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[54] PRODUCTION OF ALKYLATE

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[58] **Field of Search** 208/62, 67, 58, 61, 49;
260/683.74

[56] **References Cited**

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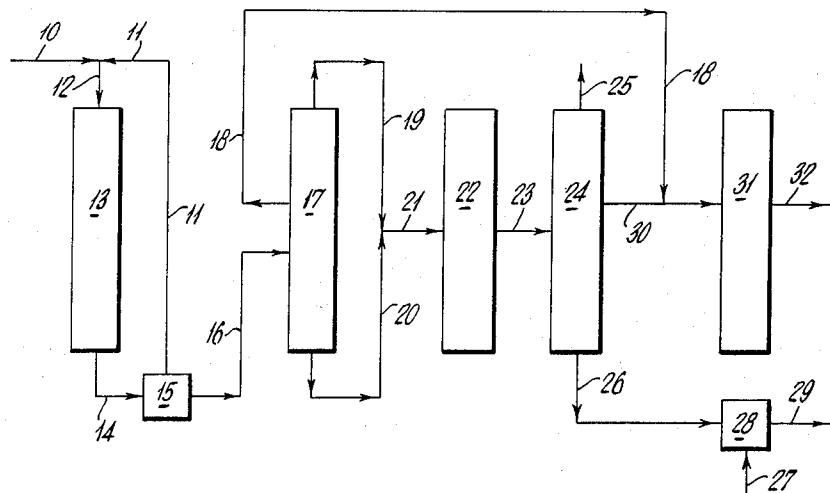
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[57] ABSTRACT

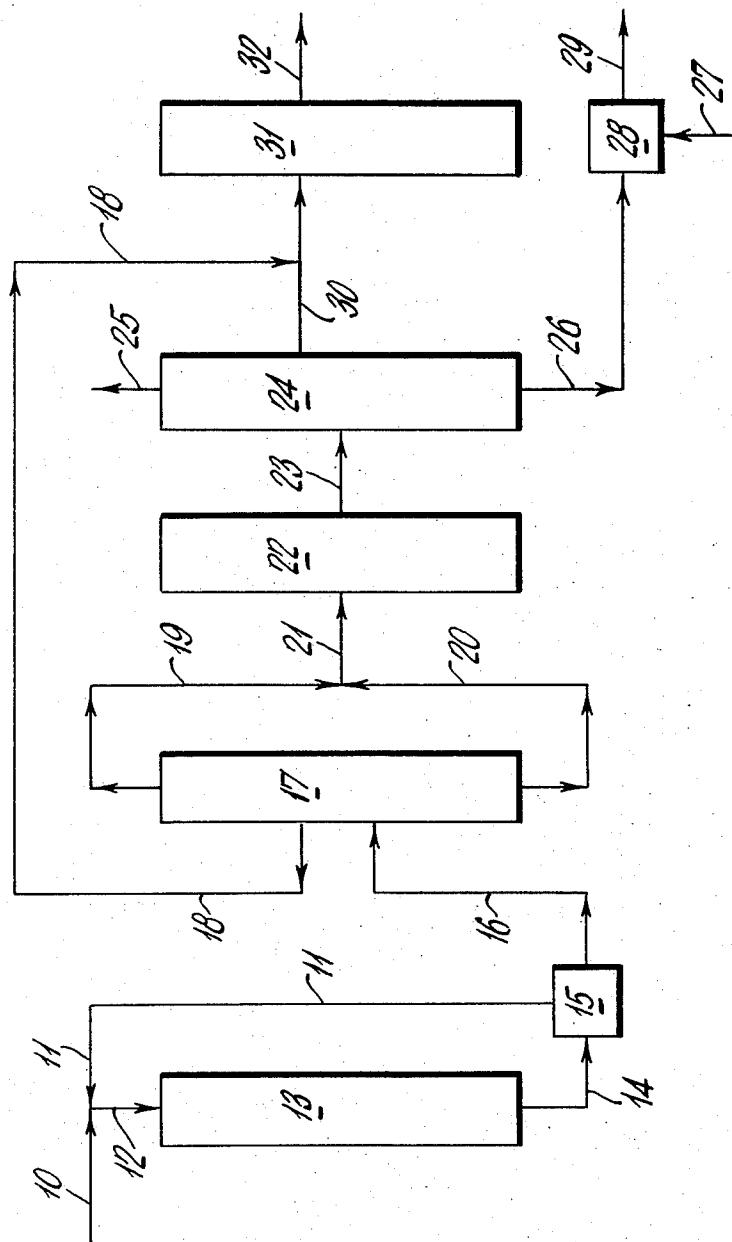
Increased yields of gasoline may be obtained by isomerizing-cracking a low octane paraffin stream and then alkyllating the isobutane fraction therein with an olefin fraction recovered by thermally steam cracking the deisobutanized isomerized-cracked stream.

15 Claims, 1 Drawing Figure



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3,816,294



PRODUCTION OF ALKYLATE

This invention relates to the production of alkylate. More specifically it relates to the conversion of light paraffinic gasoline blending components into alkylate and light olefins.

BACKGROUND OF THE INVENTION

As is well known to those skilled in the art, continuing improvements in the quality of gasoline engines, particularly automotive engines, have resulted in the need for better fuels. The octane requirements of the gasolines continue to increase with resultant need for processes which permit recovery of gasoline of increased octane rating. It has always been desirable to upgrade petroleum charge stocks and available refinery streams to permit their use in the gasoline pool; and this need is increasing with the continuing demand for high octane lead-free gasolines.

It is an object of this invention to provide a process for preparing alkylate gasoline from paraffinic charge compositions. Another object of this invention is to provide a process for converting light paraffinic gasoline blending components into fractions suitable for blending into lead-free gasoline. Other objects will be apparent to those skilled in the art from inspection of the following description.

STATEMENT OF THE INVENTION

In accordance with certain of its aspects, the method of this invention for preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components may comprise

passing said charge stream into contact with an isomerizing-cracking catalyst at isomerizing-cracking conditions in the presence of hydrogen thereby forming an isomerized-cracked stream containing isobutane and light and heavy paraffins;

separating an isobutane-containing stream from said isomerized-cracked stream thereby forming a deisobutanized isomerized-cracked stream;

thermally cracking said deisobutanized isomerized-cracked stream in the presence of steam thereby forming a thermally cracked product stream containing a C₄ olefin fraction;

alkylating said isobutane-containing stream with said product stream containing said C₄ olefin fraction thereby producing an alkylate gasoline fraction; and recovering said alkylate gasoline fraction.

DESCRIPTION OF THE INVENTION

The paraffinic gasoline blending components which may be treated by the process of this invention may typically be a stream which is available in a refinery. Most commonly it will be a stream containing light paraffinic components. Typical of such streams are those containing predominantly lower paraffins including butanes, pentanes, etc. and illustrative of such streams are light straight run products, various condensates, and raffinates from which aromatics have been extracted.

Although the charge may be a pure C₄ or C₅ paraffin, it more commonly may be a mixture containing C₄ to C₈ paraffins. The paraffin content may be 60-100 percent, preferably 70-90 percent, say about 80 percent. The charge may also contain naphthenes in amount of 5-30 percent, preferably 5-20 percent, say 8 percent,

and other components such as aromatics in amount of 2-15 percent, say 12 percent. Lesser amounts of other components may be present including aromatics, etc.

Commonly the octane rating (RON Clear) of the charge may be less than about 60, typically 30-50, say 45.

A typical charge stream may be a light Udex raffinate (from which the aromatics have been extracted) having the following composition:

Component	Udex Raffinate	
	Broad	Typical
Paraffins	70-90	80.7%
Naphthenes	5-20	7.8
Aromatics	2-15	11.5
		100.0

This raffinate may have a (RON Clear) octane number of 45, an IBP of 190°F, an EBP of 275°F, and a gravity of 70.1°API.

Another typical charge stream may be a light straight run distillate (obtained from debutanization of a straight run gasoline) having the following composition:

Component	Light Straight Run Distillate	
	Broad	Typical
Paraffins	80-99	94.0
Naphthenes	0-8	3.0
Aromatics	0-15	3.0

This distillate may have a (RON Clear) octane number of 60.8, an IBP of 92°F, an EBP of 300°F, and a gravity of 79.2°API.

The charge stream containing paraffinic components may be passed to an isomerizing-cracking operation wherein it is subjected to contact with an isomerizing-cracking catalyst at isomerizing-cracking conditions to form an isomerized-cracked stream containing isobutane, light paraffins, and heavy paraffins.

The isomerizing-cracking catalyst is a catalyst which is characterized by its ability to crack hydrocarbons, preferably e.g. a charge containing paraffins, typically in the C₅ to C₈ range, to a product containing typically C₃ and C₄ paraffins — and to simultaneously isomerize the product and/or the charge to permit formation of substantial quantities of isobutane e.g. as by isomerization of butane.

A typical catalyst may be an activated alumina such as that prepared by the process disclosed in U.S. Pat. No. 3,689,434 which issued to Robert M. Suggitt, John H. Estes, and Stanley Kravitz — assigned to Texaco Inc. (Also useful may be the catalysts disclosed in U.S. Pat. Nos. 3,607,959 and 3,567,796 and 3,523,142 all assigned to the same assignee).

The catalysts of that patent may be prepared by contacting alumina with an activator system comprising (a) chlorine or bromine and (b) an inorganic sulfur compound which may be hydrogen sulfide or S_m X₂ wherein m is 1-2 and X is chlorine or bromine. Activation is typically effected at 350°F-750°F. The preferred ratio of chlorine or bromine to the inorganic sulfur

compound may be 0.1:1 to 4:1; and the product catalyst may contain 3-15 percent (wt percent) chlorine or bromine.

Preferably the catalyst also contains 0.01-5 percent by weight of platinum, palladium, rhodium, or ruthenium.

A preferred catalyst may be that prepared by the process of experimental Example I of U.S. Pat. No. 3,689,434 — a chlorided platinum on alumina catalyst.

Isomerization-cracking of the charge stream containing paraffinic components in practice of the process of this invention may be effected by passing 100 parts by volume (this number serving as a basis for the numbers that follow) in liquid phase (except for the hydrogen which is in the gas phase) at 300°-400°F, preferably 310°F-375°F, say 325°F and pressure of 100-1000 psig, preferably 300-700 psig, say 300 psig to an isomerization-cracking operation.

There is also passed to said isomerizing-cracking operation, hydrogen in amount of 0.1-5, preferably 0.2-3.0, say 1.5 moles per mole of hydrocarbon charge. This may correspond to a hydrogen rate of 300-15,000, preferably 600-10,000, say 5,000 SCFB. The hydrogen purity may be 50-100 percent, preferably 80-100 percent, say 95 percent by volume. The space velocity (LHSV) of the total charge through the catalyst bed may be 0.5-8, preferably 1-3, say 2.

During contact with the catalyst in the isomerization-cracking stage, paraffins may be converted to an isomerized-cracked product stream containing isobutane and light and heavy hydrocarbons. In the preferred embodiment, the paraffins, typically containing butane may be converted to a product containing iso-butane.

This product stream, may be withdrawn and passed to a high pressure separator, wherein 50 - 100 parts, preferably 70 - 98 parts, say 95 parts of hydrogen may be flashed off at 300-700 psig, say 490 psig, and recirculated to the isomerization-cracking operation.

The product stream, from which hydrogen has been separated, contains (a) light paraffins i.e. paraffins having boiling points lower than that of isobutane and including typically C₃ and C₂, (b) isobutane, and (c) heavy paraffins i.e. paraffins having boiling points higher than that of isobutane and including n-butane, C₅ and C₆.

This product stream in the preferred embodiment may be passed to a fractionating or separating operation wherein light paraffins, isobutane, and heavy paraffins and hydrogen are separated; it is preferred however that the hydrogen be separated (at least in major portion thereof) prior to the fractionating operation in which the other three components may be separated. Thus the preferred fractionation product will include (a) a light paraffin stream, (b) an isobutane-containing stream, and (c) a heavy paraffin stream.

As will be apparent to those skilled in the art, the mode of separation may depend upon the relative proportions of the various components. It may for example be desirable to effect fractionation in a first operation wherein an isobutane and lighter fraction is separated as overhead from a heavier bottom fraction, followed by a second fractionation operation in which isobutane bottoms are separated from a lighter second overhead fraction. In another embodiment, fractionation in a first step may yield as overhead a lighter fraction and

as bottoms isobutane and a heavier fraction — the latter bottoms being further fractionated to yield isobutane overhead and as second bottoms a heavier fraction.

In still another embodiment, separation may be carried out in a single fractionating tower yielding light paraffins as overhead, heavy paraffins as bottoms, and an isobutane fraction as a side-cut which latter is preferably stripped to yield a clean isobutane fraction.

10 The product streams, as recovered from separation may include the following:

Liquid-Heavy Paraffin Stream

Component	% by Volume	
	Broad	Typical
Paraffins	15-70	43.2
Naphthenes	60-50	28.1
Aromatics	below 5	0
RON Clear	60-80	71

This liquid stream may typically be recovered in amount of 50-80 parts, preferably 60-75 parts, say 68.3 parts.

Vapor-Light Paraffin Stream

Component	% by Volume	
	Broad	Typical
Methane	0-4	0
Ethane	0-5	0
Propane	0-15	6
n-butane	0-15	2.5
n-pentane	0-10	0.4
i-pentane	0-25	4.8

35 The isobutane fraction may typically contain 10-70 parts, preferably 15-65 parts, say 23.3 parts.

In practice of the process of this invention, the light paraffin fraction and the heavier paraffin fraction may be combined to yield a deisobutanized, isomerized-cracked stream.

40 The deisobutanized isomerized-cracked stream, in total amount of 30-95 parts, preferably 35-90 parts, say 82 parts may be passed to a thermal cracking operation wherein the reaction is controlled to yield maximum proportions of C₃ and C₄ olefins.

45 Thermal cracking is preferably carried out in a non-catalytic tubular furnace or oil heater in the presence of steam. The temperature of thermal steam cracking may be 1,100°F-1,700°F, preferably 1,200°F-1,600°F, say 1,400°F at 0-100 psig, preferably 3-50 psig, say 25 psig with a steam to hydrocarbon mole ratio of 0.1-10, preferably 0.2-8, say 5.

50 The thermally cracked product stream containing an olefin fraction may preferably be fractionally distilled to yield (a) a light olefinic distillate fraction, (b) a thermal naphtha fraction, and (c) a C₃ to C₄ olefin fraction. 5-95 parts, preferably 15-85 parts, say 61.2 parts of the light olefinic distillate fraction may contain components having a boiling point below propylene. Typically this stream may contain the following (based on the charge to thermal cracking):

Component	% by Volume	
	Broad	Typical
hydrogen	5-20	12.5

Continued

Component	% by Volume	
	Broad	Typical
methane	10-40	28.5
acetylene	0-5	0.4
ethylene	20-70	27.6
ethane	2-12	5.7

Property	Broad	Typical
RON CLEAR	90-102	98.0
MON clear	82-92	86.0
Aromatics vol %	30-80	50.0

Fractional distillation of the thermally cracked stream may yield a thermal naphtha or dripolene (which is a heavier fraction) in amount of typically 5-50 parts, preferably 7-40 parts, say 13.8 parts.

The C₃ to C₄ olefin fraction recovered from the fractional distillation of the thermally cracked stream may be characterized by the following composition based on the charge to thermal cracking:

Component	% by Volume	
	Broad	Typical
propane	0-8	1.8
propylene	5-30	12.5
butadiene	0-8	2.3
butene	2-15	5.3
n-butane	1-10	3.2
i-butane	0-4	0.2

This C₃ to C₄ olefin stream, in total amount of 5-45 parts, preferably 7-40 parts, say 12.4 parts is passed to an alkylation operation wherein it may be used to alkylate the isobutane-containing stream recovered from fractionation of the isomerized-cracked stream.

Alkylation may be effected at 40°F-70°F, preferably 45°F-60°F, say 55°F in the presence of 85-98 percent, preferably 90-97 percent, say 95 percent sulfuric acid and at a space velocity (GPM butylene per gallon of acid in contactor) of 0.1-0.6, preferably 0.15-0.40, say 0.25. The internal mole ratio of isobutane to olefin may be 100-700, preferably 150-550, say 250; and the external mole ratio may be 2-40, preferably 4-30, say 10.

The product alkylate gasoline fraction, recovered in total amount of 10-60 parts, preferably 15-50 parts, say 31.5 parts may be characterized by an octane (RON Clear) number of 91-102, say 95.0.

It will be noted that the product alkylate gasoline may be obtained in amount of 10-60 parts, preferably 15-50 parts, say 31.5 parts per 100 parts of charge to the initial isomerization-cracking operation. This amount of gasoline may be increased by hydrogenation of the dripolene or thermal naphtha. Typically hydrogenation of this stream at 500°F.-750°F., preferably 525°F.-725°F., say 650°F. and 100-1000 psig, preferably 150-800 psig, say 500 psig may be carried out over a nickel-molybdenum, on alumina catalyst such as that sold under the trademark American Cyanimid HDS-3 catalyst. The ratio of hydrogen to thermal naphtha may be 200-5,000 SCFB, preferably 300-2,000 SCFB say 1,000 SCFB; and the LHSV may be 0.2-10, preferably 0.4-8, say 2.0.

Product hydrogenated thermal naphtha (a gasoline cut), obtained in amount of 5-50 parts, preferably 7-40 parts, say 13.9 parts, may be characterized by the following:

DESCRIPTION OF PREFERRED EMBODIMENT

Practice of the process of this invention will be apparent to those skilled in the art from inspection of the following illustrative embodiment wherein, as elsewhere in the description, all parts are parts by volume unless otherwise specifically stated.

In the drawing, there is disclosed a schematic flow sheet according to which the process of this invention may be carried out. The charge to the process in line 10 may include 10,000 BPD of light Udex Raffinate having a RON Clear octane number of 45 and containing 80.7 percent paraffins, 7.8 percent naphthenes, and 11.5 percent aromatics. This charge in liquid phase is mixed with 5000 SCFB of pure hydrogen admitted through line 11; and the mixture is passed through line 12 to isomerizing-cracking operation 13.

The catalyst in operation 13 is that prepared in accordance with the experimental catalyst of Example I of U.S. Pat. No. 3,689,434 — a chloride-activated planarized alumina catalyst. Conditions during operation 13 include a temperature of 325°F, a pressure of 300 psig, and an LHSV of 2. Effluent leaving through line 14 is passed through separation operation 15 at 325°F. and 380 psig to yield a recycle stream of hydrogen which is withdrawn through line 11.

Also withdrawn from separation operation 15, is the hydrogen-free stream in line 16; and this stream is passed to fractionation operation 17 schematically represented. In operation 17, there is separated an isobutane-containing stream, withdrawn through line 18 containing 2,330 BPD of isobutane. Also recovered is a light paraffin stream, withdrawn through line 19, containing principally propane (590 BPD) and n-butane (250 BPD) — and a heavy paraffin stream, withdrawn through line 20, containing naphthenes and paraffins of heavier molecular weight than C₄ — in amount of 6,830 BPD.

The light paraffin stream in line 19 and the heavy paraffin stream in line 20 are combined in line 21 and passed to thermal steam cracking operation 22 operated at 1,400°F. and 25 psig with a steam to hydrocarbon mole ratio of 5.

During thermal steam cracking, the charge stream is converted to a thermally cracked product stream containing an olefin fraction. This stream, withdrawn through line 23 is characterized by the following composition:

Component	Parts
hydrogen	12.5
methane	28.5
acetylene	0.4
ethylene	27.6
ethane	5.7
propylene	12.5
propane	1.8
butadiene	2.3
butene	5.3
n-butane	3.2
i-butane	0.2

Continued

Component	Parts
C ₅ +	17.9

The thermally cracked product containing an olefin fraction is fractionally distilled in operation 24 to yield a light olefinic distillate, containing ethylene as the main olefin, in amount of 61.2 parts (withdrawn through line 25) and a heavier thermal naphtha or dipolene withdrawn through line 26 in amount of 1,375 BPD. This latter pentane plus stream is partially hydrogenated (with 1,000 SCFB of hydrogen admitted through line 27) at 650°F and 500 psig in the presence of nickel-molybdenum on alumina (American Cyanamid HDS-3) hydrogenation catalyst in operation 28 and the hydrogenated naphtha, in amount of 1,390 BPD, passed through line 29 to the gasoline pool. The product in line 29 has an octane (RON Clear) number of 98.0.

The olefin cut recovered in fractional distillation operation 24, containing 370 BPD of C₄ olefins, 250 BPD of n-butane, and 870 BPD of propylene, is passed through line 30 (and together with 2,330 BPD of isobutane passing through line 18) is admitted to alkylation operation 31.

Alkylation is effected at 55°F in the presence of 95 percent sulfuric acid at a space velocity of 0.25. The internal mole ratio of isobutane to olefin is 250; and the external mole ratio is 10.

The product alkylate gasoline fraction, withdrawn through line 32 in amount of 3,150 BPD, is characterized by an octane number (RON Clear) of 95.0.

It will be apparent to those skilled in the art that the novel process of this invention permits attainment of outstanding results. It makes it possible to produce maximum yields of alkylate and valuable olefin by-products from a lower value paraffinic stream. It further provides a mode of increasing gasoline production while simultaneously providing a means of consuming paraffinic products which, because of their low octane number, are not otherwise suitable for blending into lead-free gasolines.

Although this invention has been illustrated by reference to specific embodiments, it will be apparent to those skilled in the art that various changes and modifications may be made which clearly fall within the scope of this invention.

We claim:

1. The method of preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components which comprises

passing said charge stream into contact with an isomerizing-cracking catalyst at isomerizing-cracking conditions in the presence of hydrogen thereby forming an isomerized-cracked stream containing isobutane and light and heavy paraffins;

separating an isobutane-containing stream from said isomerized-cracked stream thereby forming a deisobutanized isomerized-cracked stream;

thermally cracking said deisobutanized isomerized-cracked stream in the presence of steam thereby forming a thermally cracked product stream containing a C₄ olefin fraction;

alkylating said isobutane-containing stream with said product stream containing said C₄ olefin fraction

thereby producing an alkylate gasoline fraction; and

recovering said alkylate gasoline fraction.

2. The method of preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components as claimed in claim 1 wherein said charge stream contains C₄ to C₈ paraffins.

3. The method of preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components as claimed in claim 1 wherein said charge stream is a raffinate stream from which aromatics have been extracted.

4. The method of preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components as claimed in claim 1 wherein said charge stream contains at least about 60 percent paraffins.

5. The method of preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components as claimed in claim 1 wherein said isomerizing-cracking catalyst is an activated alumina.

6. The method of preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components as claimed in claim 1 wherein said isomerizing-cracking catalyst includes platinum, palladium, rhodium, or ruthenium on an alumina which has been activated by (a) chlorine or bromine and (b) hydrogen sulfide or S_m X₂ wherein m is 1-2 and X is chlorine or bromine at activation temperature of 350°F-750°F.

7. The method of preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components as claimed in claim 1 wherein hydrogen is separated from said isomerized-cracked stream prior to further processing.

8. The method of preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components as claimed in claim 1 wherein, in said separating operation, said isomerized-cracked stream is separated into (a) a light paraffin stream, (b) an isobutane-containing stream and (c) a heavy paraffin stream.

9. The method of preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components as claimed in claim 8 wherein said light paraffin stream and said heavy paraffin stream are combined and passed to said thermal cracking operation.

10. The method of preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components as claimed in claim 1 wherein the effluent stream from thermal cracking is fractionally distilled to separate at least a C₄ olefin fraction and a thermal naphtha fraction.

11. The method of preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components as claimed in claim 10 wherein the thermal naphtha fraction is hydrogenated to yield a gasoline cut.

12. The method of preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components as claimed in claim 11 wherein said hydrogenated thermal naphtha is added to said alkylate gasoline fraction.

13. The method of preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components as claimed in claim 1 which comprises

passing said charge stream into contact with an isomerizing-cracking catalyst at isomerizing-cracking conditions in the presence of hydrogen thereby forming an isomerized-cracked stream containing isobutane and light and heavy paraffins;

separating said isomerized-cracked stream into (a) a light paraffin stream, (b) an isobutane-containing stream, and (c) a heavy paraffin stream;

combining said light paraffin stream and said heavy paraffin stream thereby forming a deisobutanized isomerized-cracked stream;

thermally cracking said deisobutanized isomerized-cracked stream thereby forming a thermally cracked product stream containing a C₄ olefin fraction;

alkylating said isobutane-containing stream with said product stream containing said C₄ olefin fraction thereby producing an alkylate gasoline fraction; and

recovering said alkylate gasoline fraction.

14. The method of preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components as claimed in claim 1 which comprises

passing said charge stream into contact with an

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isomerizing-cracking catalyst at isomerizing-cracking conditions in the presence of hydrogen thereby forming an isomerized-cracked stream containing isobutane and light and heavy paraffins;

separating said isomerized-cracked stream into (a) a light paraffin stream, (b) an isobutane-containing stream, and (c) a heavy paraffin stream;

combining said light paraffin stream and said heavy paraffin stream thereby forming a deisobutanized isomerized-cracked stream;

thermally cracking said deisobutanized isomerized-cracked stream thereby forming a thermally cracked product stream containing a C₄ olefin fraction;

separating from said thermally cracked product stream (a) a light olefinic distillate fraction, (b) a thermal naphtha, and (c) a C₄ olefin fraction; alkylating said isobutane-containing stream with said C₄ olefin fraction thereby producing an alkylate gasoline fraction; and

recovering said alkylate gasoline fraction.

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15. The method of preparing a product stream containing alkylate gasoline from a charge stream containing paraffinic components as claimed in claim 14 wherein said thermal naphtha is hydrogenated thereby forming a hydrogenated thermal naphtha, and said hydrogenated thermal naphtha is passed to a gasoline pool.

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