



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 138 750 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
11.10.2006 Bulletin 2006/41

(51) Int Cl.:
C10G 69/12 (2006.01)

(21) Application number: **01107717.9**

(22) Date of filing: **30.03.2001**

(54) **Integrated hydroisomerization/alkylation process**

Integriertes Hydroisomerisierungs- und Alkylierungsverfahren

Procédé intégré d'hydroisomérisation et d'alkylation

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**

(30) Priority: **31.03.2000 US 539948**

(43) Date of publication of application:
04.10.2001 Bulletin 2001/40

(73) Proprietor: **ConocoPhillips Company
Bartlesville, OK 74004 (US)**

(72) Inventor: **Randolph, Bruce B.
Bartlesville, OK 74006 (US)**

(74) Representative: **Bublak, Wolfgang et al
Bardehle, Pagenberg, Dost, Altenburg, Geissler,
Galileiplatz 1
81679 München (DE)**

(56) References cited:
**EP-A- 0 505 843 US-A- 2 264 447
US-A- 2 276 171 US-A- 2 387 309**

EP 1 138 750 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

Background of the Invention

5 [0001] This invention relates to a process for producing gasoline blending components. More specifically, this invention relates to the processing of paraffinic and olefinic hydrocarbons in an integrated system to produce gasoline blending components.

[0002] Recent governmental regulations in response to the 1990 Clean Air Act have resulted in the requirement that motor gasoline be reformulated to include greater concentration levels of oxygenates and lower concentrations of aromatic and olefinic hydrocarbons. Other such regulations require reductions in permissible gasoline vapor pressure.

10 [0003] However, the removal of at least some of the aromatic and olefinic hydrocarbons from the gasoline pool, due to restrictions on aromatic and olefinic hydrocarbon concentrations, and the removal of normal butane from the gasoline pool, due to restrictions on permissible vapor pressure, will result in reducing the available gasoline pool octane.

[0004] In addition, C₅ olefins contained in some gasoline blending stocks have good octane characteristics but are also very volatile and contribute greatly to ozone and smog formation in the lower atmosphere. For this reason, there is an incentive to remove C₅ olefins from gasoline, however, the octane lost from such removal has to be replaced.

15 [0005] Therefore, development of a process to convert C₅ olefins to a high octane, low vapor pressure gasoline blending stock would be a significant contribution to the art and to the economy.

[0006] EP-A-0 505 843 discloses an integrated olefin processing process, wherein the olefins are subjected to hydroisomerization, followed by etherification. Those olefin compounds which are not etherified are alkylated. US-A-2 387 309 relates to the conversion of hydrocarbon oils, including cracking and alkylation processes. US-A-2 276 171 relates to a process wherein volatile gasolines are converted by a combination of treatment steps to high octane gasoline.

Summary of the Invention

25 [0007] It is an object of the present invention to provide an integrated process for upgrading paraffins and olefins to produce valuable gasoline blending components.

[0008] It is a further object of the present invention to provide an integrated process for upgrading paraffins and olefins which reduces the operating costs associated with the produced gasoline blending components.

30 [0009] It is yet a further object of the present invention to provide an integrated process for upgrading a gasoline blending stock by reducing the C₅ olefin concentration while maintaining its octane rating.

[0010] In accordance with the present invention, a process as defined in claim 1 for upgrading paraffins and olefins has been discovered comprising the steps of:

- 35 a) hydroisomerizing said hydrocarbon feedstock in a hydroisomerization zone so as to produce a hydroisomerate stream; and
b) passing said hydroisomerate stream to an alkylation unit and alkylating said hydroisomerate stream by a branched chain paraffin hydrocarbon to produce an alkylate stream.

40 [0011] Other objects and advantages will become apparent from the detailed description and the appended claims.

Brief Description of the Drawing

[0012]

45 The Figure is a schematic flow diagram presenting an embodiment of the present invention.

Detailed Description of the Invention

50 [0013] The process of the present invention as defined in claim 1 comprises, consists of, or consists essentially of hydroisomerizing a hydrocarbon feedstock comprising, consisting of, or consisting essentially of at least one C₅ olefin so as to produce a hydroisomerate stream; and, alkylating at least a portion of the hydroisomerate stream by a branched chain paraffin hydrocarbon to produce an alkylate stream.

[0014] The C₅ olefin of the hydrocarbon feedstock can comprise, consist of, or consist essentially of an olefin selected from the group consisting of 2-pentene, 2-methyl-butene-2, 1-pentene, 3-methyl-butene-1, 2-methyl-butene-1, isoprene, piperylene, cyclopentene, and combinations of any two or more thereof.

55 [0015] The hydrocarbon feedstock can be any gasoline range hydrocarbon stream which contains at least one C₅ olefin. Most typically, the hydrocarbon feedstock is a C₅ fraction separated from a gasoline range hydrocarbon stream

EP 1 138 750 B1

comprising hydrocarbons having at least three carbon atoms per molecule and, preferably at least 5 carbon atoms per molecule, with the other separated fraction being a C₆+ gasoline blending stock. The gasoline range hydrocarbon stream can include gasolines obtained from a catalytic cracking process, a thermal cracking process, naphthas, gas oils, reformates, straight-run gasoline, and the like. The most suitable source for the gasoline range hydrocarbon stream is a catalytic cracking process.

[0016] The hydroisomerization of the hydrocarbon feedstock includes: 1) hydrogenation of isoprene and piperylene to mono-olefins; 2) conversion of a portion of the cyclopentene to cyclopentane; and 3) isomerization of a portion of the 1-pentene to 2-pentene.

[0017] The hydroisomerization of the hydrocarbon feedstock is performed in a hydroisomerization zone which includes a hydroisomerization catalyst, the presence of hydrogen, and which is operated under hydroisomerization conditions sufficient to hydrogenate diolefins to mono-olefins and to isomerize mono-olefins. Preferably, the hydroisomerization conditions include a temperature in the range of from -18 to 260°C (0°F to 500°F), more preferably from 24 to 204 °C (75°F to 400°F), and most preferably from 37.8 to 93.3°C (100°F to 200°F), a pressure in the range of from 0.69 to 10.35 MPa gauge (100 psig to 1500 psig), more preferably from 1.04 to 6.9 MPa gauge (150 psig to 1000 psig), and most preferably from 1.38 to 4.14 MPa gauge (200 psig to 600 psig); and a liquid hourly space velocity (LHSV) in the range of from 0.01 hr.⁻¹ to 100 hr.⁻¹, more preferably from 1 hr.⁻¹ to 50 hr.⁻¹, and most preferably from 5 hr.⁻¹ to 15 hr.⁻¹.

[0018] The term LHSV, as used herein, shall mean the numerical ratio of the rate at which a hydrocarbon feed is charged to the hydroisomerization zone in cubic centimeters/per hour divided by the number of cubic centimeters of catalyst contained in the hydroisomerization zone.

[0019] The hydroisomerization catalyst is preferably a dual function catalyst capable of hydrogenating diolefins to mono-olefins and isomerizing mono-olefins. The more preferred hydroisomerization catalyst comprises palladium and alumina.

[0020] Hydrogen is present in the hydroisomerization zone at a level such that the hydrogen to diolefin mole ratio is in the range of from 0.5 to 50, more preferably from 1 to 20, and most preferably from 3 to 6.

[0021] The hydroisomerate stream produced contains reduced concentrations of isoprene, piperylene and cyclopentene as compared to the hydrocarbon feedstock. The presence of isoprene, piperylene and cyclopentene in a feed to an alkylation process can result in increased acid soluble oil (ASO) production. ASO is an undesirable alkylation by-product comprising conjunct polymers which are highly olefinic oils.

[0022] Also, due to the isomerization of 1-pentene to 2-pentene, the mole ratio of 2-pentene to 1-pentene in the hydroisomerate stream is higher than the mole ratio of 2-pentene to 1-pentene in the hydrocarbon feedstock.

[0023] The alkylation of the hydroisomerate stream is performed in an alkylation unit and under alkylation conditions suitable for alkylating the hydroisomerate stream by a branched chain paraffin hydrocarbon to produce an alkylate stream.

[0024] Optionally, a light olefin stream comprising, consisting of, or consisting essentially of an olefin selected from the group consisting of i-propylene, i-butene, 2-butenes, 1-butenes, and combinations of any two or more thereof, can be combined with and become a part of the hydroisomerate stream prior to alkylation of the hydroisomerate stream.

[0025] Suitable alkylation units include, but are not limited to, those employing hydrofluoric (HF) acid, or sulfuric acid, or a solid acid as an alkylation catalyst. The most suitable alkylation unit is an HF alkylation unit wherein isoparaffins and olefins are alkylated by contact with an alkylation catalyst comprising hydrofluoric acid, and optionally, a volatility reducing additive, in a riser (upwardly flowing) reactor with a subsequent routing of the alkylation reaction mixture to a settler for separation into a hydrocarbon phase comprising an alkylate product and an alkylation catalyst mixture phase comprising the alkylation catalyst and an ASO reaction by-product. At least a portion of the hydrocarbon phase is withdrawn from the settler to form an alkylate stream.

[0026] The branched chain paraffin hydrocarbon can comprise, consist of, or consist essentially of a hydrocarbon selected from the group consisting of i-butane, i-pentane, and combinations thereof.

[0027] The alkylate stream comprises, consists of, or consists essentially of alkylated hydrocarbons having from 5 to 20 carbon atoms per molecule, unreacted branched chain paraffin hydrocarbons, and i-pentane.

[0028] In one embodiment, the alkylate stream is separated into a C₅+ alkylate stream comprising, consisting of, or consisting essentially of hydrocarbons having greater than 4 carbon atoms per molecule, preferably from 5 to 20 carbon atoms per molecule, and most preferably from 5 to 10 carbon atoms per molecule. The C₅+ alkylate stream, which will have enhanced octane as compared to the hydroisomerate stream, can be utilized as a gasoline blending stock.

[0029] The C₅+ alkylate stream can be separated into an i-pentane stream and a deisopentane C₅+ alkylate stream. The i-pentane stream, high in octane, can be added to the C₆+ gasoline blending stock, or otherwise utilized as a gasoline blending stock, to replace the octane lost from the removal of the high octane C₅ olefins from the gasoline range hydrocarbon stream, as described above. This results in a gasoline blending stock that has good octane quality and a lower olefin content as compared to the unprocessed gasoline range hydrocarbon stream described above.

[0030] The deisopentane C₅+ alkylate stream can also be used as a separate gasoline blending stock having good octane quality.

[0031] In another embodiment, in addition to separating the alkylate stream into a C₅+ alkylate stream, the alkylate

stream can also be separated into a n-butane stream and an i-butane stream. The i-butane stream can be recycled to the alkylation unit for use as the branched chain paraffin hydrocarbon, or used as a gasoline blending component. The n-butane stream can also be used as a gasoline blending component, or isolated for use as liquefied petroleum gas (LPG).

5 [0032] In yet another embodiment, in addition to blending the i-pentane stream into the C₆+ gasoline blending stock, the i-pentane stream can also be sent downstream for further processing which can include disproportionation in a disproportionation zone operated under conditions suitable to convert i-pentane to i-butane and i-hexane. Typical, but certainly not the only, methods for disproportionating i-pentane are disclosed in U.S. Patent No.'s 5,900,522; 5,414,184; and 5,489,727.

10 [0033] Now referring to the Figure, there is depicted by schematic representation an integrated hydroisomerization/alkylation process system 10. A gasoline range hydrocarbon stream comprising, consisting of, or consisting essentially of hydrocarbons having at least three carbon atoms per molecule is introduced to first separator 12, which defines a first separation zone, via conduit 14. A hydrocarbon feedstock comprising at least one C₅ olefin is removed overhead from first separator 12 via conduit 16 and is introduced to hydroisomerization reactor 18, which defines a hydroisomerization zone. A C₆+ gasoline blending stock is removed from first separator 12 via conduit 20. A hydrogen stream is charged to hydroisomerization reactor 18 via conduits 22 and 16. A hydroisomerate stream passes from hydroisomerization reactor 18 to an alkylation unit 24 via conduit 26. A light olefin stream comprising i-propylene, i-butene, 2-butenes, 1-butenes, and combinations of any two or more thereof, is optionally charged to alkylation unit 24 via conduits 28 and 26. An alkylate stream is passed from alkylation unit 24 to a second separator 30, defining a second separation zone, via conduit 32, wherein the alkylate stream is separated into various products. A propane containing stream is removed from second separator 30 via conduit 34 and is sent downstream for further processing. A n-butane stream is removed from second separator 30 via conduit 36.

15 [0034] A C₅+ alkylate stream is removed from separator 30 via conduit 38 and can be sent downstream for use as a gasoline blending stock. At least a portion of the C₅+ alkylate can also be sent to a third separator 40, defining a third separation zone, via conduits 38 and 42 for separation into an i-pentane stream and a deisopentanzied C₅+ alkylate stream. The i-pentane stream is removed from third separator 40 via conduit 44 and can be used as a gasoline blending stock, preferably added to the C₆+ gasoline blending stock to improve its octane. The deisopentanzied C₅+ alkylate stream is removed from third separator 40 via conduit 46 and can be used as a gasoline blending stock.

20 [0035] The following examples demonstrate the advantages of the present invention. These examples are for illustration purposes only and they are not intended to limit the invention as set out in the specification and the appended claims.

30 Example I

[0036] This example illustrates the benefits of hydroisomerizing a C₅ olefin containing hydrocarbon feed prior to alkylation.

35 [0037] The alkylation batch reactor was a monel autoclave of 300 ml capacity connected at one end to a monel sight gauge via 6.35 mm (1/4") monel tubing, and connected at the other end to a feed introduction line via 3.18 mm (1/8") monel tubing.

40 [0038] For each run, the catalyst was circulated through the reactor at a stirring rate of 1500 rpm. The catalyst composition contained 92 wt. % HF, 1-2 wt. % water with the balance comprising acid soluble oil and dissolved light hydrocarbons.

Run 1 (Control)

45 [0039] For Run 1, a feed composition (presented in Table 1) was prepared, by mixing pure components, to be representative of an alkylation unit feed containing an i-butane component and a C₅ olefin component. The C₅ olefin component was blended to be representative of a raw C₅ olefin stream similar to a C₅ cut from a catalytic cracker gasoline stream. The feed was alkylated in a batch reactor in which 127.5 grams of HF were stirred at 1500 rpm. The reactor temperature was about 35.8°C (96.5°F) and the volume to volume ratio of HF acid to hydrocarbon was 1:1. The HF and alkylate product were collected in a settler and allowed to separate. The alkylate product was drawn off into a suitable sample cylinder, contacted with 8.5% KOH solution (to destroy free HF), collected, and analyzed by standard gas chromatography using a GC sample injection valve so that no light materials were lost. The separated alkylate product was collected and analyzed at the end of the run (1.5 minutes). Test data results are provided in Table 2.

55 Run 2 (Control)

[0040] For Run 2, a feed composition (presented in Table 1) was prepared, by mixing pure components, to be representative of an alkylation unit feed containing an i-butane component and a C₅ olefin component. The C₅ olefin component was blended to be representative of a C₅ olefin stream produced by sequentially hydroisomerizing and etherifying a raw

EP 1 138 750 B1

C₅ olefin stream similar to that of Control Run 1. The feed was alkylated in a batch reactor in which 127.0 grams of HF were stirred at 1500 rpm. The reactor temperature was about 35.4°C (95.8°F) and the volume to volume ratio of HF acid to hydrocarbon was 1:1. The HF and alkylate product were collected in a settler and allowed to separate. The alkylate product was drawn off into a suitable sample cylinder, contacted with 8.5% KOH solution at an ambient temperature (to destroy free HF), collected, and analyzed by standard gas chromatography using a GC sample injection valve so that no light materials were lost. The separated alkylate product was collected and analyzed at the end of the run (1.5 minutes). Test data results are provided in Table 2.

Run 3 (Inventive)

[0041] For Run 3, a feed composition (presented in Table 1) was prepared, by mixing pure components, to be representative of an alkylation unit feed containing an i-butane component and a C₅ olefin component. The C₅ olefin component was blended to be representative of a C₅ olefin hydroisomerate stream produced by hydroisomerizing a raw C₅ olefin stream similar to that of Control Run 1. The feed was alkylated in a batch reactor in which 127.9 grams of HF were stirred at 1500 rpm. The reactor temperature was about 35.1°C (95.1°F) and the volume to volume ratio of HF acid to hydrocarbon was 1:1. The HF and alkylate product were collected in a settler and allowed to separate. The alkylate product was drawn off into a suitable sample cylinder, contacted with 8.5% KOH solution at an ambient temperature (to destroy free HF), collected, and analyzed by standard gas chromatography using a GC sample injection valve so that no light materials were lost. The separated alkylate product was collected and analyzed at the end of the run (1.5 minutes). Test data results are provided in Table 2.

Table 1			
Component	Run 1 (Control)	Run 2 (Control)	Run 3 (Inventive)
<u>Paraffins</u>			
Lights	0.002	0.003	0.002
propane	0.803	0.827	0.818
i-butane	89.811	89.603	90.019
n-butane	1.978	1.967	1.967
i-pentane	0.003	0.002	0.005
<u>Olefins</u>			
1-pentene	0.656	0.512	0.269
2-methyl-butene-1	0.199	0.027	0.216
(t) 2-pentene	2.029	4.332	2.048
(c) 2-pentene	0.931	2.042	0.965
2-methyl-butene-2	3.090	0.369	3.306
pentadienes	0.276	-----	-----
cyclopentene	0.083	0.263	0.221
C ₆ +	0.104	0.017	0.085
unknowns	0.035	0.036	0.079
Total	100	100	100
I/O ratio ¹	12.85	11.88	12.81
isopentene/ n-pentene ratio	0.909	0.057	1.073
¹ I/O ratio = Isoparaffin to Olefin ratio, weight/weight			

Table 2 Alkylation Product			
Component	Run 1 (Control)	Run 2 (Control)	Run 3 (Inventive)
ethane	0.001	0.001	0.001

EP 1 138 750 B1

(continued)

Component	Run 1 (Control)	Run 2 (Control)	Run 3 (Inventive)
propane	0.669	0.698	0.692
i-butane	81.196	80.522	80.557
n-butane	2.052	2.021	2.035
organic fluorides	0.066	0.067	0.072
i-pentane	4.253	3.186	4.483
n-pentane	0.153	0.424	0.136
C ₆ paraffins	0.230	0.168	0.288
C ₇ paraffins	0.186	0.130	0.193
C ₈ paraffins	6.027	4.269	6.171
C ₉ paraffins	2.873	5.477	3.044
unknown/residue	2.294	3.037	2.326
Total	100	100	100
C ₅ + wt. % yield ¹	2.31	2.23	2.39
Net C ₅ + Product			
i-pentane	26.531	19.087	26.890
n-pentane	0.957	2.535	0.815
C ₆ paraffins	1.434	1.009	1.729
C ₇ paraffins	1.160	0.782	1.159
C ₈ paraffins	37.632	25.595	37.066
C ₉ +paraffins	31.879	50.780	31.942
unknowns	0.375	0.261	0.314
Total	100	100	100
RON ²	91.8	89.8	91.9
MON ³	90.6	89.0	90.6
(R+M)/2 ⁴	91.2	89.4	91.3
¹ C ₅ + wt. % yield is equal to the wt. % C ₅ + in the product divided by the wt. % olefins in the feed. ² Estimated by Gas Chromatograph according to the Hutson and Logan method, Hydrocarbon Processing, Sept. 1975, pages 107-110. ³ Estimated by Gas Chromatograph according to the Hutson and Logan method, Hydrocarbon Processing, Sept. 1975, pages 107-110. ⁴ Numerical average of collected RON and MON			

[0042] The test results presented in Table 2 show that the inventive process (Run 3) of hydroisomerizing a hydrocarbon feed containing C₅ olefins followed by alkylating the resulting intermediate product results in a product having a higher octane rating and increased C₅+ wt. % yield per wt. of C₅ olefin in the feed as compared to Control Run 1 which includes only the alkylation of the hydrocarbon feed, and, as compared to Control Run 2 which includes hydroisomerization of the hydrocarbon feed followed by etherification to convert isopentenes (such as 2-methyl-butene-2) to oxygenates (such as methyl-tertiary-butyl ether), which are then removed, and alkylation of the remaining intermediate product.

[0043] Inventive Run 3 demonstrated a 0.1% increase in octane (R+M/2) and a 3.5% increase in C₅+ wt. % yield per wt. of C₅ olefin in the feed over Control Run 1.

[0044] Inventive Run 3 demonstrated a 2.1 % increase in octane (R+M/2) and a 7.2 % increase in C₅ + wt. % yield per wt. of C₅ olefin in the feed over Control Run 2.

EP 1 138 750 B1

Example II

[0045] This example illustrates the benefits of hydroisomerizing a C₅ olefin containing hydrocarbon feed prior to alkylation.

[0046] The reactor was a section of monel schedule 40 pipe 0.6 m (2 feet) in length and 25.4 mm (1 inch) in diameter connected at one end to a monel sight gauge via 6.35 mm (1/4") monel tubing, and connected at the other end to a feed introduction nozzle, having a 0.25 mm (0.01 inch) diameter orifice, via 3.18 mm (1/8") monel tubing.

[0047] For each run, the catalyst was circulated through the reactor and monel sight gauge at a flow rate in the range of from about 50 ml/min to about 100 ml/min. The catalyst composition contained approximately 87-88 wt. % HF, 1-2 wt. % water with the balance comprising acid soluble oil and dissolved light hydrocarbons.

Control Run 4

[0048] The composition of the hydrocarbon feed for Control Run 4 is presented in Table 3, and is a mixture of three components, 1) a C₅ olefin fraction from a full range FCC gasoline; 2) a typical propylene and butylene alkylation unit feed and; 3) a typical isobutane alkylation unit feed. The hydrocarbon feed was pumped through the feed introduction nozzle into the reactor at a rate of about 300 ml/hour. The reactor effluent flowed into the monel sight gauge wherein the hydrocarbon product and any catalyst carryover were separated.

[0049] The hydrocarbon product was drawn off into a suitable sample cylinder, passed over alumina at an ambient temperature (to adsorb free HF), collected, and analyzed by standard gas chromatography using a GC sample injection valve so that no light materials were lost. Test data results for Control Run 4 are summarized in Table 4.

Inventive Run 5

[0050] The composition of the hydrocarbon feed for Inventive Run 5 is presented in Table 3, and is a mixture of three components, 1) a typical propylene and butylene alkylation unit feed; 2) a typical isobutane alkylation unit feed, and; 3) a C₅ olefin fraction from a full range FCC gasoline which had first been hydroisomerized over a palladium on alumina catalyst at 40-52.8 °C (104-127°F), at a LHSV of 6 hr.⁻¹, and at a H₂/diolefin mole ratio of 4.3.

[0051] The hydrocarbon feed was pumped through the feed introduction nozzle into the reactor at a rate of about 300 ml/hr. The reactor effluent flowed into the monel sight gauge wherein the hydrocarbon product and any catalyst carryover were separated.

[0052] The hydrocarbon product was drawn off into a suitable sample cylinder, passed over alumina at an ambient temperature (to adsorb free HF), collected, and analyzed by standard gas chromatography using a GC sample injection valve so that no light materials were lost. Test data results for Inventive Run 5 are summarized in Table 4.

Component	Run 4 (Control)	Run 5 (Inventive)
i-butane	87.17	86.69
olefins	7.64	7.80
% C ₃ = in olefins	23.7	23.3
% C ₄ = in olefins	53.4	53.9
% C ₅ = in olefins	22.9	22.6
C ₅ dienes ¹ (ppmw)	386	21
I/O ratio ²	11.4	11.1
¹ isoprene and piperylene		
² Isoparaffin to Olefin ratio, weight/weight		

EP 1 138 750 B1

Table 4		
Component	Alkylate Product Net Basis	
	Run 4 (Control)	Run 5 (Inventive)
i C ₅ paraffin (wt. %)	10.3	9.62
C ₆ paraffin (wt. %)	2.94	2.34
C ₇ paraffin (wt. %)	12.3	11.8
C ₈ paraffin (wt. %).	44.4	48.9
C ₉ + paraffin (wt. %)	15.3	13.2
RON ¹	91.8	92.9
MON ²	91.3	91.9
(R+M)/2 ³	91.6	92.4
C ₅ + Yield (vol C ₅ + /vol olefin in feed)	1.89	1.90
ASO Rate (kg/m ³ (lbs ASO/bbl C ₅ + product))	2.28 (0.8)	0.86 (0.3)
T50 (°C(°F)) ⁴	108 (226)	106 (223)
T90 (°C(°F)) ⁴	147 (297)	132 (269)
Endpoint (°C(°F)) ⁴	217 (422)	202 (395)
Reactor Temp., °C(°F)	34.8 (94.6)	35.8 (96.4)
¹ Determined using ASTM Engine Test D-2699-97 ae1 ² Determined using ASTM Engine Test D-2700-97 el ³ Average of RON and MON ⁴ Determined using ASTM test method D-86-99 ae1 T-50 - boiling point at which 50 volume % of the sample has boiled overhead T-90 - boiling point at which 90 volume % of the sample has boiled overhead endpoint - boiling point at which 100 volume % of the sample has boiled overhead		

[0053] The test data results in Table 4 demonstrate the following advantages of first hydroisomerizing a C₅ olefin containing hydrocarbon feed prior to alkylation as compared to a process not including such hydroisomerization: 1) increased octane rating ((R+M)/ 2); 2) increased C₅+ yield; 3) decreased ASO production rate; 4) decreased C₉+ paraffin concentration in product; and 5) lower T50, T90 and endpoint boiling points.

[0054] Inventive Run 5 demonstrated a 0.9 % increase in octane rating, a 0.5 % increase in C₅ + yield, a 62.5 % decrease in ASO production rate (kg (lbs)ASO/m³ (bbl) C₅ + in product), and a 13.7 % decrease in C₉+ paraffin wt. % as compared to Control Run 4.

[0055] Inventive Run 5 also, unexpectedly, demonstrated a 1.3 % decrease in the T50 boiling point, a 9.4% decrease in the T90 boiling point, and a 6.4 % decrease in the endpoint boiling point for the product as compared to Control Run 4. This decreased endpoint, in particular, results in a much higher quality gasoline blend stock as compared to Control Run 4.

[0056] Also, the data show that, unexpectedly, C₅ dienes have a large impact on heavy alkylate production. Reducing the C₅ dienes from 386 ppmw in Control Run 4 to 21 ppmw in Inventive Run 5 contributes to the decrease in C₉+ production, and this, in turn, leads to lower i-pentane production and lower T90, and endpoint values. The i-pentane production is cut by 6.6%, which will lead to lower RVP of the C₅+ product.

Example III

[0057] This example illustrates the benefits of hydroisomerizing a C₅ olefin containing hydrocarbon feed prior to alkylation.

[0058] The reactor was a section of monel schedule 40 pipe 0.6 m (2 feet) in length and 25.4 mm (1 inch) in diameter connected at one end to a monel sight gauge via 6.35 mm (1/4") monel tubing, and connected at the other end to a feed introduction nozzle, having a 0.25 mm (0.01 inch) diameter orifice, via 3.18 mm (1/8") monel tubing.

[0059] For each run, the catalyst was circulated through the reactor and monel sight gauge at a flow rate in the range

EP 1 138 750 B1

of from about 50 ml/min to about 100 ml/min. The catalyst composition contained approximately 87-88 wt. % HF, 1-2 wt. % water with the balance comprising acid soluble oil and dissolved light hydrocarbons.

Control Run 6

[0060] The composition of the hydrocarbon feed for Control Run 6 is presented in Table 5, and is a mixture of two components, 1) a typical mixed olefin alkylation unit feed and; 2) a typical isobutane alkylation unit feed. The hydrocarbon feed was pumped through the feed introduction nozzle into the reactor at a rate of about 300 ml/hour. The reactor effluent flowed into the monel sight gauge wherein the hydrocarbon product and any catalyst carryover were separated.

[0061] The hydrocarbon product was drawn off into a suitable sample cylinder, passed over alumina at an ambient temperature (to adsorb free HF), collected, and analyzed by standard gas chromatography using a GC sample injection valve so that no light materials were lost. Test data results for Control Run 6 are summarized in Table 6.

Control Run 7

[0062] The composition of the hydrocarbon feed for Control Run 7 is presented in Table 5, and is a mixture of three components, 1) a C₅ olefin fraction from a full range FCC gasoline; 2) a typical mixed olefin alkylation unit feed and; 3) a typical isobutane alkylation unit feed. The hydrocarbon feed was pumped through the feed introduction nozzle into the reactor at a rate of about 300 ml/hour. The reactor effluent flowed into the monel sight gauge wherein the hydrocarbon product and any catalyst carryover were separated.

[0063] The hydrocarbon product was drawn off into a suitable sample cylinder, passed over alumina at an ambient temperature (to adsorb free HF), collected, and analyzed by standard gas chromatography using a GC sample injection valve so that no light materials were lost. Test data results for Control Run 7 are summarized in Table 6.

Inventive Run 8

[0064] The composition of the hydrocarbon feed for Inventive Run 8 is presented in Table 5, and is a mixture of three components, 1) a typical mixed olefin alkylation unit feed; 2) a typical isobutane alkylation unit feed, and; 3) a C₅ olefin fraction from a full range FCC gasoline which had first been hydroisomerized over a palladium on alumina catalyst at 83.9-89.4°C (183 - 193°F), at a LHSV of 10 hr.⁻¹, and at a H₂/diolefin mole ratio of 4.0.

[0065] The hydrocarbon feed was pumped through the feed introduction nozzle into the reactor at a rate of about 300 ml/hr. The reactor effluent flowed into the monel sight gauge wherein the hydrocarbon product and any catalyst carryover were separated.

[0066] The hydrocarbon product was drawn off into a suitable sample cylinder, passed over alumina at an ambient temperature (to adsorb free HF), collected, and analyzed by standard gas chromatography using a GC sample injection valve so no light materials were lost. Test data results for Inventive Run 8 are summarized in Table 6.

Component	Run 6 (Control)	Run 7 (Control)	Run 8 (Inventive)
<u>Paraffins</u>			
propane	1.213	0.807	0.876
i-butane	85.708	85.595	84.855
n-butane	3.150	2.830	3.325
i-pentane	1.059	1.328	1.139
n-pentane	0.072	0.313	0.438
cyclopentane	0.000	0.095	0.139
<u>Olefins</u>			
propylene	3.124	2.078	2.257
butylenes	4.849	3.887	4.277
2-methyl-butene-2	0.181	1.031	1.064
2-methyl-butene-1	0.220	0.474	0.268
3-methyl-butene-1	0.089	0.068	0.063

EP 1 138 750 B1

(continued)

<u>Olefins</u>			
1-pentene	0.105	0.247	0.101
2-pentene	0.230	1.004	0.918
<u>Dienes</u>			
iso + n-pentadienes	0.000	0.093	0.000
cyclopentene	0.000	0.158	0.090
Olefin Only Basis			
propylene	35.51	23.64	25.22
butylene	55.11	44.23	47.80
i-pentenes	5.58	17.90	15.59
1-pentene	1.19	2.81	1.13
2-pentene	2.61	11.42	10.26
i-pentene/ n-pentene Ratio (w/w)	1.47	1.26	1.37
I/O Ratio (w/w) ¹	9.74	9.74	9.48
i-pentane/ olefin Ratio (w/w)	0.120	0.149	0.122
¹ I/O Ratio = Isoparaffin to Olefin ratio, weight/weight			

Table 6
Alkylate Product Net Basis

Component	Run 6 (Control)	Run 7 (Control)	Run 8 (Inventive)
i-pentane	6.91	14.16	9.61
n-pentane	0.17	0.21	0.27
C ₆ paraffins	3.42	6.07	3.67
C ₇ paraffins	20.50	12.76	14.31
C ₈ paraffins	58.07	37.64	58.46
C ₉ + paraffins	10.84	29.07	13.54
unknowns	0.099	0.093	0.131
trimethylpentane (TMP)	48.59	28.53	48.83
dimethylhexane (DMH)	9.48	9.06	9.62
TMP/DMH	5.13	3.15	5.07
Reactor Temp., °C(°F)	40.6 (105)	36.8 (98.2)	38.9 (102)
RON ¹	92.4	88.5	93.1
MON ²	92.0	88.4	92.0
(R+M)/2	92.2	88.5	92.6
EP (°C (°F)) ³	198 (388)	227 (441)	202 (396)
C5+ Yield (vol C5+/vol olefin in feed) ³	1.80	1.88	1.90
ASO Rate (kg/m ³ (lb/bbl C5+))	0.57 (0.2)	9.13 (3.2)	1.14 (0.4)
¹ Determined using ASTM engine test D-2699-97 ae1			
² RON and MON determined using ASTM engine test D-2700-97e1 (R+M)/2 = average of RON and MON			
³ Estimated by Gas Chromatograph according to the Hutson and Logan method, Hydrocarbon Processing, September 1975, pages 107-110			

EP 1 138 750 B1

[0067] The test data results in Table 6 demonstrate the following advantages of first hydroisomerizing a C₅ olefin containing hydrocarbon feed prior to alkylation as compared to a process not including such hydroisomerization: 1) increased octane rating ((R+M)/2); 2) increased C₅+ yield; 3) decreased ASO production rate; 4) decreased C₉+ paraffin concentration in product; 5) lower endpoint boiling point; 6) reduced net i-pentane; 7) increased C₈ paraffin yield; and an increase in trimethylpentane production.

[0068] Inventive Run 8 demonstrated a 4.6 % increase in octane rating, a 1.1 % increase in C₅ + yield, an 88 % decrease in ASO production rate (kg (lbs) ASO/m³ (bbl) C₅ + in product), a 53 % decrease in C₉+ paraffin wt. %, a 32% reduction in net i-pentane production, a 55% increase in C₈ paraffin yield, and a 71% increase in trimethylpentane production, as compared to Control Run 7.

[0069] Inventive Run 8 also, unexpectedly, demonstrated a 10.2 % decrease in the endpoint boiling point for the product as compared to Control Run 7. This decreased endpoint, in particular, results in a much higher quality gasoline blend stock as compared to Control Run 7.

[0070] In addition, the lower I/O Ratio for Inventive Run 8 (9.48) as compared to the I/O Ratio for Control Run 7 (9.74) would lead one skilled in the art to expect a lower alkylate quality for Inventive Run 8 as compared to Control Run 7. However, as demonstrated above, the alkylate quality for Inventive Run 8 is significantly better than the alkylate quality for Control Run 7.

Claims

1. A method for processing a hydrocarbon feedstock (16) comprising at least one C₅ olefin comprising the steps of:
 - a) hydroisomerizing said hydrocarbon feedstock (16) in a hydroisomerization zone (18) so as to produce a hydroisomerate stream (26); and
 - b) passing said hydroisomerate stream (26) to an alkylation unit (24) and alkylating said hydroisomerate stream (26) by a branched chain paraffin hydrocarbon to produce an alkylate stream (32).
2. The method of claim 1, wherein said at least one C₅ olefin of said hydrocarbon feedstock (16) is an olefin selected from 2-pentene, 2-methyl-butene-2, 1-pentene, 3-methyl-butene-1, 2-methyl-butene-1, isoprene, piperylene, cyclopentene, and combinations of any two or more thereof.
3. The method of claim 1 or 2, wherein said hydroisomerizing of step a) includes: 1) hydrogenation of isoprene and piperylene to mono-olefins; 2) conversion of a portion of the cyclopentene to cyclopentane; and 3) isomerization of 1-pentene to 2-pentene.
4. The method of any of claims 1 to 3, wherein said hydroisomerization zone (18) includes the presence of hydrogen, a hydroisomerization catalyst and is operated at a temperature in the range of from -18 to 260 °C (0 to 500 °F), a pressure in the range of from 0.69 to 10.35 MPa gauge (100 to 1500 psig), and a LHSV in the range of from 0.01 to 100 h⁻¹, in particular wherein the hydrogen to diolefin mole ratio in said hydroisomerization zone (18) is in the range of from 0.5 to 50.
5. The method of claim 4, wherein said hydroisomerization catalyst comprises palladium and alumina.
6. The method of any of the preceding claims, wherein said branched chain paraffin hydrocarbon comprises a hydrocarbon selected from i-butane, i-pentane, and combinations thereof.
7. The method of any of the preceding claims, wherein said alkylate stream (32) is separated into a C₅+ alkylate stream (38), a n-butane stream (36) and an i-butane stream; and wherein said C₅+ alkylate stream (38) is utilized as a gasoline blending stock, in particular wherein said i-butane stream is recycled to said alkylation unit (24) for use as said branched chain paraffin hydrocarbon.
8. The method of any of the preceding claims, wherein said alkylate stream (32) is separated thereby forming a C₅+ alkylate stream (38); said C₅+ alkylate stream (38) is separated into an i-pentane stream (44) and a deisopentanized C₅+ alkylate stream (46); said i-pentane stream (44) is utilized as a first gasoline blending stock; and said deisopentanized C₅+ alkylate stream (46) is utilized as a second gasoline blending stock.

9. The method of any of the preceding claims, wherein, prior to step a), a gasoline range hydrocarbon stream (14) comprising hydrocarbons having at least three carbon atoms per molecule is separated into a C₆+ gasoline blending stock (20) and into said hydrocarbon feedstock (16) comprising at least one C₅ olefin.

5 10. The method of any of the preceding claims, wherein a light olefin stream (28, 26) comprising an olefin selected from i-propylene, i-butene, 2-butenes, 1-butenes, and combinations of any two or more thereof is combined with and becomes a part of said hydroisomerate stream prior to step b).

10 **Patentansprüche**

1. Verfahren zur Verarbeitung eines mindestens ein C₅-Olefin umfassenden Kohlenwasserstoffausgangsmaterials (16), umfassend die Schritte:

15 a) Hydroisomerisieren des Kohlenwasserstoffausgangsmaterials (16) in einer Hydroisomerisationszone (18) derart, dass ein Hydroisomerisatstrom (26) hergestellt wird; und
 b) Leiten des Hydroisomerisatstroms (26) zu einer Alkylierungseinheit (24) und Alkylieren des Hydroisomerisatstroms (26) durch einen verzweigten Paraffinkohlenwasserstoff zur Herstellung eines Alkylatstroms (32).

20 2. Verfahren nach Anspruch 1, wobei das mindestens eine C₅-Olefin des Kohlenwasserstoffausgangsmaterials (16) ein Olefin ist, ausgewählt aus 2-Penten, 2-Methylbuten-2-, 1-Penten, 3-Methylbuten-1-, 2-Methylbuten-1-, Isopren, Piperlylen, Cyclopenten und Kombinationen von beliebigen zwei oder mehreren davon.

25 3. Verfahren nach Anspruch 1 oder 2, wobei das Hydroisomerisieren von Schritt a) einschließt: 1) Hydrieren von Isopren und Piperlylen zu Monoolefinen; 2) Umwandlung eines Teils des Cyclopentens zu Cyclopentan und 3) Isomerisation von 1-Penten zu 2-Penten.

30 4. Verfahren nach einem der Ansprüche 1 bis 3, wobei die Hydroisomerisationszone (18) die Gegenwart von Wasserstoff, eines Hydroisomerisationskatalysators einschließt und bei einer Temperatur im Bereich von -18 bis 260°C (0 bis 500°F), einem Druck im Bereich von 0,69 bis 10,35 MPa gauge (100 bis 1500 psig) und einer Katalysatorbeladung (LHSV) im Bereich von 0,01 bis 100 h⁻¹ betrieben wird, wobei insbesondere das Molverhältnis von Wasserstoff zu Diolefin in der Hydroisomerisationszone (18) im Bereich von 0,5 bis 50 liegt.

35 5. Verfahren nach Anspruch 4, wobei der Hydroisomerisationskatalysator Palladium und Aluminiumoxid umfasst.

6. Verfahren nach einem der vorangehenden Ansprüche, wobei der verzweigte Paraffinkohlenwasserstoff einen Kohlenwasserstoff umfasst, ausgewählt aus i-Butan, i-Pentan und Kombinationen davon.

40 7. Verfahren nach einem der vorangehenden Ansprüche, wobei der Alkylatstrom (32) in einen C₅⁺-Alkylatstrom (38), einen n-Butanstrom (36) und einen i-Butanstrom aufgetrennt wird; und wobei der C₅⁺-Alkylatstrom (38) als Kraftstoffgemischmaterial verwendet wird, wobei insbesondere der i-Butanstrom der Alkylierungseinheit (24) zur Verwendung als verzweigter Paraffinkohlenwasserstoff rückgeführt wird.

45 8. Verfahren nach einem der vorangehenden Ansprüche, wobei der Alkylatstrom (32) abgetrennt wird, wodurch ein C₅⁺-Alkylatstrom (38) gebildet wird;
 der C₅⁺-Alkylatstrom in einen i-Pentanstrom (44) und einen deisopentanisierten C₅⁺-Alkylatstrom (46) aufgetrennt wird;
 der i-Pentanstrom (44) als erstes Kraftstoffgemischmaterial verwendet wird; und
 der deisopentanierte C₅⁺-Alkylatstrom (46) als zweites Kraftstoffgemischmaterial verwendet wird.

50 9. Verfahren nach einem der vorangehenden Ansprüche, wobei vor Schritt a) ein Kohlenwasserstoffstrom (14) der Kraftstoffklasse, umfassend Kohlenwasserstoffe mit mindestens drei Kohlenstoffatomen pro Molekül, in ein C₆⁺-Kraftstoffgemischmaterial (20) und in das mindestens ein C₅-Olefin umfassende Kohlenwasserstoffausgangsmaterial (16) aufgetrennt wird.

55 10. Verfahren nach einem der vorangehenden Ansprüche, wobei ein Leichtolefinstrom (28, 26), umfassend ein Olefin, ausgewählt aus i-Propylen, i-Buten, 2-Butenen, 1-Butenen und Kombinationen von beliebigen zwei oder mehreren davon vor Schritt b) mit dem Hydroisomerisatstrom kombiniert und ein Teil davon wird.

Revendications

- 5
1. Procédé pour traiter une charge d'hydrocarbures (16) comprenant au moins une oléfine en C₅, comprenant les étapes consistant à :
- a) hydro-isomériser ladite charge d'hydrocarbures (16) dans une zone d'hydro-isomérisation (18) de façon à produire un courant d'hydro-isomérats (26) ; et
 (b) faire passer ledit courant d'hydro-isomérats ((26) dans une unité d'alkylation (24) et alkyler ledit courant d'hydro-isomérats (26) avec un hydrocarbure paraffinique à chaîne ramifiée pour produire un courant d'alkylats (32).
- 10
2. Procédé selon la revendication 1, dans lequel au moins une oléfine en C₅ de ladite charge d'hydrocarbures (16) est une oléfine choisie parmi le 2-pentène, le 2-méthylbutène-2, le 1-pentène, le 3-méthylbutène-1, le 2-méthylbutène-1, l'isoprène, le pipérylène, le cyclopentène, et leurs combinaisons de deux quelconques ou davantage.
- 15
3. Procédé selon la revendication 1 ou 2, dans lequel ladite hydro-isomérisation de l'étape a) comprend : 1) l'hydrogénation d'isoprène et de pipérylène en mono-oléfines ; 2) la conversion d'une partie du cyclopentène en cyclopentane ; et 3) l'isomérisation de 1-pentène en 2-pentène.
- 20
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel ladite zone d'hydro-isomérisation (18) comprend la présence d'hydrogène, d'un catalyseur d'hydro-isomérisation, et opère à une température située dans la plage allant de -18 à 260°C (0 à 500°F), sous une pression située dans la plage allant de 0,69 à 10,35 MPa au manomètre (100 à 1500 psig), et à une VSHL située dans la plage allant de 0,01 à 100 h⁻¹, en particulier dans lequel le rapport molaire de l'hydrogène aux dioléfines dans ladite zone d'hydro-isomérisation (18) est situé dans la plage allant de 0,5 à 50.
- 25
5. Procédé selon la revendication 4, dans lequel ledit catalyseur d'hydro-isomérisation comprend du palladium et de l'alumine.
- 30
6. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit hydrocarbure paraffinique à chaîne ramifiée comprend un hydrocarbure choisi parmi l'isobutane, l'isopentane, et leurs combinaisons.
- 35
7. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit courant d'alkylates (32) est séparé en un courant d'alkylates en C₅+ (38), un courant de n-butane (36) et un courant d'isobutane ; et dans lequel ledit courant d'alkylates en C₅+ (38) est utilisé en tant que base pour carburant essence, en particulier dans lequel ledit courant d'isobutane est recyclé vers ladite unité d'alkylation (24) pour être utilisé en tant qu'hydrocarbure paraffinique à chaîne ramifiée.
- 40
8. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit courant d'alkylates (32) est séparé, formant ainsi un courant d'alkylates en C₅+ (38) ; ledit courant d'alkylates en C₅+ (38) est séparé en un courant d'isopentane (44) et un courant d'alkylates en C₅+ dé-isopentanisé (46) ; ledit courant d'isopentane (44) est utilisé en tant que première base pour carburant essence ; et ledit courant d'alkylates en C₅+ dé-isopentanisé (46) est utilisé en tant que seconde base pour carburant essence.
- 45
9. Procédé selon l'une quelconque des revendications précédentes, dans lequel, avant l'étape a), un courant d'hydrocarbures de la gamme essence (14) comprenant des hydrocarbures ayant au moins trois atomes de carbone par molécule est séparé en une base pour carburant essence en C₆+ (20) et en ladite charge d'hydrocarbures (16) comprenant au moins une oléfine en C₅.
- 50
10. Procédé selon l'une quelconque des revendications précédentes, dans lequel, avant l'étape b), un courant d'oléfines légères (28, 26) comprenant une oléfine choisie parmi l'isopropylène, l'isobutène, les 2-butènes, les 1-butènes, et leurs combinaisons de deux quelconques ou davantage, est combiné avec ledit courant d'hydroisomérats, et devient partie intégrante de celui-ci.
- 55

