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(12) Patent:

(54) ISOPARAFFINIC JET FUEL

(54)

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1 The present invention is directed to the production
2 of jet fuel from a quality-deficient kerosene fraction by isom-
3 erization followed by hydrogenation. It may be utilized to make
4 commodity-type fuels from kerosenes otherwise unsuitable for
5 that purpose, or special "super" fuels from commodity-type
6 fuels.

7 Stocks for producing jet fuel of acceptable quality
8 are in short supply. Quality objectives, particularly freeze
9 point (possibly as low as -50°F . maximum) and luminometer num-
10 ber (approximately 50 minimum) make it difficult to produce
11 acceptable jet fuel without suffering substantial volume losses
12 in processing. For example, the prior art discloses a method
13 of producing a jet fuel which is high in BTU/gallon in a three-
14 step process comprising (1) hydrocracking, (2) distillation,
15 and (3) hydrogenation. In accordance with the known process
16 paraffinic hydrocarbons are selectively hydrocracked and the
17 residue is removed so as to leave a liquid product boiling
18 above 400°F . which is substantially 100 percent aromatic in
19 nature. This aromatic fraction is then hydrogenated to produce
20 a concentrate of Decalins as the jet fuel product. The present
21 invention avoids the losses due to hydrocracking in the known
22 process by isomerizing rather than cracking the normal paraf-
23 fins in the feedstock.

24 The present invention contemplates isomerization of
25 the n-paraffins (rather than cracking them) and thereafter hy-
26 drogenating the isomerized product. By the isomerization step
27 the freeze point of the mixture is lowered and the efficacy of
28 the following hydrogenation step is enhanced (i.e., it is bet-
29 ter able to reduce the aromatics content and thereby to improve
30 the luminometer number). Paraffins are considered to be premi-
31 um jet fuel components, providing more BTU/lb. and burning more
32 evenly than naphthenic hydrocarbons. Consequently, it is de-

1 desirable to retain them in the jet fuel if possible, rather than
2 cracking them and removing the residue as in the known process.
3 The present invention allows the refiner to retain the paraffins
4 in the fuel, with a concomitant increase in quality and with
5 the added advantage of minimizing volumetric loss during pro-
6 cessing.

7 The present invention may be understood by reference
8 to the drawing which is a schematic diagram of the process.

9 A crude oil is introduced by way of line 100 and frac-
10 tionated in a fractionating tower 101 to provide a kerosene
11 fraction 102 which is the feedstock to the present process.
12 This kerosene fraction is transferred by way of line 102, ad-
13 mixed with hydrogen introduced by way of line 104, and heated
14 by way of the furnace 106 before introduction by way of line
15 108 into an isomerization zone 110. In the isomerization zone
16 110 the n-paraffinic constituents in the kerosene are isomer-
17 ized into isoparaffins, under conditions chosen to minimize the
18 hydrocracking activity of the catalyst so that the final pro-
19 duct does not suffer more than about a 10% loss of the n-paraf-
20 fins due to cracking. The effluent from the isomerization zone
21 is transferred by way of line 112 into a separator 114, from
22 whence hydrogen and noncondensable gases are removed by way of
23 line 116 while the liquid product is passed by way of line 118,
24 admixed with hydrogen which is introduced by way of line 120,
25 and heated in the furnace 122 before introduction into the hydro-
26 genation zone 126 by way of line 124.

27 In the hydrogenation zone the aromatic hydrocarbons
28 which are present in the kerosene fraction originally (as well
29 as those which have been created by dehydrogenation of naphthen-
30 ic constituents) are hydrogenated so that the resulting product
31 contains less than 5% aromatic hydrocarbons, preferably less
32 than 2%. The hydrogenated products are passed by way of line

1 128 into a separator 130 from whence hydrogen and nonconden-
2 sable gases are removed by way of line 132 for suitable treat-
3 ment and possible recycle, while the liquid constituents are
4 removed by way of line 134 for fractionation if desired.

5 The hydrogenated product may be fractionated in a
6 column 140 so as to remove by way of line 142 the small amount
7 of fragments from n-paraffins which have unavoidably been hydro-
8 cracked as an overhead lower boiling stream, while the final
9 product is removed by way of line 144 as a superior jet fuel
10 fraction.

11 There have been indications that shortages of kero-
12 sene and kerosene-type jet fuels might develop because of qual-
13 ity limitations, specifically freeze point and luminometer num-
14 ber (LN). If presently available, but quality deficient, kero-
15 sene boiling range material could be upgraded to meet a goal of
16 -50°F. maximum freeze point and 50 minimum LN, the shortage
17 would be alleviated.

18 The upgrading of present stocks to meet the LN and
19 freezing point requirement should preferably be done with a
20 minimal loss of volume in the requisite treatment for such im-
21 provement. The LN can be improved by extraction to remove the
22 aromatics, but this reduces substantially the volume of the hy-
23 drocarbon stream available as a jet fuel. Likewise, the n-
24 paraffins can be removed from the kerosene range stocks, and
25 the freezing point lowered, by contact with molecular sieves or
26 cracking, but this again reduces the volume which is available
27 as a jet fuel and deprives the resulting fuel of the even-burn-
28 ing characteristics which the paraffinic content can provide.

29 The present invention improves both the luminometer
30 number and the freeze point characteristics of the kerosene
31 range feedstocks by isomerizing the kerosene boiling range ma-
32 terial without substantial hydrocracking, under conditions

1 chosen to minimize cracking, and then subjecting the isomerized
 2 material to hydrogenation to saturate aromatic hydrocarbons.
 3 Unexpectedly, it has been found that the isomerization pretreat-
 4 ment enhances the susceptibility of the materials to hydrogen-
 5 ation so that the aromatics content of the hydrogenated pro-
 6 duct can be substantially reduced under relatively mild condi-
 7 tions of hydrogenation. The use of mild hydrogenation is im-
 8 portant in reducing the pressure specifications which must be
 9 met, thereby minimizing the cost of plant investment.

10 The feedstock for the present process is a jet-qual-
 11 ity deficient kerosene. The kerosene feedstock may suitably
 12 boil within the range of 300-550°F., and may contain from 20
 13 to 50 volume percent naphthenes, from 20 to 50 volume percent
 14 aromatics, from 10 to 30 volume percent n-paraffins, and from
 15 15 to 40 volume percent isoparaffins. An inspection of a
 16 representative kerosene feedstock is given below in Table I.

17 TABLE I

18 Exemplary Kerosene Feedstock

19	LN	29
20	Freeze, °F.	-32
21	RI, 25°C.	1.4696
22	% n-Paraffins	18
23	% Isoparaffins	23
24	% Naphthenes	29
25	% Aromatics	30
26	IBP, °F.	366
27	10%	404
28	20%	418
29	50%	450
30	90%	500
31	FBP °F.	530

32

1 By advertence to Table I, it is seen that a typical
2 feedstock for use in the present invention has a luminometer
3 number of 29, far below the 50 minimum which is required. Al-
4 so, the freeze point of -32°F. is far too high as compared to
5 the -50°F. minimum which is desired. As will be discussed here-
6 inafter, the present invention allows the production of a jet
7 fuel having a luminometer number of about 60-80 and with a
8 freeze point of about -55 to -60°F. , while suffering only about
9 a 5-15 volume percent loss in volume due to cracking during the
10 isomerization step.

11 The first step of the present invention is liquid
12 phase isomerization, which may be suitably accomplished in con-
13 tact with a catalyst such as platinum on alumina. Suitable cata-
14 lysts will include metals of Group VI and Group VIII of the
15 Periodic Table, their oxides and sulfides, which may be sup-
16 ported on materials such as alumina, natural or processed baux-
17 ite, kieselguhr, etc. When using platinum, 0.3-0.6% platinum
18 on alumina is preferred. A halogen promoter may be employed,
19 but is not essential.

20 The conditions of isomerization will depend upon the
21 specific catalyst which is to be employed, but will be chosen
22 to minimize the cracking activity of the catalyst so that isom-
23 erization of the n-paraffin can be accomplished without sub-
24 stantial losses due to cracking.

25 When using the preferred platinum-on-alumina catalyst,
26 these conditions may include from 800°F. to 1000°F. (preferably
27 875°F.), a pressure of 150 to 500 psig (preferably 300 psig),
28 a liquid hourly space velocity (LHSV) from 0.2 to 2 V/V/Hr.
29 (preferably 1 to 1.5 V/V/Hr.), and a hydrogen feed rate of from
30 2000 to 10,000 SCF/B (preferably 5000 SCF/B).

31 The conditions are chosen so as to obtain an isomer-
32 ized product containing at least 25 volume percent paraffinic

1 hydrocarbons (at least 15% isoparaffins) while suffering no
2 more than a 15 volume percent loss of the feedstock due to
3 cracking of the paraffins into constituents which boil below
4 the boiling range of the feedstock.

5 The hydrogenation step may be accomplished in contact
6 with a suitable hydrogenation catalyst, such as the platinum-
7 on-alumina catalyst preferred for use in the isomerization zone.
8 Other suitable catalysts may be chosen from the group consist-
9 ing of nickel, cobalt and iron. These catalysts may be sup-
10 ported on materials such as alumina, silica, magnesia, kiesel-
11 guhr, zirconia, etc.

12 For the preferred platinum-on-alumina catalyst, hy-
13 drogenation conditions will include a temperature from 400 to
14 800°F. (preferably 500°F.), a pressure from 200 to 2000 psig
15 (preferably 800 psig), a liquid hourly space velocity (LHSV)
16 from 0.3 to 3 V/V/Hr. (preferably 0.5 V/V/Hr.), and a hydrogen
17 treat rate of from 500 to 10,000 SCF/B (preferably 5000 SCF/B).

18 The hydrogenation conditions are chosen to maximize
19 hydrogenation of the aromatic constituents, some of which may
20 have been formed during the isomerization step. The product
21 from the hydrogenation should contain less than 5% aromatic hy-
22 drocarbons, preferably less than 2% (by volume) and will com-
23 prise at least 25 volume percent paraffinic hydrocarbons, in-
24 cluding at least 15 volume percent isoparaffins. Thus, it is
25 seen that all of the paraffinic hydrocarbons in the isomerized
26 product remain in the hydrogenated product. The hydrogenated
27 product boils within the range from 300°F. to 500°F.

28 In order to illustrate the present invention, a number
29 of runs were made wherein the exemplary kerosene feedstock
30 shown in Table I was first subjected to isomerization in con-
31 tact with a 0.6% platinum-on-alumina catalyst, at 875°F., 300
32 psig, 1.25 V/V/Hr., and 5000 SCF/B. This product was then

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- 1 hydrogenated in contact with 0.6% platinum-on-alumina catalyst,
- 2 at 500°F., 900 psig, 0.5 V/V/Hr., and 5000 SCF/B of hydrogen.
- 3 The results of this run are summarized below in Table II.

TABLE II
Improvement of LN and Freeze Point

	<u>Operating Conditions</u>	<u>Feed</u>	<u>Isomerization</u>	<u>Hydrogenation</u>
1				
2				
3				
4	Catalyst		0.6% Platinum on Alumina	0.6% Platinum on Alumina
5	Temperature		875°F.	500°F.
6	Pressure		300 psig	900 psig
7	Space velocity, LHSV		1.25 V/V/Hr.	0.5 V/V/Hr.
8	Hydrogen rate		5000 SCF/B	5000 SCF/B
9	<u>Stream Data</u>	<u>Feed</u>	<u>Isom. Prod.</u>	<u>Hydr. Prod.</u>
10	LN	29.2	13.8	69.7
11	Freeze point, °F.	-32	-72	-70
12	Hydrocarbon Analysis			
13	Isoparaffins	22.8	28.5	97.5
14	n-Paraffins	17.1	8.2	} }
15	Napththenes	29.1	8.1	
16	Aromatics	29.5	52.5	
17	Olefins	1.5	2.5	0.5
18	Refractive Index	1.470		2.0
				1.445

1 By advertence to Table II it is seen that the lumin-
 2 ometer number of the kerosene feedstock was increased from 29.2
 3 in the feed to 69.7 in the hydrogenated product. The freeze
 4 point was improved from a -32°F. to -70°F. Note that this was
 5 accomplished by isomerizing the n-paraffins in the feedstock,
 6 which were reduced from 17.1% to 8.2% while the isoparaffins
 7 increased from 22.8% to 28.5%. Note that the naphthenes in
 8 the feedstock were dehydrogenated in the isomerization zone to
 9 form aromatics, but that in the final hydrogenation product only
 10 0.5 volume percent aromatics were present. Loss of feedstock
 11 was only about 5 volume percent. Thus, a superior jet fuel is
 12 produced in the two-step process.

13 In order to show that the hydrogenation susceptibil-
 14 ity of the kerosene fraction was unexpectedly improved by the
 15 isomerization step, runs were made wherein the feedstock with-
 16 out isomerization was contacted with a platinum-on-alumina cata-
 17 lyst under hydrogenation conditions, and these results compared
 18 to the hydrogenation of the isomerized product, using the same
 19 feedstock for the isomerization step. The results of these runs
 20 are shown below in Table III

21 TABLE III

22 IMPROVED HYDROGENATION SUSCEPTIBILITY

	Raw feed	Dehydroisomerized Feed	Run I	Run II
24 % Aromatics	29.5	52.5	0.6	25.5
25 RI, 25°C.	1.470	-	-	1.462
26 LN	29	13.8	70	-
27 Freeze, °F.	-32	-72	-65	-36
28 IBP, °F.	366	-	356	-
29 10%	404	-	381	-
30 20%	418	-	391	-
31 50%	450	-	423	-
32 90%	500	-	480	-
33 FBP, °F.	530	-	530	-

1 Hydrogenation Conditions, Run I and Run II

2	Catalyst	0.6% Platinum on Alumina
3	Temperature, °F.	500
4	Pressure, psig	400
5	LHSV (V/V/Hr.)	0.5
6	H ₂ rate, SCF/B	5000-10,000

7 By reference to Table III, it is seen that the raw
8 feedstock contained 29.5% aromatic hydrocarbons, which was re-
9 duced by hydrogenation at the standard operating conditions to
10 only 0.6 volume percent in Run 1. The isomerized feedstock in-
11 to the hydrogenation zone in this case contained about 52%
12 aromatic hydrocarbons, due to the dehydroaromatization activ-
13 ity in the isomerization zone. The hydrogenation accomplished
14 a reduction in aromatic hydrocarbons of about 92%. Comparing
15 this with the hydrogenation of the untreated feedstock in Run
16 2, it is seen that the product contained 25.5% aromatics. Com-
17 pared to the feedstock (which contained only 29.5% aromatics)
18 it is seen that the reduction in aromatic hydrocarbons without
19 the isomerization step was only about 15%. The hydrogenation
20 was carried out under the identical conditions employed in Run
21 1. Thus, the enhancement of hydrogenation efficacy is clear.

22 Attention is also directed to the fact that the hy-
23 drogenation step was carried out under 400 pounds pressure,
24 at a temperature of only 500°F. These mild hydrogenation con-
25 ditions allow the use of equipment in the hydrogenating units
26 which is much less expensive than that which is required for
27 operation at 900 pounds and at elevated temperatures. The dis-
28 tillation data presented on the raw feed and on the Run 2 pro-
29 duct demonstrate that the product was corrected to essentially
30 the same boiling range as the feed. This was done by the re-
31 moval of 5 volume percent of the total reactor effluent by dis-
32 tillation. This 5% is the measure of the loss by cracking to

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1 lower than feed boiling range, since little if any gas is
2 formed in the reaction.

3 Having disclosed in detail the essence of the pres-
4 ent invention, and having given several specific examples there-
5 of as preferred embodiments, what is desired to be protected
6 by Letters Patent should be limited by the following claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

A 1. A method of producing a superior jet fuel which comprises sequentially (1) catalytically isomerizing^{in the liquid phase} a quality-deficient kerosene without hydrocracking more than 15 volume percent thereof into components boiling lower than said kerosene, to obtain an isomerized product containing at least 25 volume percent paraffinic hydrocarbons including at least 15 volume percent isoparaffins, and thereafter (2) catalytically hydrogenating said isomerized product to obtain a hydrogenated product boiling within the range from 300°F. to 500°F. which contains less than 5 volume percent aromatics and contains all of said paraffinic hydrocarbons.

2. A method in accordance with claim 1 wherein both the isomerization step and the hydrogenation step are carried out in contact with platinum on alumina.

3. A method in accordance with claim 1 wherein said isomerization catalyst is platinum on alumina under liquid phase isomerization conditions including a temperature from 800 to 1000°F., a pressure from 150 to 500 psig, a LHSV from 0.2 to 2.0 V/V/Hr., and a hydrogen feed rate from 2000 to 10,000 SCF/B.

4. A method in accordance with claim 3 wherein said hydrogenation catalyst is platinum on alumina and said hydrogenation conditions include a temperature from 400 to 800°F., a pressure from 200 to 2000 psig, a LHSV from 0.3 to 3 V/V/Hr., and a hydrogen feed rate from 500 to 10,000 SCF/B.

5. A method in accordance with claim 4 wherein the kerosene boils within the range of 300 to 500°F. and contains from 10 to 30 volume percent n-paraffins, from 15 to 40 volume percent isoparaffins, from 20 to 50 volume percent aromatics, and from 20 to 50 volume percent naphthenes.

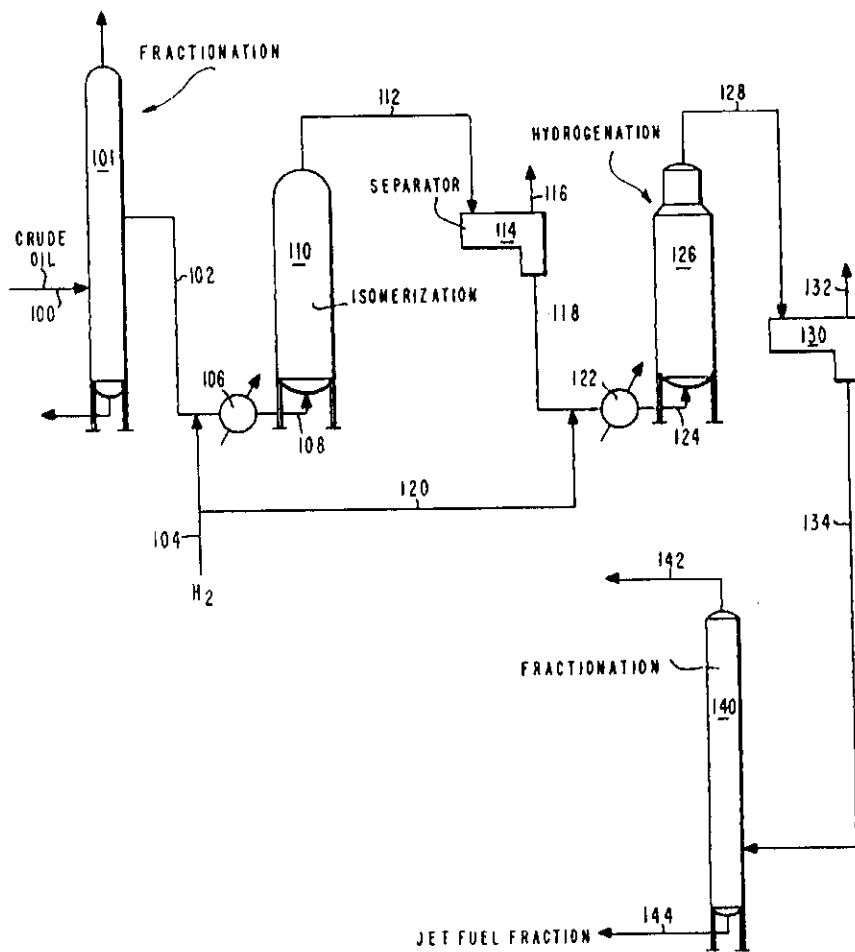
6. A method of producing a superior jet fuel which comprises in an isomerization zone, contacting a hydrocarbon mixture comprising 10 to 30 volume percent n-paraffins, 20 to 50 volume percent aromatics, and 20 to 50 volume percent naphthenes and boiling within the range from 300 to 550°F. with an isomerization catalyst chosen from the group consisting of the metals of Group VI and Group VIII of the Periodic Table, their oxides and sulfides, and admixtures thereof, under liquid phase isomerization conditions including a temperature from 800 to 1000°F., a pressure from 150 to 500 psig, a space velocity from 0.2 to 2 V/V/Hr., and a hydrogen rate from 2000 to 10,000 SCF/B, said conditions being chosen to minimize hydrocracking so that not more than 15 volume percent of said hydrocarbon mixture is hydrocracked, whereby an isomerized product stream is obtained which contains at least 25 volume percent paraffinic hydrocarbons, including at least 15 volume percent isoparaffins, and, in a hydrogenation zone, contacting said isomerized product stream with a hydrogenation catalyst chosen from the group consisting of platinum, cobalt, and iron, under liquid phase hydrogenation conditions including a temperature from 400 to 500°F., a pressure from 200 to 2000 psig, a space velocity from 0.3 to 3 V/V/Hr., and a hydrogen treat rate from 500 to 10,000 SCF/B, whereby a hydrogenated product is obtained boiling substantially within the range from 300 to 500°F. and comprising at least 25 volume percent paraffinic hydrocarbons, including at least 15 volume percent isoparaffins, and less than 5 volume percent aromatics.

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7. A method of producing a superior jet fuel which comprises sequentially subjecting a hydrocarbon stream boiling substantially within the range from 366 to 530°F. and containing from 10 to 30 volume percent n-paraffins, from 20 to 50 volume percent aromatics, and from 20 to 50 volume percent naphthenes first to dehydroisomerization in contact with a platinum-on-alumina catalyst at a temperature of about 875°F., a pressure of about 300 psig, a LHSV of about 1.25 V/V/Hr., and a hydrogen feed rate of about 5000 SCF/B, and then to hydrogenation in contact with a platinum-on-alumina catalyst at a temperature from 400 to 800°F., a pressure from about 200 to about 1000 psig, a LHSV from about 0.3 to about 3 V/V/Hr., and a hydrogen feed rate from about 500 to 10,000 SCF/B, to obtain a hydrogenated product boiling within the range from 356 to 530°F. and containing about 97.5 volume percent paraffins and naphthenes, and about 0.5 volume percent aromatics.

8. A method in accordance with claim 7 wherein the hydrogenation conditions include a temperature of about 500°F., a pressure of about 900 psig, a LHSV of about 0.5 V/V/Hr., and a hydrogen rate of about 5000 SCF/B.





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