaffins which have lower freezing points than paraffins containing the same number of carbon atoms per molecule; and they should not have substantial amounts of benzene, o-xylene and p-xylene for these compounds have relatively high solidification points. The net heat of combustion should be at least 18,890 British thermal units per pound (B.t.u./lbs.), and a high luminometer number (ASTM test D1740–60T) of at least about 90 is also sought to avoid excessive smoking during operation. In addition, the fuel should have a high flash point of at least 150° F. in combination with a low vapor pressure of less than 50 pounds per square inch (p.s.i.) at 500° F. High grade fuels for supersonic aircraft and their manufacture are described in detail in the copending application Ser. No. 173,044, filed Feb. 13, 1962 of Halik, Smith, and Streed, which application was later abandoned.

In the manufacture of jet fuels from kerosines, the principal conversion of hydrocarbons involves the dehydrogenation of naphthenes to aromatic hydrocarbons with liberation of hydrogen, and secondarily isomerization reactions. The aforesaid conversion may be carried out at elevated temperatures and pressures in the presence of large amounts of hydrogen in the form of hydrogen-rich refinery gases over a catalyst of the same type employed for reforming naphthas to upgrade their octane ratings.

Although the preferred kerosine feedstocks have a high content of normal and isoparaffins, difficulties are often encountered in converting them in the manner described as a result of an inadequate or borderline production of hydrogen during the catalytic conversion. This particular problem is of no great moment in refineries that have two or more naphtha reformers as one of the reforming units can easily generate enough by-product hydrogen in the routine reforming of naphtha to make up any hydrogen deficiency encountered in another reformer used for jet fuel production. However, very few refineries have more than a single catalytic reforming unit and commercial hydrogen from other sources is relatively expensive. In addition, it is usually necessary to pretreat the kerosine feed with hydrogen in order to avoid poisoning of the dehydrogenation catalyst by compounds containing sulfur, nitrogen or metals. Such a hydrogen treatment consumes some hydrogen which must be obtained from the dehydrogenation reaction if the overall process is to operate in a self-contained manner.

In the conversion of kerosines to jet fuels by such processes, it has been found that a production of about 300 standard cubic feet measured at 60° F. and standard atmospheric pressure (s.c.f.) of hydrogen per barrel (42 U.S. gallons) of normally liquid feed charged to the conversion zone constitutes a borderline operation and that producing about 340 s.c.f./b. or more is necessary to avoid hydrogen deficiencies. Approximately one-half of this hydrogen is needed to make up for leakage, mechanical losses and the hydrogen dissolved in the liquid product, while the balance is required for any preliminary purification of the feed with hydrogen that may be necessary and for venting from the system to avoid accumulating excessive amounts of inert gases in the recycle gas.

An object of the invention is to provide an improved process for the manufacture of jet fuels.

Another object of the invention is to provide adequate production of hydrogen in the manufacture of jet fuels from highly paraffinic feedstocks.

A further object of the invention is to provide a combined and self-sufficient process for the manufacture of jet fuels and selected aromatic hydrocarbons.

Still another object of the invention is to provide a self-sufficient conversion process for the manufacture of jet fuels from various charging stocks of a highly paraffinic nature.

A still further object of the invention is to provide a process for the manufacture of fuels for supersonic aircraft, which requires no external supply of hydrogen.

Still another object of the invention is to produce improved yields of jet fuel.

Other objects and advantages of the invention will be apparent to those skilled in the art upon consideration of the detailed disclosure hereinafter.

Unless otherwise indicated herein all temperatures are expressed as degrees Fahrenheit (° F.), pressures as pounds per square inch gage (p.s.i.g.), boiling points or ranges in degrees Fahrenheit at atmospheric pressure by the ASTM procedure, proportions in terms of weight and space velocities as volumes of normally liquid charge per volume of catalyst bed or beds per hour (LHSV). Furthermore, the expressions "major" and "minor" are used to describe more than half and less than half respectively of any given quantity.

The present invention is a process for the production of jet fuels which comprises blending a hydrocarbon feedstock containing paraffinic hydrocarbons and a relatively low content of naphthenes with a hydrocarbon mixture having a substantially higher naphthene content, subjecting a charge containing said blend to dehydrogenation conditions in the presence of a recycled hydrogen-rich gas and a dehydrogenation catalyst for naphthenes, separating the normally gaseous and normally liquid fractions of the dehydrogenation reaction effluent, recycling a substantial portion of said gaseous fraction to the dehydrogenation reaction as the hydrogen-rich gas, removing at least a substantial proportion of the aromatic hydrocarbon content of said liquid fraction and withdrawing the remainder of said liquid fraction as a product of the process.

Other more specific embodiments of the invention involve such features as the highly paraffinic principal feedstock which is a kerosine boiling within the range of about 300–600° F. (preferably between 350 and 550°

F.) and containing less than about 25% of naphthenes by volume; the dehydrogenation-isomerization catalyst, for example, a noble metal, such as 0.1–1% platinum supported on alumina; specified ranges of reaction conditions; generating hydrogen at a rate of at least 340 s.c.f./b. in the conversion step; a preliminary hydrotreating operation in the presence of hydrogen-rich gas recycled from the conversion reaction effluent; the characteristics of the blending stock, and the fractionation and employment of fractions in the conversion effluent. The hydrocarbon blending stock desirably has a naphthene content of about 32% or more by volume, and it is employed in sufficient proportions to raise the percentage of naphthenes in the blended charge to at least about 25%. The blending stock may boil anywhere in between about 150 and 700° F. Thus, its volatility may be the same as kerosine or greater or less.

The present invention may be practiced in combination with the invention described in my concurrently filed application Ser. No. 311,833 wherein such combinations are claimed.

Besides freeing jet fuel production from dependence on extraneous sources of hydrogen, a number of other significant benefits are derived from the process of the present invention. A more highly paraffinic feedstock may be employed than was heretofore possible in the absence of outside sources of hydrogen, and this produces a higher yield of paraffinic jet fuel. Operating flexibility is enhanced by the ability to use of naphthene-rich blending stocks having volatilities outside or overlapping the kerosine boiling range. For instance, a naphtha and/or gas oil may be blended with kerosine, then dehydrogenated, and the conversion reaction effluent fractionated prior to the removal of the aromatic hydrocarbons therefrom so that the boiling range of the product is held within the range suitable for jet fuels. With a naphtha as the blending stock, the portion of the normally liquid product, which boils below 300 or 350° F. is a volatile, partly reformed, naphtha that is an excellent motor fuel blending stock. The presence of naphtha in the conversion reaction does not appear to produce any deleterious effects whatsoever. Also, the blending stock may be selected with a view to the selective formation of certain aromatic hydrocarbons such as benzene, toluene and xylenes in the conversion reaction from cyclohexane, methyl cyclohexane and polymethyl cyclohexanes, respectively in the blending stock, such aromatic by-products being later extracted from the product stream. In addition, it is possible to manufacture extra quantities of hydrogen-rich gas in excess of that required in the instant process for use in other sections of the refinery or elsewhere by selecting a highly naphthenic blending stock and using higher proportions of it than normal in the blend.

The blended charging stock is subjected to conditions conducive to the dehydrogenation of naphthenes to aromatic hydrocarbons and also the isomerization of paraffins and naphthenes over a suitable catalyst for such reactions in the presence of substantial amounts of hydrogen. This conversion may be carried out in a catalytic reformer of the type used for upgrading naphthas by dehydroaromatization and cyclization reactions under somewhat different conditions than are employed here, or units designed specifically for the instant process may be used.

The present invention is intended for principal hydrocarbon feedstocks of relatively low naphthene content, for example below about 25% by volume, and preferably but not necessarily having high proportions of paraffins and isoparaffins. Aromatic hydrocarbons may be present in substantial percentages in the feed as these, plus the aromatics produced in the conversion reaction, are eventually separated for the most part from the jet fuel product. The principal feedstock is desirably of the kerosine type which may be described for the present purposes as a petroleum distillate boiling within the range of about 300 to 600° F., and preferably between about 350 and 550° F. This primary feed is supplemented by blending naphthene-rich, liquid hydrocarbon mixtures of similar or different boiling characteristics for various purposes so that the material charged to the dehydrogenation reaction contains substantial quantities of naphthenes, for example, at least about 25%, and preferably at least about 28%, of the total liquid volume of normally liquid hydrocarbons in the charge. Material in the conversion effluent which is outside the kerosine volatility range is removed subsequently by a fractionation procedure.

A large amount of hydrogen is also charged to the conversion reactor in a recycled gaseous mixture. This may range from about 1000 to 15,000 s.c.f. of hydrogen per barrel of normally liquid feed to the dehydrogenation zone and about 4000 to 10,000 s.c.f./b. is usually preferred for the purpose. Although the hydrogen is typically in admixture with the substantial amounts of normally gaseous hydrocarbons, especially methane, it will be appreciated that these rates refer only to the hydrogen content of these gaseous mixtures. The purpose of this high concentration of hydrogen in the conversion zone is to prolong the life of the catalyst between regenerations, and it has little effect upon the production of hydrogen.

The dehydrogenation-isomerization conversion is conducted in the vapor phase at elevated temperatures and pressures. Accordingly, the mixture of liquid hydrocarbons and hydrogen-rich gas is preheated to a temperature of about 800 to 1000° F. in a conventional type heater or furnace. The overall conversion is of an endothermic nature, and the temperature of the gaseous effluent from the conversion reactor is maintained between about 640 and 980°, the range of about 780–900° being preferred for optimum hydrogen production. If the temperature of the reaction effluent is raised gradually through the 640–980° range with other reaction conditions held constant, first the hydrogen production increases, then it reaches a maximum and finally decreases in the upper part of said range. Temperatures that are too low (insufficient conversion severity) require lowering space velocities so much that the productive capacity of the equipment is unnecessarily reduced; moreover, they promote the unwanted hydrogenation of aromatic to naphthenic hydrocarbons with an attendant high consumption of hydrogen that is also undesirable. Unduly high temperatures (excessive conversion severity) tend to promote the formation of olefins and the cracking of hydrocarbons. Olefin formation is particularly undesirable here since these olefins are subsequently hydrogenated, thereby consuming extra hydrogen; moreover, the cracking eliminates valuable hydrocarbons from the product boiling range.

The partial pressure of hydrogen in the conversion reaction may be as low as about 20 or as high as about 1400 p.s.i. and controlling it within the range of about 100–500 p.s.i. is especially recommended for the instant process. If the hydrogen pressure is gradually decreased within the range of about 500 to 100 p.s.i. with other reaction conditions constant, the hydrogen make increases for a while and then levels off; however, the catalyst life decreases if the hydrogen partial pressure is allowed to drop too low. The total reaction pressure, which is of less significance, may be within the range of about 30 to 2000 p.s.i.g.

The overall space velocity (LHSV) of the gaseous charge through the dehydrogenation catalyst bed or beds may range from about 0.5 to 60, and it is usually set at a value within the range of about 1 to 20. An excessive space velocity for any given temperature within the stated range produces an insufficient conversion severity with attendant lowering of both naphthene dehydrogenation

and hydrogen production; whereas an inadequate space velocity results in both an excessive conversion severity and an uneconomically low jet fuel production rate.

While any contact material capable of catalyzing the dehydrogenation of naphthenes to aromatic hydrocarbons may be employed in the present process, it is desirable that it serve the duel purpose of also catalyzing the isomerization reactions. Paraffins are converted to isoparaffins by adding methyl groups or shifting such radicals along the chains of carbon atoms, and cyclopentanes are isomerized to cyclohexanes which are then dehydrogenated to aromatic hydrocarbons. It is also preferable that the catalyst have little or no activity of the type that promotes undesired side reactions to any substantial extent including the dealkylation of aromatic hydrocarbons and the cracking of any hydrocarbons to smaller molecules. One of the benefits of this invention is high conservation of paraffinic hydrocarbon content without reduction of the number of carbon atoms per molecule thereof, so substantial cracking is particularly undesirable here.

Accordingly, such catalysts as tungsten and/or nickel sulfides on kieselguhr, oxides of chromium on alumina, etc. may be used in the instant conversion, but noble metal catalysts of the platinum series including platinum, palladium, rhodium, etc., are greatly preferred; and these are desirably dispersed in the finely divided state on inert carrier materials in particle form such, as the various aluminas (especially the eta, gamma and chi varieties), low activity silica-alumina, etc. The carrier may contain halogen, such as chlorine or fluorine, in small quantities that do not exceed the noble material content and preferably amount to less, as the halogen component provides isomerization activity. Low activity silica-alumina also catalyzes isomerization or alternatively the catalyst may contain a constituent such as sulfided molybdena for the purpose.

The conventional catalysts for reforming naphthas in the presence of hydrogen by dehydroaromatization, cyclization, etc. provide good results here. Moreover, these possess the advantage of enhancing the flexibility of operations in a refinery because the same catalyst and reactor may be used alternatively either for reforming naphthas or for producing jet fuels. Accordingly, platinum reforming catalysts containing about 0.1 to 1.0% of platinum supported on either eta or gamma type alumina of a particle size within the 1/16 to 3/16" range are especially recommended for the instant process. Although moving bed or fluidized catalysts may be utilized, in the present state of the art a fixed catalyst bed is considered more economical for the dehydrogenation-isomerization reactions of this invention.

Various conversion reaction conditions mentioned hereinbefore are interrelated, and a change in one may require adjustment of another reaction condition. Accordingly, hydrogen is generated at a rate of 340 s.c.f./b. or more—a higher rate than is commercially feasible with the unblended principal feed—in the conversion of the blended charge stock by controlling the conversion severity in relation to the naphthene content of the charge (which contains at least about 25 volumes percent of naphthenes). Such control of conversion severity is exercised by selection and adjustment within the stated limits of certain reaction conditions especially temperature, space velocity and selection of the catalyst. Moreover, these conversion reaction conditions are desirably correlated along the lines described in said application Ser. No. 173,044 for substantial conversion of the high boiling (e.g. 350–550° F.) paraffinic hydrocarbons in the charge. Excellent results are obtained with kerosines which have low proportions of naphthenes and high contents of paraffinic hydrocarbons, such as those derived from Qatar and West Texas Bright crudes.

The raw petroleum distillates commonly employed as feedstocks usually contain sufficient amounts of sulfur and/or nitrogen in organic components to temporarily poison or deactivate many dehydrogenation catalysts including platinum and palladium. In such instances sulfur and/or nitrogen removal is a necessity for economical processing. This may be accomplished in conventional fashion by preheating the liquid charge along with about 190 to 3000 s.c.f./b. of hydrogen in a recycle gas to a temperature between about 550 and 850° F. at a hydrogen partial pressure within the range from 145 to 1000 p.s.i., and space velocity (LHSV) of 0.5 to 10. The preheated charge in the vapor state is passed through a reactor containing a bed of typical desulfurization catalyst, as for instance, cobalt molybdate supported on gamma alumina to convert organic sulfur in the charge to hydrogen sulfide and organic nitrogen to ammonia. Metal contaminants in the feed are also removed by deposition on the desulfurization catalyst. After cooling the effluent, the hydrogen sulfide and/or ammonia are stripped from the purified liquid. The hydrogen consumption in this pretreating or hydrogenation step typically runs between 25 and 150 s.c.f./b. of the normally liquid charge depending on the initial sulfur and nitrogen content thereof, and, to some extent on the nature of the hydrocarbons present; accordingly, most of the hydrogen-rich gas charged to the hydrotreater is recycled to the overall process after scrubbing the stripped hydrotreater effluent in order to conserve hydrogen.

The hydrocarbon blending operation may be performed at any stage prior to heating the charge up to a temperature suitable for the dehydrogenation-isomerization conversion. It is usually carried out before any other steps in the instant process in order to obtain the full benefit of any hydrotreating operation. However, this sequence may be reversed, especially if only the kerosine or only the blending stock requires purification.

The reaction effluent of the dehydrogenation-isomerization conversion is subjected to a fractionation step, after the hot gaseous effluent has been at least partially cooled. In cases where all of the normally liquid components of the charge to the conversion reactor are within the kerosine boiling range, the gaseous effluent is cooled almost to ambient temperature, say within 30° thereof, and then separated into gas and liquid phases in an ordinary separator.

Whenever either the blending stock or the principal feedstock boils at least partially outside of the desired jet fuel range, a somewhat more complex fractionation is necessary. Fractional distillation is then recommended, and conversion reaction products are split into three or more fractions. The gas phase rich in hydrogen is taken overhead and a dehydrogenated kerosine cut boiling at about 300–600° F., and preferably between about 350 and 550°, is taken off for further processing into a jet fuel. In addition, cuts are taken off boiling below or above said range, or both, depending upon the composition of the material charged. For example, a heavy naphtha of 400° F. end point may be utilized as the blending stock and a lighter naphtha (350° E.P.) that has been reformed in part during the conversion treatment may be taken as a by-product from a level higher on the fractionating tower than the kerosine fraction. In another embodiment wherein the charge includes heavier hydrocarbons, a gas oil fraction may be withdrawn as the tower bottoms. If the volatility range of the normally liquid components of the conversion charge is that broad, both naphtha and gas oil by-product streams may be taken off simultaneously. When such fractional distillation is employed, the effluent gases from the converter need not be cooled to the atmospheric temperature levels.

Any of the known methods of removing aromatic hydrocarbons from mixtures of these compounds with naphthenic and paraffinic hydrocarbons is suitable for their removal from the dehydrogenated kerosine. For example, that kerosine may be subjected to extraction with various solvents, azeotropic or extractive distillation, treat-

ment with strong sulfuric acid or oleum or adsorption on silica gel. Inasmuch as the aforesaid techniques are well known in the art, it is not necessary to describe them here other than to mention that extraction with sulfur dioxide is generally recommended. A major proportion of the aromatic compounds present may be removed in this step, and it is preferred that this removal be as complete as is consistent with economic processing. To obtain a superior product, it is desirable to produce a jet fuel containing less than about 5% of aromatic hydrocarbons, and preferably below about 3% by volume.

For a better understanding of the nature and objects of the present invention, reference should be had to the detailed disclosure hereinafter taken in conjunction with the accompanying drawing which is a flow sheet or schematic representation of a system suitable for the practice of the present process. For simplicity, many conventional elements, including valves, regulators, instruments, etc., have been omitted from the drawing.

Turning now to the flow sheet depicting one embodiment of the process, a paraffin-rich kerosine feedstock of the type described hereinbefore (20% naphthenes by volume) is charged by means of conduit **10** to the mixing tank **12**. Through the valved line **14**, a naphtha (44% naphthenes) with a lower boiling range which overlaps that the kerosine is charged at a controlled rate to the same tank wherein it is blended with the kerosine by a rapidly rotating agitator (not shown) which induces thorough mixing of the contents of the tank. On a volumetric basis, the kerosine charging rate is twice that of the naphtha and the blended charge contains 28 vol. percent of naphthenic hydrocarbons.

The transfer line **16** carries the mixed charge to the high pressure pump **18** which pumps the liquid at a pressure slightly above 500 p.s.i.g. through the valved conduit **20**, where the liquid meets a stream of recycle gas entering from conduit **22**. This recycled material consisting predominantly of hydrogen along with minor amounts of methane and other gaseous hydrocarbons is charged at a rate sufficient to introduce 1000 s.c.f. of hydrogen per barrel of liquid flowing through line **20**.

The gas-liquid mixture is completely vaporized in the heater or furnace **24** in which its temperature is raised to 700° F. prior to passing through the pipe **26** en route to the catalytic pretreating unit **28** wherein its sulfur content is reduced from 1000 to less than 5 parts per million (p.p.m.) in flowing downward through a bed of cobalt molybdate-alumina catalyst of ⅛ inch particle size at an average temperature of 700° F., a hydrogen partial pressure of 465 p.s.i. and a liquid hourly space velocity of 3.0.

The hydrotreated material is withdrawn in conduit **30**, cooled in cooler **32** to a temperature of 125° and then transferred via line **33** to the stripper **34**. Here the gaseous phase rich in hydrogen and containing substantially all of the hydrogen sulfide and ammonia produced in hydrotreater **28** is stripped from the liquid phase by a stream of recycle gas introduced from line **31** and then withdrawn through the conduit **35** along with the stripping gas. An appropriate proportion of the stripped gas mixture is vented through pipe **36** and the balance is passed through line **37** to the bottom of scrubber **38**. This scrubbing unit is divided into two sections. Aqueous caustic soda is introduced into the lower section and travels downward countercurrent to the gas stream to remove hydrogen sulfide from the gas stream. In the upper section, which is provided with separate drainage for the liquid, a water wash absorbs any ammonia in the stream of gas. The purified gas phase is then carried to the main gas recycle system in valved conduit **39**. The liquid phase leaves stripper **34** through the lower line **40** in which it meets another stream of the recycle gas introduced from conduit **42** at a hydrogen charging rate of 8000 s.c.f./b. of total hydrotreated liquid charge.

In those instances where purification of the feedstock is not required, the aforesaid heating, hydrotreating, stripping and scrubbing equipment is shutdown and the blended charge stock is by-passed from line **20** to the conduit **40** by means of the valved line **44** after the valves in lines **20, 39** and **40** are closed.

Next, the gas-liquid mixture entering pipe furnace **46** from line **40** is heated to a temperature of 910° F. and transferred through conduit **48** to the conversion reactor **50** which contains a bed of catalyst particles of 1/16 inch size. This catalyst consists of 0.35% finely dispersed platinum and 0.20% chlorine on eta alumina.

The conversion of the hydrocarbon charge takes place while passing downwardly through the catalyst bed in this reactor at total pressure of 450 p.s.i.g. and space velocity of 1.5 (LHSV) with the product gases maintained at a reactor outlet temperature of 835° F. This temperature is controlled by suitable regulation of the firing of furnace **46**. These conditions produce a dehydrogenation of about 80% of the naphthenes charged to the reactor as well as the isomerization of a considerable quantity of the paraffinic components and a minor amount of the naphthenes.

The vapor phase effluent from this conversion is withdrawn at the bottom of the reactor in pipe **52** and directed through a cooler **54** and conduit **56** in being transferred to the fractionation unit **58**. The latter unit is a fractional distillation tower (schematically represented) in the instant embodiment inasmuch as it is necessary to separate three fractions here by reason of the introduction of the lower boiling, blending naphtha through charge line **14**.

A normally gaseous fraction composed predominantly of hydrogen plus methane and other light hydrocarbons formed by cracking side reactions in a minor degree in reactor **50** is taken overhead through conduit **60**. This is the major portion of the recycle gas which is joined by a minor amount in the purified stream from pipe **39** and then compressed to a pressure of 525 p.s.i.g. in recycle compressor **62** before delivery to the line **64**. Most of the compressed gas is then directed into the valved line **42** as the hydrogen-rich circulating gas for the dehydrogenation reaction. A smaller amount of it is recycled via valved line **22** to supply hydrogen for the hydrogen pretreatment, and another stream of this gas is carried in conduit **31** to stripper **34** to serve as the stripping gas. Alternatively, when the hydro-treating step is omitted, an amount similar to that vented through line **36** is taken off through the valved conduit **66** for use as fuel or other purposes to avoid the build-up of inerts in the system.

A second or middle fraction of the reactor effluent is withdrawn through line **68** for use as a motor fuel blending stock. This naphtha, partly reformed under the relatively mild conversion conditions, which boils below the jet fuel range, that is below about 350° F. It is usually desirable to separate the naphtha at this stage in order to reduce the load on the final dearomatization unit and also to allow this liquid motor fuel fraction to retain aromatic hydrocarbons which enhance its antiknock rating. However, the extraction of aromatic compounds from the conversion product stream should precede fractionation in instances where it is desired to maximize the yield of byproduct benzene, toluene or xylenes in order to keep most of these substances out of the by-product naphtha.

The third fraction which boils within the preferred 350–550° F. range is withdrawn through the lower line **70** and passed through the cooler **72** and conduit **74** in transit to the aromatics removal unit **76**. Aromatic hydrocarbons are removed from the kerosine conversion product here at temperatures in the—10° to +20° F. range by the sulfur dioxide extractant charged through the line **78**. The extract containing about 90% of the aromatic hydrocarbons charged to the unit is removed through the bottom conduit **80**; while the product, a jet fuel containing only a small percentage of aromatic hydrocarbons, is withdrawn through the upper line **82**.

A bottoms line **69** is also provided in the fractionation system for the separation of heavier hydrocarbons

which boil at temperatures above the preferred jet fuel range. When naphthene-rich gas oil (500–600° F. boiling range) is employed as the blending stock to be charged with a kerosine feedstock of low naphthene content, the overhead gas and the dehydrogenated kerosine are withdrawn in pipes **60** and **70** respectively as before, and a gas oil boiling above 550° F. is taken off through the bottoms line **69** while the naphtha line **68** is usually shut off. Alternatively, the total charge to the plant may include as naphthene-rich blending stocks both a fraction lighter than kerosine and another fraction heavier than kerosine, plus the principal kerosine feed, in which case the conversion effluent will be separated in the fractionator into four or more recycle, product and by-product fractions.

Further illustrations of the practice in the present invention are set forth in the examples which follow. These examples have been simplified by exclusion of certain details in order to better illustrate the present invention.

Examples

The table of examples hereinafter depicts the charge and jet fuel characteristics obtainable by processing a straight kerosine of relatively low naphthenic hydrocarbon content in comparative Example A in comparison with employing naphthenic enriched blends of the same kerosine and two different naphthas according to the present invention in illustrative Examples 1 and 2. The same processing conditions are employed throughout except for omitting the blending step and fractional distillation of the liquid conversion product when charging straight kerosine in Example A.

Hydrogen pretreatment is carried out after the blending operation under the following conditions:

	Cobalt molybdate-on-alumina
Hydrotreating catalyst:	
Average temperature, ° F.	700
Total pressure, p.s.i.g.	500
H_2 partial pressure p.s.i.	465
H_2 circ. rate, s.c.f./b.	1000
Space velocity, LHSV	2
H_2 consumption, s.c.f./b.	75

This treatment does not appreciably alter composition of the charge except for the reduction in sulfur and nitrogen contents.

The selected dehydrogenation-isomerization conditions are as follows:

	0.35% pt. on eta-alumina
Conversion catalyst:	
Total pressure, p.s.i.g.	400
H_2 partial pressure, p.s.i.	355
H_2 circ. rate, s.c.f./b.	8000
Space velocity, LHSV	1.5
Reactor effluent temp., ° F.	835

Fractional distillation is employed to separate the conversion effluent into a partly reformed naphtha boiling below 350° F. and a kerosine fraction boiling above that temperature. Then the final jet fuel is prepared by using sulfur dioxide to extract most of the aromatic hydrocarbons from this dehydrogenated kerosine. Meanwhile the normally gaseous portion of the conversion effluent is recycled to the hydrogen pretreatment and to the dehydrogenation reactions at the stated hydrogen rates.

TABLE OF EXAMPLES

Example	A		1		2
Charge	Kerosine Q	Naphtha C	Blend Q:C	Naphtha M	Blend Q:M
Type	Qatar	Calif.-Kuwait		Mid-Continent	
Kerosine, vol. ratio	100		80:20		50–50
Boiling range, ° F.	356–467	260–380		280–398	
Composition, vol. percent:					
Paraffins	57.8	47.5	55.7	47.4	52.6
Olefins	0.5		0.4	0.5	0.5
Naphthenes	22.8	34.4	25.1	49.2	36.0
Aromatics	18.9	18.1	18.7	2.9	10.9
Sulfur, p.p.m.	1,000	480	896	150	575
Nitrogen, p.p.m.	8	0.7	6.5	Nil	4
Final Fuel—					
Composition, vol. percent:					
Paraffins	88.4		89.1		89.4
Olefins	1.0		0.7		0.6
Naphthenes	7.6		7.2		7.0
Aromatics	3.0		3.0		3.0
Sulfur, p.p.m.	Nil		Nil		Nil
Freeze Point, ° F.	−40		−39		−38
Luminometer No.	110		111		112
Net heat of Combustion, B.t.u./lb.	18,910		18,910		18,910
Hydrogen make, s.c.f./b.	300		350		440

It is apparent from these tabulated results that the hydrogen production of the straight kerosine in comparative Example A is at a border line rate unsuitable for actual commercial operation. However, sufficient hydrogen is liberated from the blended charging stock of illustrative Example 1 to render the overall process, including the hydrogen pretreating step, self-sufficient in hydrogen. Example 2 illustrates processing according to the instant invention a blend which is even richer in naphthenes, and the hydrogen make here is sufficient to provide extra hydrogen for use in other processes in a refinery. The products of Examples 1 and 2 both display excellent combustion characteristics as denoted by the high luminometer numbers and high heats of combustion coupled with low freezing points, hence both constitute excellent fuels for supersonic jet aircraft. Moreover, a small but desirable luminometer number apparently accompanies increases in hydrogen production under the present process.

While the invention has been described with particular reference to a few detailed examples and embodiments, it is to be understood that these have been set forth for the purpose of illustrating rather than restricting the invention. Those skilled in the art will appreciate that various modifications can be made in the specific embodiments without departing from the scope or the spirit of the invention. Accordingly, the present invention should not be contrued as limited in any particular conditions or aspects as may be set forth in the appended claims or required by the prior art.

I claim:

1. In producing jet engine fuels, the process which comprises blending a hydrocarbon feedstock containing paraffinic hydrocarbons and a relatively low content of naphthenes with a hydrocarbon mixture having a substantially higher naphthene content, subjecting a charge containing said blend to dehydrogenation conditions in the presence of a recycled hydrogen-rich gas and a dehydrogenation catalyst for naphthenes with the conversion severity controlled to minimize cracking and olefin formation, separating the normally gaseous and normally liquid fractions of the dehydrogenation reaction effluent, recycling a substantial portion of said gaseous fraction to the dehydrogenation reaction as the hydrogen-rich gas, removing at least a substantial proportion of the aromatic hydrocar-

bon content of said liquid fraction and withdrawing the remainder of said liquid fraction as a product of the process, whereby the dehydrogenation reaction produces hydrogen at a rate at least equivalent to the requirements of said process.

2. A process according to claim 1 in which said feedstock contains less than about 25% of naphthenes and said blend contains more than about 25% naphthenes by volume.

3. A process according to claim 1 in which said dehydrogenation catalyst is a finely divided noble metal supported on a particle form carrier.

4. A process according to claim 1 in which said feedstock is a kerosine.

5. In producing jet engine fuels, the process which comprises blending a kerosine of relatively low naphthene content boiling within the range of about 300 to 600° F. with a sufficient quantity of a hydrocarbon mixture of substantially higher naphthene content to raise the naphthene content of the resulting blend to at least 25% by volume, thereafter reacting a charge containing said blend under dehydrogenation and isomerization conditions in the presence of a recycled hydrogen-rich gas and a dehydrogenation-isomerization catalyst with the conversion severity controlled to minimize cracking and olefin formation, separating the normally gaseous and normally liquid fractions of the reaction effluent, recycling a substantial portion of said gaseous fraction to the reaction as the hydrogen-rich gas, removing at least a substantial proportion of the aromatic hydrocarbon content of said liquid fraction and withdrawing the remainder of said liquid fraction as a product of the process, whereby the dehydrogenation reaction produces hydrogen at a rate at least equivalent to the requirements of said process.

6. A process according to claim 5 in which said dehydrogenation-isomerization catalyst contains between about 0.1 and 1.0% platinum supported on particle form alumina.

7. A process according to claim 5 in which said hydrocarbon mixture employed in said blending step contains cyclohexane, and benzene is recovered from said liquid fraction of the reaction effluent.

8. A process according to claim 5 in which said hydrocarbon mixture employed in said blending step contains methyl cyclohexane, and toluene is recovered from said liquid fraction of the reaction effluent.

9. A process according to claim 5 in which said hydrocarbon mixture employed in said blending step contains a naphthene of the group consisting of dimethyl cyclohexanes and trimethyl cyclohexanes, and xylene is recovered from said liquid fraction of the reaction effluent.

10. A process according to claim 5 in which at least a portion of said charge is hydrotreated under desulfurization conditions in the presence of a hydrogen-rich gas and a desulfurization catalyst prior to said dehydrogenation-isomerization reaction.

11. In producing jet engine fuels, the process which comprises blending a kerosine having a relatively low naphthene content with a hydrocarbon mixture of substantially higher naphthene content and having a boiling range at least partially outside the kerosine boiling range; subjecting the blend to dehydrogenation conditions in the presence of a recycled hydrogen-rich gas and a dehydrogenation catalyst for naphthenes with the conversion severity controlled to minimize cracking and olefin formation; fractionating the dehydrogenation reaction effluent into a normally gaseous fraction, a dehydrogenated kerosine boiling within the range of about 300 to 600° F. and at least one liquid fraction boiling outside said range; recycling a substantial portion of said gaseous fraction to the dehydrogenation reaction as the hydrogen-rich gas; removing at least a substantial proportion of the aromatic hydrocarbon content from said dehydrogenated keorsine and withdrawing the remainder of said dehydrogenated kerosine as a product of the process, whereby the dehydrogenation reaction produces hydrogen at a rate at least equivalent to the requirements of said process.

12. A process according to claim 11 in which said dehydrogenation conditions include a hydrogen partial pressure between about 20 and 1400 p.s.i., a reaction effluent temperature between about 640 and 980° F., a hydrogen charging rate between about 1000 and 15,000 s.c.f./b. of said blend and a liquid hourly volumetric space velocity between about 0.5 and 60.

13. In producing jet engine fuels, the process which comprises blending a kerosine boiling within the range of about 300 to 600° F. and having a naphthene content below about 25% by volume with a sufficient amount of a hydrocarbon mixture of a substantially higher naphthene content and having a boiling range at least partially outside said kerosine boiling range to raise the naphthene content of the resulting blend to at least about 25%; generating at least about 340 s.c.f. of hydrogen per barrel of said blend under dehydrogenation conditions in the presence of a recycled hydrogen-rich gas and a dehydrogenation catalyst for naphthenes with the conversion severity controlled to minimize cracking and olefin formation; fractionating the dehydrogenation reaction effluent into a normally gaseous fraction, a dehydrogenated kerosine boiling within the range of about 300 to 600° F. and at least one liquid fraction boiling outside said kerosine range; recycling a substantial portion of said gaseous fraction to the dehydrogenation reaction as the hydrogen-rich gas; removing at least a substantial proportion of the aromatic hydrocarbon content of said dehydrogenated kerosine and withdrawing the remainder of said dehydrogenated kerosine as a product of the process, whereby the dehydrogenation reaction produces hydrogen at a rate at least equivalent to the requirements of said process.

14. In the production of jet engine fuels, the steps which comprises blending a kerosine boiling within the range of about 300 to 600° F. of relatively low naphthene content with a hydrocarbon mixture of a substantially higher naphthene content, and hydrotreating the kerosine under desulfurization conditions in the presence of a recycled hydrogen-rich gas and a desulfurization catalyst to produce a hydrotreated hydrocarbon blend containing more than about 25% of naphthenes by volume; thereafter subjecting said blend to dehydrogenation conditions in the presence of a recycled hydrogen-rich gas and a dehydrogenation catalyst for naphthenes with the conversion severity controlled to minimize cracking and olefin formation; fractionating the dehydrogenation reaction effluent into a normally gaseous fraction, a dehydrogenated kerosine and at least one liquid fraction boiling outside the kerosine range; recycling a minor portion of said gaseous fraction to said hydrotreating step; recycling a major portion of said gaseous fraction to said dehydrogenation reaction as the hydrogen-rich gas; removing at least a substantial proportion of the aromatic hydrocarbon content of said dehydrogenated kerosine and withdrawing the remainder of said dehydrogenated kerosine as a jet fuel; whereby the dehydrogenation reaction produces all of the hydrogen required in said process.

15. A process according to claim 14 in which said dehydrogenation conditions include a hydrogen partial pressure between about 20 and 1400 p.s.i., a reaction effluent temperature between about 640 and 980° F., a hydrogen charging rate betwen about 1000 and 15,000 s.c.f./b. of said blend and a liquid hourly volumetric space velocity between about 0.5 and 60.

16. A process for the production of jet engine fuels which comprises blending a kerosine boiling within the range of about 350° to 550° F. and having a naphthene content below about 25% by volume with a sufficient quantity of a hydrocarbon mixture having a boiling range at least partially outside said kerosine range and having a naphthene content of at least about 32% to raise the

naphthene content of the resulting blend to at least about 25%; hydrotreating said blend under desulfurization conditions in the presence of a recycled hydrogen-rich gas and a desulfurization catalyst; thereafter generating at least about 340 s.c.f. of hydrogen per barrel of the hydrotreated blend under dehydrogenation-isomerization conditions in the presence of a recycled hydrogen-rich gas and a noble metal catalyst for the dehydrogenation of naphthenes and the isomerization of paraffins with the conversion severity controlled to minimize cracking and olefin formation; fractionating the dehydrogenation-isomerization reaction effluent into a normally gaseous fraction, a dehydrogenated kerosine boiling within the range of about 350 to 550° F. and at least one liquid fraction boiling outside said dehydrogenated kerosine range; recycling a minor portion of said gaseous fraction to said hydrotreating step; recycling a major portion of said gaseous fraction to the dehydrogenation-isomerization reaction as the hydrogen-rich gas; removing at least a major proportion of the aromatic hydrocarbons in said dehydrogenated kerosine and withdrawing the remainder of said dehydrogenated kerosine as a jet fuel; whereby the dehydrogenation-isomerization reaction produces all of the hydrogen required in said process.

17. A continuous process according to claim **16** in which said dehydrogenation-isomerization conditions include a hydrogen partial pressure between about 100 and 500 p.s.i., a reaction effluent temperature between about 780 and 900° F., a hydrogen charging rate between about 4000 and 10,000 s.c.f./b. of said hydrotreated blend, a liquid hourly volumetric space velocity between about 1 and 20 and a catalyst composite comprising between about 0.1 and 1.0% by weight of a noble metal supported on an inert particle form carrier; and said conditions are correlated within said ranges for high retention of paraffinic hydrocarbons in the kerosine boiling range.

18. A process according to claim **16** in which said hydrocarbon mixture employed in said blending is a petroleum distillate boiling within the range of about 500 to 600° F. and said liquid fraction of the reaction effluent boils above about 550° F.

19. A process according to claim **16** in which said hydrocarbon mixture employed in said blending is a naphtha boiling below about 400° F. and said liquid fraction of the reaction effluent is a partially reformed gasoline blending stock boiling below about 350° F.

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