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BLENDING HYDROGENATED FRACTIONS TO MAKE A JET FUEL

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ABSTRACT OF THE DISCLOSURE

A high thermal stability, low vapor pressure jet engine fuel for Mach 3 to 3.5 aircraft containing from 30 to 60 percent isoparaffins, from 20 to 50 percent monocyclic naphthenes, and from 10 to 25 percent polycyclic naphthenes. The fuel is formed by removing n-paraffins from a highly paraffinic crude and/or by blending isoparaffinic stocks together with straight run stocks to form the desired proportion of constituents. Preferred blending materials are alkylation unit solvent rerun bottoms, alkyl trimers, propylene tetramers, specific thermally cracked stocks boiling within the stove oil range, and specific straight run stocks boiling in the stove oil range. The thermally cracked stocks and straight run stocks used are first hydrogenated to completion in two hydrogenation steps, treated to remove n-paraffins and then blended to form the specific fuel composition. The alkylation unit solvent rerun bottoms and propylene tetramer are substantially isoparaffinic and require only a single hydrogenation step prior to blending.

CROSS REFERENCE TO RELATED APPLICATIONS

This is a division of patent application Ser. No. 658,066, filed Aug. 3, 1967, now abandoned, for Jet Fuel, which is a continuation-in-part of application Ser. No. 588,237, filed Oct. 13, 1966, now Patent No. 3,367,860 which is a continuation-in-part of application Ser. No. 324,881, filed Nov. 19, 1963, now abandoned.

BACKGROUND OF THE INVENTION

This invention is directed to a high thermal stability, low vapor pressure fuel for jet engines in Mach 3 to 3.5 aircraft and to the process for producing such fuels and operating such engines. These engines require fuel having a high luminometer number, a high heat of combustion, a low freeze point, a low viscosity at low temperatures and a moderately high flash point. In addition to these burning properties, the fuel must be of high thermal stability at temperatures of about 700° F. The required burning properties and thermal stability have been found to be generally unattainable with straight run stocks.

The heat of combustion may be expressed both as B.t.u./gal. and B.t.u./lb. For simplicity in nomenclature, the heat of combustion expressed in B.t.u./gal. will be referred to herein as "fuel density." All percentages of fuel components given herein are intended to refer to percent by volume unless specified otherwise.

Many of the fuels developed thus far for use in Mach 3 to 3.5 aircraft have been unsatisfactory in that the luminometer number has been undesirably low. The luminometer number is indicative of the tendency of the fuel to smoke during combustion in the engine. High luminometer number fuels burn cleaner than those of lower luminometer number and, consequently, provide a more

desirable jet fuel. Preferably, the luminometer number of a Mach 3 to 3.5 jet aircraft fuel should be 75 or greater.

The luminometer number of a jet fuel can be increased generally by increasing its paraffinicity. Increased paraffinicity, however, also normally causes a rise in the fuel freeze point and a decrease in the fuel density due to the comparatively high hydrogen to carbon ratio of the paraffins. It has now been discovered that the removal of normal paraffins from the paraffin content of the fuel significantly reduces the detrimental effect of the paraffins on fuel freeze point without otherwise reducing the beneficial effects of high paraffinicity. The branched or isoparaffins still beneficially increase the fuel luminometer number but the freeze point remains low and surprisingly only a mild reduction in fuel density has been observed. Also, contrary to some teachings of the prior art, it has been found that jet fuels of this invention having high isoparaffin content also have good stability at high temperatures.

The most desirable fuel, it has now been discovered comprises narrow compositional ranges of isoparaffins, monocyclic naphthenes and polycyclic naphthenes. A small amount of normal paraffins can also be tolerated when the ratio of isoparaffins to normal paraffins is kept high.

SUMMARY OF INVENTION

The low vapor pressure, high thermal stability jet fuel compositions of this invention contain from 30 to 60 percent isoparaffins, up to about 6.5 percent n-paraffins, from a 20 to 50 percent monocyclic naphthenes and from 10 to 25 percent polycyclic naphthenes. The fuels are hydrogenated to completion and contain substantially no aromatics. These fuel compositions possess excellent burning characteristics and are thermally stable at temperatures on the order of 700° F. They have a heat of combustion of greater than 18,750 B.t.u./lb., a fuel density of greater than 124,000 B.t.u./gal., and a luminometer number of greater than 75. The fuel freeze points of these fuels are about −75° F. or lower. These jet fuels are formed by blending select, completely hydrogenated stocks in the proper proportions to obtain the ranges of components and properties set forth.

In particular, blending components which have shown exceptionally beneficial characteristics are hydrogenated alkylation unit rerun bottoms, hydrogenated propylene tetramers, thermally cracked stock which has been hydrogenated and treated to remove n-paraffins, and hydrogenated stove oils from high normal paraffin content crudes which have been treated with a molecular sieve or in some other manner to remove n-paraffins.

The alkylation unit rerun bottoms blending components of this invention boil in the range of 370 to 525° F. and typically are a distribution of C_{10} to C_{15} isoparaffins in the following ranges:

	Percent by volume
C_{10}	8–15
C_{11}	30–40
C_{12}	10–25
C_{13}	10–25
C_{14}	8–15
C_{15}	8–15

When hydrogenated this material is substantially 100 percent isoparaffin and has been found to be an outstanding blending stock for Mach 3 to 3.5 jet aircraft fuels. For convenience, and in accordance with the terminology commonly used in this art, these alkylation unit rerun bottoms will be referred to here as alky trimers. The alkyl trimers typically have an API gravity of about 51, a heat of combustion of about 19,000 B.t.u./lb., a fuel density of about

122,500 B.t.u./gal. and a freze point below —80° F. The viscosity of the alky trimers and their luminometer number are also excellent so that they provide a low boiling point high heat of combustion stock which can be used for blending to provide the desired properties of a high Mach jet fuel.

The propylene tetramer blending component of this invention is also a refinery product boiling in the range from 365 to 445° F. and comprising olefins from 50 to 70 percent C_{12}, up to about 27 percent C_{11}, from 3 to 45 percent C_{13} and up to 5 percent C_{14}. The tetramer when hydrogenated has an API gravity of 53.5, a heat of combustion of 18,980 B.t.u./lb., a fuel density of 120,860 B.t.u./gal., a freeze point below —80° F. and a luminometer number of 115 and is substantially 100 percent isoparaffin. The preferred tetramer blending component is the light tetramer which contains about 27 percent C_{11} olefins, about 70 percent C_{12} olefins, and about 3 percent C_{13} olefins.

One object of this invention is to produce a fuel for jet engines of Mach 3 to 3.5 aircraft.

Another object of this invention is to provide a jet fuel which has a flash point of 150° F. minimum, a gravity (API) of 44 minimum, a viscosity at —30° F. of 15 maximum, a freeze point of —70° F. maximum, a heat of combustion of at least 18,750 B.t.u./lb., a fuel density of at least 124,000 B.t.u./gal., and a luminometer number of at least 80.

Another object of this invention is to produce a jet fuel which is substantially free of normal paraffins and has an isoparaffin content of from 30 to 60 percent by volume with the balance naphthenes.

These and other objects of this invention will become more apparent from the following discussion and the appended claims.

PREFERRED EMBODIMENTS AND DISCUSSION

The preferred ranges of constituents in the fuel of this invention are from 40 to 55 percent isoparaffins, from 30 to 40 percent monocyclic naphthenes, from 15 to 20 percent polycyclic naphthenes, and substantially no n-paraffins. The isoparaffin content is especially critical since, if the fuel contains less than 40 percent isoparaffins, the luminometer number and the heat of combustion are adversely affected. If the isoparaffin content is greater than about 55 percent, the fuel density is adversely affected.

The most preferred jet fuel composition consists of about 52 percent isoparaffins, about 30 percent monocyclic naphthenes and the balance polycyclic naphthenes with substantially no n-paraffins.

Small quantities of n-paraffins can be tolerated in the fuels of this invention, but the n-paraffin content should never exceed about 6.5 percent because of the detrimental effect of n-paraffin on the freeze point. Preferably, the n-paraffins are substantially all removed from the jet fuel.

Briefly, the fuels of this invention are formed in four primary ways. First, they can be produced by totally hydrogenating a stove oil cut from selected straight run crudes and blending these hydrogenated stove oil cuts with hydrogenated propylene tetramer or with hydrogenated alky trimers. Propylene tetramer is substantially 100 percent isoparaffins after hydrogenation. The alky trimers, as noted, are a mixture of C_{10} to C_{15} hydrocarbons and are substantially 100 percent isoparaffins prior to hydrogenation so that the single stage hydrogenation does not have to be severe.

Second, the fuels can be produced by hydrogenating a stove oil cut from a straight run stock to completion in two stages and removing n-paraffins, as by means of a molecular sieve or by extraction with a urea complex.

Thirdly, these fuels can be produced by hydrogenating the stove oil cut from a straight run stock to completion, extracting the normal paraffins from the hydrogenated stock, as through the use of molecular sieves, and blending the resultant product with hydrogenated tertamer and/or alky trimers.

Fourth, the fuels can be made by hydrogenating to completion a stove oil fraction from a selected thermally cracked stock, removing n-paraffins, as through the use of molecular sieves, and blending with hydrogenated alky trimers to form a low vapor pressure, high thermal stability fuel.

The purpose of the single stage hydrogenation of the alky trimers is primarily to increase the thermal stability of these materials and the fuel into which they are blended. The hydrogenation is carried out at a temperature of from 250 to 850° F., a pressure of from 300 to 2,000 p.s.i.g., a liquid hourly space velocity of from 0.2 to 6.0 and a hydrogen to oil ratio of from 1,500 to 8,500 s.c.f./bbl.

By blending alky trimers with a hydrogenated straight run stove oil or refinery stream of high paraffinicity, the preferred proportions of constituents for high Mach aircraft jet engine fuel can easily be obtained. The trimers must be blended since they have a fuel density less than that required for high Mach aircraft fuels and, due to their weight, they have a very high viscosity at temperatures on the order of —30° F. and lower. The alky trimers when used as blending stock, due to their high isoparaffinicity, may generally be used in quantities up to 20 percent by volume of the fuel blend with a straight run hydrogenated stove oil constituting the remainder. Greater than about 20 percent by volume of the alky trimers detrimentally affects the viscosity of the fuel at low temperatures. The preferred range of additions of alky trimers is from 10 to 15 percent by volume.

Propylene tetramer is available as a refinery stream product and has also been found, when hydrogenated, to make an excellent blending component for the jet fuel of this invention. The tetramer, as noted, is an olefin boiling in the range of 365° to 445° F. and is sulfur free so that it can be hydrogenated in a single step. Hydrogenation of the tetramer can be accomplished under substantially the same range of conditions as for hydrogenation of alky trimers.

Suitable blending agents for the tetramer have been found to be a mixture of hydrogenated stove oils from naphthenic and intermediate crudes such as a stove oil mixture containing from 25 to 40 percent paraffins of which 99 percent are isoparaffins, from 38 to 48 percent monocyclic naphthenes, from 22 to 28 percent dicyclic naphthenes and up to 2 percent tricyclic naphthenes. The use of hydrogenated propylene tetramer in the place of alky trimers is beneficial in some cases because the tetramer has an extremely low viscosity at low temperatures since it is a lighter weight stock and has shorter carbon chains than the alky trimers. The major limitation on the tetramer as a blending component is its poor fuel density. Up to about 50 percent by volume tetramer can be used without adverse effects. The preferred range of tetramer addition, however, has been found to be from about 25 to 45 percent by volume. Usually 25 percent by volume tetramer is required to bring the fuel isoparaffin level within the desired range. If greater than 45 percent by volume tetramer is used, however, the fuel density decreases to a value very close to the minimum 124,000 B.t.u./gal. level.

The alky trimers and propylene tetramers are convenient to use as blending stocks since they require only a single hydrogenation step and since they both are obtainable as by-products of petroleum refinery processes.

A highly isoparaffin blending stock can also be obtained by the elimination of n-paraffins from an initially high n-paraffin content hydrogenated thermally cracked stock boiling in the stove oil range by treatment with molecular sieves. For example, a hydrogenated thermally cracked stock boiling in the range of 292 to 672° F. having a high initial paraffin content with a large percentage of n-paraffins may be treated with a molecular sieve to remove the n-paraffins. A typical thermally cracked stock of this

nature is a refinery Combination Unit Bubble Tower sidestream boiling in the range of 292 to 672° F. which after complete hydrogenation comprises about 12 to 20 percent n-paraffins, about 12 to 20 percent isoparaffins, about 44 to 52 percent monocyclic naphthenes and about 15 to 23 percent polycyclic naphthenes. Although the n-paraffin content of the stock is reduced by the sieve treatment, the isoparaffin content is not affected. A molecular sieve having a pore size of 5 angstroms has been found to be most suited for use in separation since it passes the n-paraffins but not the isoparaffins. The n-paraffins, alternatively, may be removed from the thermally cracked stocks by other methods such as by extraction with a urea complex to provide the isoparaffinic blending component desired.

It has been found that the thermally cracked stocks must be hydrogenated in two stages. The first stage hydrogenation or hydrofinishing is necessary to remove sulfur and nitrogen from the stock and may be conducted at a temperature from 250 to 850° F., a pressure from 300 to 2,000 p.s.i.g., a liquid hourly space velocity of from 0.2 to 6.0, and a hydrogenation rate of from 1,500 to 8,000 s.c.f./bbl. The preferred first stage conditions are a temperature from 600 to 800° F., a pressure from 450 to 850 p.s.i.g., a liquid hourly space velocity from 0.5 to 2.0 and a hydrogenation rate of 2,500 to 3,500 s.c.f./bbl.

The hydrogenation catalyst for the first stage must also be a hydrodenitrogenation and hydrodesulfurization catalyst. Therefore, it must be a catalyst which is not fouled by sulfur and nitrogen such as a supported metal combination of a Group VIII metal and Group VI–B metal oxides and sulfides. Typical catalysts of this variety are cobalt-molybdenum oxide, nickel-molybdenum oxide, cobalt-molybdenum sulfide, nickel-molybdenum sulfide, cobalt-tungsten sulfide, nickel-tungsten sulfide and molybdenum-tungsten sulfide on a conventional support material such as alumina or silica-alumina. The first stage hydrogenation should be at least to 80 percent saturation and preferably to 90 or 95 percent saturation.

The second stage hydrogenation conditions are a temperature from 200 to 850° F., a pressure of from 100 to 2,000 p.s.i.g., a liquid hourly space velocity of 1.5 to 6.0, and a hydrogenation rate of 1,500 to 6,000 s.c.f./bbl. The preferred conditions are temperatures from 400 to 750° F., pressures from 500 to 1,000 p.s.i.g., a liquid hourly space velocity from 0.5 to 4.0, a hydrogenation rate of 3,500 to 4,500 s.c.f./bbl. Hydrogenation in the second stage should be substantially to completion and at least 98 percent to form the component of the jet fuels of this invention. Platinum group metal catalysts and preferably platinum have been found to produce the best results in the second stage.

Low boiling cracked and partially cracked products of the initial hydrogenation step may be removed by a convenient separation process such as distillation of a 370 to 520° F. heart cut prior to second stage hydrogenation. Separation may also be accomplished by other means such as hydrogen stripping or with molecular sieves. With some thermally cracked stocks, it may be possible to eliminate the initial hydrogenation step since the sulfur content is sufficiently low initially and the necessity for the first stage hydrogenation is dependent on the sulfur content of the oil.

The final product of the hydrogenation and sieve treatment comprises a highly isoparaffinic blending component comparable to but not as heavy as the alky trimers discussed.

It has been found that a highly isoparaffinic blending material can also be provided by selecting a straight run stove oil which, after hydrogenation, is relatively high in paraffins and has a high heat of combustion and fuel density and by removing substantially all n-paraffins from the oil. Stove oil from Four Corners crude has been found to be the only straight run stock which satisfies these requirements. Typically, the stove oil fraction, boiling in the range of from 290 to 520° F., of this crude when hydrogenated contains from 22 to 30 percent isoparaffins, from 15 to 20 percent n-paraffins, from 35 to 41 percent monocyclic naphthenes and from 15 to 20 percent polycyclic naphthenes when hydrogenated in the two-stage hydrogenation process already discussed. The preferred conditions and catalysts for the two-stage hydrogenation have been found to be the same as those discussed for thermally cracked stocks.

The hydrogenated Four Corners stove oil typically has a heat of combustion of 18,771 B.t.u./lb., a fuel density of 124,658 B.t.u./gal., a luminometer number of 84 and a freeze point of −40° F. After removal of the n-paraffins from the oil, the heat of combustion, fuel density and luminometer number remained substantially constant while the freeze point decreased to below −80° F. providing a full scope of excellent properties for a jet fuel.

This invention may be further understood from a consideration of the foregoing discussion in conjunction with the following specific examples of the high Mach jet fuel prepared in accordance with our invention. The examples are not intended to limit the scope of this invention beyond that of the appended claims.

EXAMPLE 1

A fuel was prepared by blending 35 volume percent hydrogenated alky trimers with 65 volume percent of a hydrogenated straight run stove oil blend. The alkyl trimers used as a blending component in the fuel boiled in the range of from 372 to 522° F. and contained:

	Percent by volume
C_{10}	10
C_{11}	40
C_{12}	15
C_{13}	15
C_{14}	10
C_{15}	10

These alky trimers were hydrogenated in a single step in the presence of a platinum group metal catalyst at 600 p.s.i.g., 500° F., a liquid hourly space velocity of 1.0, and a hydrogen rate of 4,000 s.c.f./bbl.

The stove oil blend comprised a mixture of 2 parts of a stove oil from a naphthenic type crude, i.e., a crude having from 55 to 65 percent naphthenes, less than 20 percent paraffins and the balance aromatics and 1 part of a stove oil from an intermediate type crude, i.e., a crude having from 45 to 55 percent naphthenes, about 30 percent paraffins and the remainder aromatics. The stove oil blend was hydrogenated in two steps the first of which was carried out at 750 p.s.i.g., 750° F., 1.0 liquid hourly space velocity, and 3,000 s.c.f./bbl. in the presence of a cobalt-molybdenum oxide catalyst on alumina. The second stage was at 600 p.s.i.g., 500° F., 1.0 liquid hourly space velocity, and 4,000 s.c.f./bbl. in the presence of a platinum catalyst. The final fuel contained:

	Percent by volume
n-Paraffins	0.8
Isoparaffins	52.1
Monocyclic naphthenes	29.5
Dicyclic naphthenes	17.2
Tricyclic naphthenes	0.4

This fuel was tested in the laboratory and found to have the following properties:

Gravity, ° API	43.8
Heat of combustion, B.t.u./lb.	18,770
Fuel density, B.t.u./gal.	126,025
Freeze point, ° F.	Below −80
Viscosity, CS at −30° F.	17.4
Luminometer number	74

Distillation, ° F.:	
IBP	378
10%	391
50%	414
90%	475
EP	511
Rec. percent	97.0
Flash point, PMCC, ° F.	164

The fuel had good thermal stability at 700° F. The addition of substantially 100 percent isoparaffinic alky rerun bottoms to the blend of stove oils, as shown, provided a fuel which was suitable as a high Mach jet engine fuel. Although the paraffin content exceeded 50 percent the freeze point of the fuel was still excellent.

EXAMPLE 2

A mixture of 10 percent hydrogenated alky trimers and 90 percent of a hydrogenated Mid-east stove oil comprising 42.5 percent by volume isoparaffins, 38.6 percent by volume monocyclic naphthenes and 18.9 percent by volume dicyclic naphthenes was prepared. The alky trimers were hydrogenated in a single step in the presence of a platinum catalyst at a temperature of 500° F., a pressure of 600 p.s.i.g., a liquid hourly space velocity of 1.0 and a hydrogen to oil ratio of 4,000 s.c.f./bbl. The stove oil was hydrogenated to completion in two stages under the following conditions:

First stage.—Nickel-molybdenum oxide on alumina catalyst, 750 p.s.i.g., 750° F., 1.0 liquid hourly space velocity, and 3,000 s.c.f./bbl.

Second stage.—Platinum catalyst, 600 p.s.i.g., 500° F., 1.0 liquid hourly space velocity, and 4,000 s.c.f./bbl.

The fuel blend consisted of 48.3 percent by volume isoparaffins, 34.7 percent by volume monocyclic naphthenes and 17 percent by volume dicyclic naphthenes.

This fuel was tested in the laboratory and found to possess the following properties:

Gravity, ° API	43.5
Heat of combustion, B.t.u./lb.	18,750
Fuel density, B.t.u./gal.	126,225
Freeze point, ° F.	−80
Viscosity, CS at −30° F.	16.7
Luminometer number	80
Distillation, ° F.:	
IBP	388
10%	403
50%	427
90%	479
EP	514
Flash point	164

EXAMPLE 3

Propylene tetramer was hydrogenated to completion in one step under the following conditions:

Platinum catalyst, 700 p.s.i.g., 500° F., 6.0 liquid hourly space velocity and 4,000 s.c.f./bbl.

The hydrogenated tetramer was blended with a hydrogenated naphthenic and an intermediate stove oil blend, as described in Example 1, to form a fuel containing 45 percent by volume propylene tetramer and 55 percent by volume of the stove oil blend. This fuel has the following composition:

	Percent by volume
n-Paraffins	0.7
Isoparaffins	59.5
Monocyclic naphthenes	24.9
Dicyclic naphthenes	14.5
Tricyclic naphthenes	0.4

When tested in the laboratory this fuel exhibited the following properties:

Gravity, ° API	46.0
Heat of combustion, B.t.u./lb.	18,760
Fuel density, B.t.u./gal.	124,543
Freeze point, ° F.	−84
Viscosity, CS at −30° F.	12
Luminometer number	85
Distillation:	
IBP	372
10%	380
50%	407
90%	453
EP	500
Rec. percent	98
Flash point, PMCC, ° F.	148

Generally, the viscosity and luminometer number of the tetramer blend were better than the alky trimer-stove oil blend but the fuel density was not as good.

EXAMPLE 4

Propylene tetramer, hydrogenated as in Example 3, was blended with a stove oil, hydrogenated as in Example 1, having the following composition:

42.5 percent isoparaffins, 38.6 percent monocyclic naphthenes and 18.9 percent dicyclic naphthenes.

The fuel blend formed was 20 percent by volume propylene tetramer and 80 percent by volume stove oil and had a composition consisting of:

	Percent by volume
n-Paraffins	7.7
Isoparaffins	50.7
Monocyclic naphthenes	27.9
Dicyclic naphthenes	13.7

This fuel composition was tested in the laboratory and had the following properties:

Gravity, ° API	46.8
Heat of combustion, B.t.u./lb.	18,815
Fuel density, B.t.u./gal.	124,310
Freeze point, ° F.	−40
Viscosity, CS at −30° F.	16
Luminometer number	>78

The freeze point of this fuel was above that required for use in high Mach jet engines and, thus, the fuel was treated with a Lindy 5A molecular sieve to remove n-paraffins. The resultant fuel had the following composition:

	Percent by volume
Isoparaffins	54.0
Monocyclic naphthenes	30.9
Dicyclic naphthenes	15.1

This fuel blend was then tested in the laboratory and was found to have the following properties:

Gravity, ° API	45.0
Heat of combustion, B.t.u./lb.	18,750
Fuel density, B.t.u./gal.	125,150
Freeze point, ° F.	below −80
Viscosity, CS at −30° F.	Less than 15
Luminometer number	80

Treatment of the fuel composition to remove n-paraffins thus produced a very beneficial effect on the freeze point and luminometer number of the fuel without serious detrimental effect on the heat of combustion.

EXAMPLE 5

A fuel was prepared by blending 7.5 percent by volume propylene tetramer with 7.5 percent by volume alkyl trimers and 85 percent by volume of a hydrogenated stove oil having the composition of that used in Example 4. The

alky trimers and the tetramers were hydrogenated in a single step, as in Examples 1 and 3 respectively. The stove oil was hydrogenated in 2 steps as in Example 1. The blended fuel was then passed through a Lindy 5A molecular sieve to remove n-paraffins. The sieved fuel had the following composition:

51.1 percent by volume isoparaffins, 32.8 percent by volume monocyclic naphthenes, and 16.1 percent by volume dicyclic naphthenes.

This fuel was found to have the following properties:

Gravity, ° API	4.39
Heat of combustion, B.t.u./lb.	18,750
Fuel Density, B.t.u./gal.	125,945
Freeze point, ° F.	Below −80
Viscosity at −30° F., CS	15.3
Luminometer number	75.4
Flash point, PMCC, ° F.	162
Distillation:	
IBP	387
10%	401
50%	424
90%	481
EP	517
Rec. percent	98.0

EXAMPLE 6

A stove oil cut from a Four Corners crude was hydrogenated to completion under the two stage hydrogenation conditions of Example 1 and then passed through a Lindy 5A molecular sieve to remove n-paraffins. The resultant stove oil was 30.3 percent by volume isoparaffins, 48.3 percent by volume monocyclic naphthenes, and 21.4 percent by volume tricyclic naphthenes.

This Four Corners stove oil had the following properties after hydrogenation and prior to removal of the n-paraffins.

Gravity, ° API	45.9
Heat of combustion, B.t.u./lb.	18,771
Fuel density, B.t.u./gal.	124,658
Freeze point, ° F.	−42
Viscosity, CS at −30° F.	—
Luminometer number	84

After removal of the n-paraffins, the fuel had the following properties:

Gravity, ° API	46.0
Heat of combustion, B.t.u./lb.	18,740
Fuel density, B.t.u./gal.	124,375
Freeze point, ° F.	Below −80
Viscosity, CS at −30° F.	10.94
Luminometer number	82.0
Flash point	166

After removal of the n-paraffins the fuel had an excellent viscosity and freeze point. Four Corners Crude of the composition given has been found to be the only crude which could be hydrogenated and sieved and then directly used as a fuel without blending.

EXAMPLE 7

A thermally cracked stock obtained from a refinery combination unit bubble tower side stream boiling in the range of 292 to 672° F. was hydrogenated under the two stage conditions set forth in Example 1 and a 375 to 520° F. heart cut was distilled off to form a stock comprising by volume 49.7 percent paraffins about 10 percent of which were n-paraffins, 32.8 percent monocyclic naphthenes, and 17.5 percent dicyclic naphthenes.

This thermally cracked stock was blended with alky trimers hydrogenated as in Example 1 to produce a fuel comprising 85 percent by volume of the thermally cracked stock and 15 percent by volume of the alky trimers. This stock was tested in the laboratory and found to have the following properties:

Gravity, ° API	44.8
Heat of combustion, B.t.u./lb.	18,755
Fuel density, B.t.u./gal.	125,320
Freeze point, ° F.	−60
Viscosity at −30° F., CS	13.51
Luminometer number	83
Distillation, ° F.:	
IBP	384
10%	398
50%	421
90%	469
EP	503

Although the stove oils of many crude oils were examined and none was found which could be hydrogenated and used directly as a high Mach aircraft jet fuel, it is theoretically possible that such a stove oil might be available. Accordingly, with such a stove oil it would be possible to produce high Mach aircraft jet fuels of the disclosed composition using only the two stage hydrogenation described.

Many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof and therefore only such limitations should be applied as are indicated in the appended claims.

We claim:

1. A process for forming a jet engine fuel for Mach 3 to 3.5 aircraft comprising the steps of hydrogenating alky trimers at a temperature from 250 to 850° F., a pressure from 300 to 2,000 p.s.i.g., a liquid hourly space velocity of from 0.2 to 6.0, and a hydrogen rate of from 1,500 to 8,5000 s.c.f./bbl. in the presence of a platinum group metal catalyst to substantial completion to form a mixture of C_{10} to C_{15} isoparaffins; blending 7.5 to 20 percent by volume of said hydrogenated alky trimers with a hydrogenated stove oil fraction to form a fuel having up to 6.5 percent by volume n-paraffins, from 20 to 50 percent by volume monocyclic naphthenes, from 10 to 25 percent polycyclic naphthenes and the balance isoparaffins.

2. A process as defined in claim **1** wherein the alky trimers are a mixture of C_{10} to C_{15} isoparaffins consisting essentially of 8 to 15 percent by volume C_{10}, 30 to 40 percent by volume C_{11}, 10 to 25 percent by volume C_{12}, 10 to 25 percent by volume C_{13}, 8 to 15 percent by volume C_{14} and 8 to 15 percent by volume C_{15} isoparaffins.

3. A process as defined in claim **1** wherein said fuel is formed by blending about 7.5 percent by volume hydrogenated propylene tetramer with 7.5 percent by volume of said hydrogenated alkyl trimer and about 85 percent by volume of a hydrogenated stove oil consisting essentially of from 40 to 45 percent by volume isoparaffins 35 to 40 percent by volume monocyclic naphthenes, and the balance polycyclic naphthenes.

4. A process as defined in claim **3** wherein said hydrogenated propylene tetramer consists essentially of up to 27 percent by volume C_{11} isoparaffins, from 50 to 70 percent by volume C_{12} isoparaffins, from 3 to 45 percent by volume C_{13} isoparaffins and up to 5 percent by volume C_{14} isoparaffins and said hydrogenated alky trimers consist essentially of 8 to 15 percent by volume C_{10} isoparaffins, 30 to 40 percent by volume C_{11} isoparaffins, 10 to 25 percent by volume C_{12} isoparaffins, 10 to 25 percent by volume C_{13} isoparaffins, 8 to 15 percent by volume C_{14} isoparaffins and 8 to 15 percent by volume C_{15} isoparaffins.

5. A process for forming a high Mach jet engine aircraft fuel comprising:

hydrogenating a refinery tetramer stream consisting essentially of by volume up to 30 percent C_{11} olefins, from 50 to 70 percent C_{12} olefins, from 3 to 45 percent C_{13} olefins and up to 5 percent C_{14} olefins, at a temperature of from 250 to 850° F., a pressure

of from 300 to 2,000 p.s.i.g., a liquid hourly space velocity of from 0.2 to 6.0 and a hydrogen rate of from 1,500 to 8,500 s.c.f./bbl. in the presence of a platinum group metal catalyst;

providing a hydrogenated stove oil consisting essentially of from 30 to 45 percent by volume isoparaffins, from 35 to 50 percent by volume monocyclic napthenes, from 15 to 25 percent by volume polycyclic naphthenes and substantially no n-paraffins;

blending a sufficient quantity of said tetramer with said stove oil to form a jet engine fuel having 20 to 50 percent by volume tetramer and the balance stove oil, said fuel having a heat of combustion of at least 18,750 B.t.u./lb., a fuel density of at least 124,000 B.t.u./gal., a luminometer number of at least 75, a freeze point of —75° F. or lower and a viscosity of less than 15 centistokes at —30° F.

6. A process as defined in claim **5** wherein said hydrogenated stove oil is prepared by hydrogenating at a temperature from 250 to 850 ° F., a pressure from 300 to 2,000 p.s.i.g., a liquid hourly space velocity from 0.5 to 6.0, and a hydrogen rate of from 1,500 to 8,000 s.c.f./bbl. in the prescence of a hydrodesulfurizing catatyst;

separating a 370 to 520° F. heart cut from said hydrogenated product; and

hydrogenating said heart cut at a temperature of from 200 to 850° F., a pressure of from 100 to 2,000 p.s.i.g., a liquid hourly space velocity of from 1.5 to 6.0, and a hydrogen rate of from 1,500 to 6,000 s.c.f./bbl. in the presence of a platinum group metal catalyst.

7. A process for forming a jet engine fuel for Mach 3 to 3.5 aircraft comprising the steps of:

hydrogenating a thermally cracked stock boiling in the range of 292 to 672° F. to form a stock consisting essentially of from 12 to 20 percent by volume n-paraffins, from 12 to 20 percent by volume isoparaffins, from 44 to 52 percent by volume monocyclic naphthenes, and from 15 to 23 percent by volume polycyclic naphthenes;

conducting said hydrogenation in a first stage at a temperature from 250° to 850° F., a pressure from 300 to 2,000 p.s.i.g., a liquid hourly space velocity of from 0.2 to 6.0, and a hydrogen rate of from 1,500 to 8,000 s.c.f./bbl. in the presence of a hydrodesulfurization catalyst and in a second stage at a temperature from 200 to 850° F., a pressure from 100 to 2,000 p.s.i.g., a liquid hourly space velocity of from 1.5 to 6.0, and a hydrogen rate of 1,500 to 6,000 s.c.f./bbl. in the presence of a platinum catalyst; and

blending said hydrogenated thermally cracked stock with a sufficient quantity of alkyl trimers to provide a fuel containing 85 percent by volume thermally cracked stock and 15 percent by volume alky trimers and consisting essentially of from 30 to 60 percent by volume isoparaffins, up to 6.5 percent n-paraffins, from 20 to 50 percent by volume monocyclic naphthenes and the remainder from 10 to 25 percent by volume polycyclic naphthenes.

8. A process, as defined in claim **7**, wherein said thermally cracked stock consists essentially of about 49 percent paraffins, about 33 percent monocyclic naphthenes and about 18 percent polycyclic naphthenes, about 10 percent of said paraffins being n-paraffins.

9. A process, as defined in claim **7**, wherein said alky trimers comprise a distribution of C_{10} to C_{15} isoparaffins consisting essentially of from 8 to 15 percent by volume C_{10}, from 30 to 40 percent by volume C_{11}, from 10 to 25 percent by volume C_{12}, from 10 to 25 percent by volume C_{13}, from 8 to 15 percent by volume C_{14}, and from 8 to 15 percent by volume C_{15}.

10. A process as defined in claim **7** further including the step of passing said fuel through a molecular sieve of sufficient pore size to extract substantially all n-paraffins from said fuel.

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