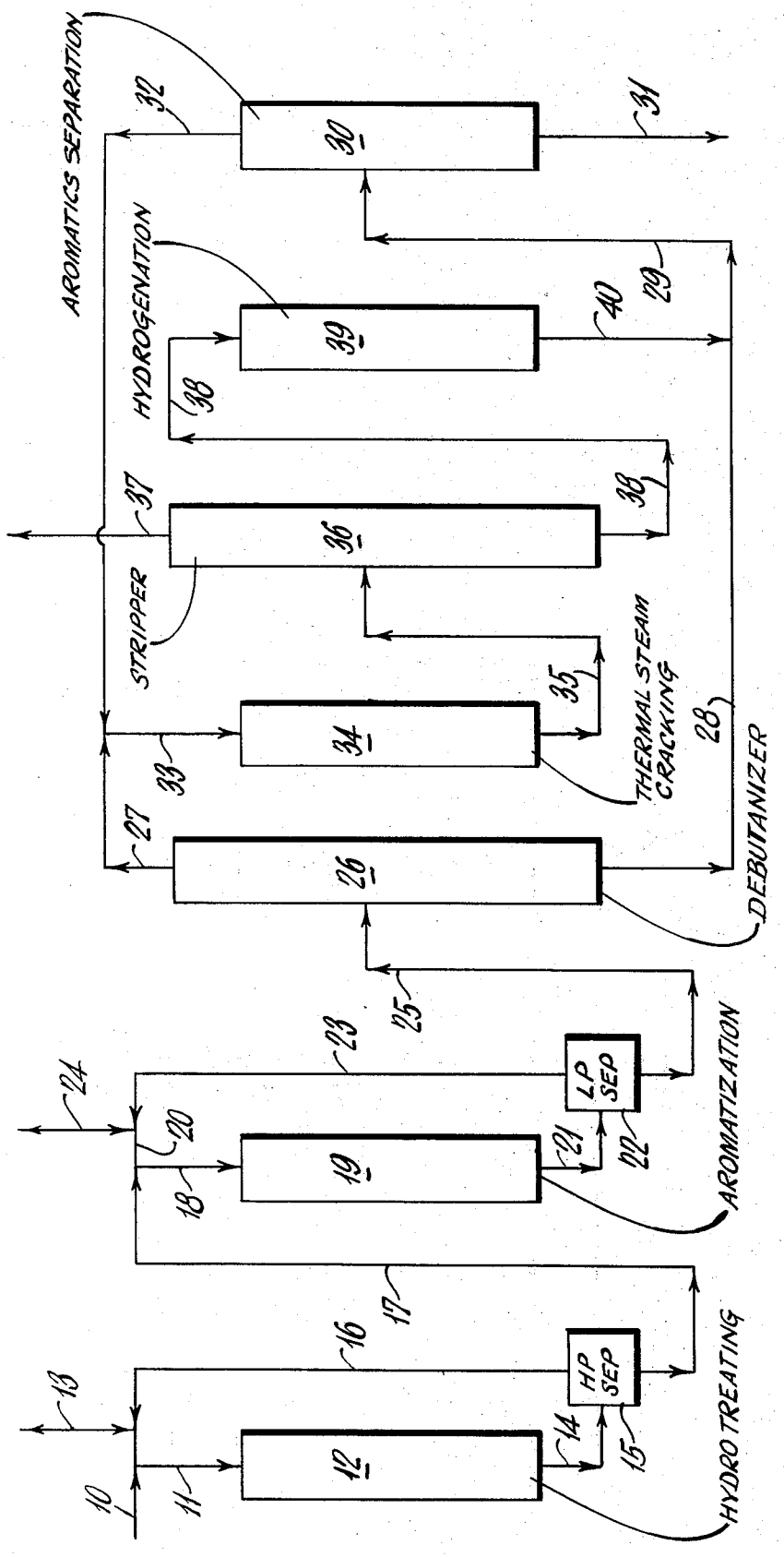
CONVERSION OF PARAFFINS

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CONVERSION OF PARAFFINS

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ABSTRACT OF THE DISCLOSURE

Paraffinic gasoline blending components may be upgraded by aromatization, recovery of aromatics, and thermally steam cracking the remaining paraffins to yield as total product, an olefin fraction and an aromatic fraction.

The novel process of this invention relates to the conversion of paraffins. More particularly, it relates to the production of aromatics and olefins from a charge paraffinic stock.

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 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 upgrading a charge paraffinic hydrocarbon may comprise

(a) aromatizing said charge paraffinic hydrocarbon stream in the presence of hydrogen and a noble metal supported catalyst thereby forming an aromatic hydrocarbon stream;
(b) debutanizing said aromatic hydrocarbon stream thereby forming (i) as overhead an unconverted paraffin stream and (ii) as bottoms an aromatic concentrate;
(c) separating said aromatic concentrate thereby forming (i) a separated paraffin stream and (ii) a separated aromatic stream;
(d) combining said overhead unconverted paraffin stream and said separated paraffin stream thereby forming a combined paraffin stream;
(e) thermally steam cracking said combined paraffinic stream thereby forming a thermally cracked combined paraffin stream; and
(f) recovering said thermally cracked combined paraffin stream.

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 C_4 or C_5 paraffin, it more commonly may be a mixture containing C_4 to C_8 paraffins. The paraffin content may be 60%–100%, preferably 70%–90%, say about 80%. The charge may also contain naphthenes in amount of 5%–30%, preferably 5%–10%, say 8%, and other components such as aromatics in amount of 0%–15%, say 12%. Lesser amounts of other components may be present.

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 heavy Udex raffinate (from which the aromatics have been extracted) having the following composition:

TABLE I.—UDEX RAFFINATE

Component	Percent by volume	
	Broad	Typical
Paraffins	70–90	80.7
Naphthenes	5–20	7.8
Aromatics	2–15	11.5
Total		100.0

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

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

TABLE II.—LIGHT STRAIGHT RUN DISTILLATE

Component	Percent by volume	
	Broad	Typical
Paraffins	80–99	94
Naphthenes	0–18	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 an API gravity of 79.2.

These paraffinic stocks may be hydrotreated e.g. hydrodesulfurized to remove sulfur compounds and to reduce the content of undesirable metals. Hydrotreating is effected by contacting the charge with hydrotreating catalyst at hydrotreating conditions. Hydrotreating may be carried out at 500° F.–850° F., say 650° F. and 100–3000 p.s.i.g., say 500 p.s.i.g. in the presence of hydrogen in amount of 100–8000 s.c.f.b., say 5000 s.c.f.b. LHSV may be 0.1–10, say 2. The catalyst may be a Group VIII metal, preferably in combination with a Group VI metal, on an inert carrier; and a preferred catalyst may be that sold under the trademark Aero HDS–3 containing 3.5% Ni- and 15% Mo on 0.125" alumina. Hydrotreating may decrease the sulfur content from 0.01%–0.4%, say 0.2% to a final value which may be 0.5–10 p.p.m., say 1.0 p.p.m. sulfur.

In the preferred embodiment, the hydrotreated, desulfurized charge paraffinic hydrocarbon in amount of 10,000 b.p.d. may be passed to an aromatizing operation wherein it is contacted with aromatizing catalyst in an aromatizing zone at aromatizing conditions in the presence of hydrogen. Most preferably, aromatizing may be carried out in a reforming operation. Aromatization is effected at 500° F.–1100° F. preferably 700° F.–1000° F., say 950° F. at 0–700 p.s.i.g., preferably 50–500 p.s.i.g., say 15 p.s.i.g. at a space velocity LHSV of 0.2–5.0, preferably 0.5–4.0, say 1.0 and a hydrogen gas rate of 500–10,000 s.c.f.b., preferably 1000–5000 s.c.f.b. say 5300 s.c.f.b.

Aromatizing caatlyst may be for example a Group VIII metal and a Group VIIB metal on an inert carrier—typi-

cally one containing 0.3% Pt and 0.3% Re on alumina such as that sold under the trademark UOP–R–16.

The aromatic hydrocarbon stream exiting the aromatizing operation (after removal of hydrogen which is flashed off and recirculated) may be characterized by the following criteria:

TABLE III

Property	Broad range	Typical
API gravity	65–85	80.0
RON clear	85–100	92.2
RON (+3 cc.)	90–105	101.1
Aromatics, vol. percent	10–50	31.8
Naphthenes, vol. percent	0–10	1.0
Saturates, vol. percent	20–80	41.1
Unsaturates, vol. percent	0–15	6.1
C_6, vol. percent	16–25	21.6
n-C_6, vol. percent	2–5	3.4
2-MP and 3-MP, vol. percent	5–8	6.1
CP, MCP, DMP, vol. percent	2–5	3.1
n-C_7, vol. percent	0–1	0.2
Benzene, vol. percent	12–30	19.4
Toluene, vol. percent	5–20	12.3
C_8+, vol. percent	1–20	5.1
Other, vol. percent	0–10	1.0
Total C_4+, vol. percent	50–90	72.2
C_1 to C_4, vol. percent	20–50	36.0

NOTE.—MP=Methyl pentane; MCP=Methyl cyclopentane; DMP=Dimethyl pentane; CP=Cyclopentane.

This aromatic hydrocarbon stream is debutanized to yield (i) an overhead unconverted paraffinic stream which may normally also contain some olefins and (ii) as bottoms an aromatic concentrate.

The overhead unconverted paraffinic stream, recovered in amount of 1000–5000 b.p.d., say 3600 b.p.d. contains mainly light gaseous paraffins including methane, ethane, propane, and butanes. Lesser amounts of light olefins may be present.

The aromatic concentrate bottoms, recovered from the debutanizing operation in amounts of 5000–9000 b.p.d., say 7220 b.p.d., may be a liquid recovered at 700°–1000° F., say 950° F. and 15–500 p.s.i.g., say 50 p.s.i.g.; and it may typically contain primarily benzene and toluene plus paraffins.

In practice of the process of this invention, the aromatic concentrate bottoms from the debutanizing operation may be passed to an aromatics separation operation which typically may be a sulfolane or a furfural extraction unit (or a molecular sieve separation operation) wherein there may be formed (i) a raffinate stream containing unreacted paraffins and (ii) an extract stream containing aromatics.

In typical operation, aromatic separation may be carried out by contacting 2–6 volumes, say 4 volumes of sulfolane solvent per volume of hydrocarbon charge at temperature of 250° F.–350° F., say 300 F. and 90–160 p.s.i.g., say 120 p.s.i.g. The extract stream, after separation and recovery, may be 1000–5000 b.p.d., say 3100 b.p.d. of an aromatic stream containing benzene and toluene.

The raffinate stream, after separation and recovery may be 2000–6000 b.p.d., say 4100 b.p.d. of a stream containing unreacted paraffins characterized by the following criteria:

TABLE IV

Property	Broad range	Typical
API gravity	60–78	68.0
IBP, ° F	100–180	147
EBP ° F	200–325	302
RON clear	40–80	63.0
RON (+3 cc.)	65–90	85.0
Aromatics, vol. percent	1–10	2.0
Napthenes, vol. percent	2–12	8.0
Saturates, vol. percent	80–95	90.1

In the preferred embodiment of the process of this invention, the overhead unconverted paraffinic stream from the debutanizing operation and the raffinate stream from the separation operation containing unreacted paraffins may be combined to form 3000–9500 b.p.d., say 7700 b.p.d. of a combined paraffin stream.

This combined paraffin stream is passed to a thermal cracking operation wherein cracking is preferably carried out non-catalytically in a tubular furnace, or oil heater, in the presence of steam. The temperature of thermal steam cracking may be 1100° F.–1700° F., preferably 1200° F.–1600° F., say 1400° F. at 0–100 p.s.i.g., preferably 3–50 p.s.i.g., say 25 p.s.i.g. with a steam to hydrocarbon mole ratio of 0.1–10, preferably 0.2–8, say 5.

The thermally cracked product stream typically has the following composition:

TABLE V

Composition:	Vol. percent
Hydrogen	14.5
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
Pentane plus	19.8

This stream may be separated in a stripping operation into (i) an olefin-containing cracked combined paraffin stream as overhead and (ii) a thermally cracked naphtha stream (i.e. a dripolene) as bottoms.

Stripping is preferably carried out in a fractionation operation to which the thermally cracked product stream is admitted. The overhead, an olefin-containing cracked combined paraffin stream, is recovered in amount of 102 volume percent of charge to the thermal cracker.

In practice of the preferred embodiment of the process of this invention, the thermally cracked naphtha stream may be hydrogenated in a hydrogenation operation carried out in the presence of hydrogenating catalyst at hydrogenating conditions to yield a hydrogenated thermally cracked naphtha stream. Hydrogenation is carried out at 300° F.–750° F., say 650° F. at 150–800 p.s.i.g., say 500 p.s.i.g. in the presence of hydrogen charged in amount of 300–5000 s.c.f.b., say 1000 s.c.f.b. of charge hydrocarbon. Hydrogenation catalyst may typically comprise a Group VIII metal or compound thereof such as nickel or platinum on a support such as carbon. Preferred is a Group VI and a Group VIII metal, oxide, or sulfide e.g. Ni, Co, Mo, W, and mixtures thereof, more preferably Ni-W or Co-Mo, supported on a refractory inorganic oxide such as alumina, silica, magnesia, zirconia, or mixtures thereof. A preferred catalyst may contain 2%–15% by weight of Group VIII metal and 5%–30% by weight of Group VI metal.

Product hydrogenated, thermally cracked naphtha recovered in amount of 1000–2500 b.p.d., say 1430 b.p.d. may be characterized by the following criteria:

TABLE V

Property	Broad range	Typical
RON clear	90–102	98
RON (+3 cc.)	82–92	86
Aromatics, vol. percent	30–80	50

It is an additional feature of the process of this invention that the product hydrogenated thermally cracked naphtha may be passed to a separation operation wherein it may be separated into a paraffin stream and an aromatic stream. In practice of a preferred embodiment, the product hydrogenated thermally cracked naphtha from the hydrogenation operation would be combined with the aromatic concentrate bottoms from the debutanizing operation to form a blended stream to be charged to aromatic separation.

It will be apparent to those skilled in the art that the novel process of this invention permits highly efficient

conversion of charge paraffin streams into maximum yield of valuable aromatics and olefins. Typically without further treatment of stripped thermally cracked naphtha stream, the process may permit conversion of the charge paraffin stream to give 10%–60%, say 31% by volume of desired aromatic product.

It will be apparent that the further treatment of the thermally cracked naphtha stream, including hydrogenation and aromatics separation (with preferred recycling of paraffins to thermal steam cracking) may permit an increase in aromatics.

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 description wherein, as elsewhere in this specification, all parts are parts by volume unless otherwise specifically set forth.

EXAMPLE I

Practice of this invention according to one of its embodiments may be carried out in accordance with the schematic process flow sheet as set forth in the drawing.

Charge to the unit in line **10** may include 10,000 b.p.d. of an Arabian Light Straight Run Naphtha having the properties set forth in the last column of Table II. This is passed through line **11** to hydrotreating operation **12** together with 5000 s.c.f.b. of hydrogen admitted through line **16**. Hydrotreating is carried out at 650° F. and 500 p.s.i.g. (LHSV of 2.0) in the presence of 3.5% Ni and 15% Mo on alumina (American Cyanamide Aero HDS–3 catalyst); and the sulfur content is reduced from 100 p.p.m. to 1 p.p.m.

Hydrotreated, desulfurized charge paraffinic hydrocarbon, shown as schematically leaving the hydrotreating operation through line **14**, is passed to high pressure separation operation **15** wherein gases including hydrogen are separated and withdrawn through line **16**. Hydrogen may be withdrawn from or added to the system through line **13**.

The net product from the H.P. Separation is passed as a hydrotreated desulfurized charge paraffinic hydrocarbon stream through lines **17** and **18** to aromatizing operation **19**, which in the preferred embodiment is a reforming operation. Aromatizing is carried out in the presence of 5300 s.c.f.b. of hydrogen admitted through line **20**.

Aromatization is carried out at 950° F. and 15 p.s.i.g. (LHSV of 1.0) in the presence of 0.3% Pt and 0.3% Re on alumina (UOP–R–16 catalyst). The product aromatic hydrocarbon stream leaving aromatization through line **21** is passed to low pressure separation operation **22** wherein gases including hydrogen are separated and withdrawn through line **23**. Hydrogen may be withdrawn from or admitted to the system through line **24**.

The net product (10,820 b.p.d.) from the L.P. Separation operation has the following composition:

TABLE III

Component:	Vol. percent
Hydrocarbons less than C_5	36.0
Pentane	21.6
Benzene	19.4
Toluene	12.3
Other	18.9
RON Clear	92.2
RON +3cc.	101.1

This product is passed as an aromatic hydrocarbon stream through line **25** to debutanizing operation **26**.

In the debutanizing operation **26**, 3600 b.p.d. of unconverted paraffin-olefin stream is withdrawn through line **27** as overhead.

Aromatic concentrate bottoms at 950° F. and 15 p.s.i.g. are withdrawn from debutanizing operation **26** through line **28**. This stream is passed through line **28** and line **29** to aromatics separation operation **30**. In this embodiment, the aromatic concentrate stream in line **28** is combined with a hydrogenated, thermally cracked naphtha stream to form a blended total charge stream in line **29** containing aromatic concentrate.

In aromatic separation operation **30**, the charge aromatic concentrate is separated into a paraffin stream and an aromatic stream. In this embodiment, this may be carried out by contacting sulfolane solvent with the charge stream at 50° F. and 150 p.s.i.g. to yield, after recovery from the extract, 3815 b.p.d. of an aromatic stream removed through line **31**. This stream may be passed to the gasoline pool.

The raffinate (containing unreacted paraffins) from aromatics separation operation **30** withdrawn through line **32**, containing 4815 b.p.d. is combined with the debutanizer overhead stream in line **27** to form a combined paraffin stream in line **33**.

The combined paraffin stream in line **33** is passed to thermal steam cracking operation **34** wherein it is cracked in vapor phase at 1400° F. and 25 p.s.i.g. with a steam to hydrocarbon mole ratio of 5. Effluent is recovered in line **35**.

The thermally steam cracked stream in line **35** is passed at 1400° F. and 25 p.s.i.g. to stripping operation **36** wherein it is separated into (i) as overhead 8550 b.p.d. of an olefin stream (withdrawn through line **37** at 200° F. and 25 p.s.i.g.) and (ii) as bottoms a thermally cracked naphtha stream withdrawn through line **38**.

The thermally cracked naphtha (or dripolene) stream is passed through line **38** to hydrogenation operation **39** wherein it is hydrogenated in the presence of hydrogen.

Product hydrogenated, thermally cracked naphtha, is withdrawn through line **40**. This stream is combined with the stream in line **28** as noted supra.

It will be apparent that in this processing technique, a light straight run naphtha may be upgraded into an aromatic stream of high octane number suitable for use in the gasoline pool and an olefin stream which is suitable for use in chemical operations.

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 upgrading a charge paraffinic hydrocarbon which comprises

(a) aromatizing said charge paraffinic hydrocarbon in the presence of hydrogen and a noble metal supported catalyst thereby forming an aromatic hydrocarbon stream;

(b) debutanizing said aromatic hydrocarbon stream thereby forming (i) as overhead an unconverted paraffin stream and (ii) as bottoms an aromatic concentrate;

(c) separating said aromatic concentrate thereby forming (i) a separated paraffin stream and (ii) a separated aromatic stream;

(d) combining said overhead unconverted paraffin stream and said separated paraffin stream thereby forming a combined paraffin stream;

(e) thermally steam cracking said combined paraffin stream thereby forming a thermally cracked combined paraffin stream containing olefins; and

(f) recovering said thermally cracked combined paraffin stream containing olefins.

2. The method of upgrading a charge paraffinic hydrocarbon as claimed in Claim **1** wherein said charge paraffinic hydrocarbon is a C_4 to C_8 paraffinic hydrocarbon.

3. The method of upgrading a charge paraffinic hydrocarbon as claimed in Claim **1** wherein said charge paraffinic hydrocarbon is a naphtha.

4. The method of upgrading a charge paraffinic hydrocarbon as claimed in Claim **1** wherein said charge paraf-

finic hydrocarbon is hydrotreated to decrease the sulfur content prior to aromatizing.

5. The method of upgrading a charge paraffinic hydrocarbon which comprises.

(a) aromatizing said charge paraffinic hydrocarbon in the presence of hydrogen and a noble metal supported catalyst thereby forming an aromatic hydrocarbon stream;

(b) debutanizing said aromatic hydrocarbon stream thereby forming (i) as overhead an unconverted paraffinic stream and (ii) as bottoms and aromatic concentrate;

(c) separating said aromatic concentrate thereby forming (i) a paraffin stream and (ii) an aromatic stream;

(d) combining said overhead unconverted paraffin stream and said overhead paraffin stream thereby forming a combined paraffin stream;

(e) thermally steam cracking said combined paraffin stream thereby forming a thermally cracked combined paraffin stream containing olefins;

(f) separating a thermally cracked naphtha stream from said thermally cracked product stream containing olefins;

(g) hydrogenating said thermally cracked naphtha stream thereby forming a hydrogenated, thermally cracked naphtha stream; and

(h) separating an aromatic concentrate from said hydrogenated, thermally cracked naphtha stream.

6. The method of upgrading a charge paraffinic hydrocarbon as claimed in Claim 5 wherein said charge paraffinic hydrocarbon is hydrotreated to reduce the sulfur content.

7. The method of upgrading a charge paraffinic hydrocarbon as claimed in Claim 5 wherein said charge paraffinic hydrocarbon is a light naphtha.

8. The method of upgrading a charge paraffinic hydrocarbon as claimed in Claim 5 wherein said aromatization is carried out in a reforming operation.

9. The method of upgrading a charge light naphtha paraffinic hydrocarbon which comprises:

(a) reforming said charge light naphtha paraffinic hydrocarbon at 500° F.–1100° F. in the presence of hydrogen and a supported catalyst containing a Group VIII metal and a Group VIIB metal thereby forming an aromatic hydrocarbon stream;

(b) debutanizing said aromatic hydrocarbon stream thereby forming (i) as overhead an unconverted paraffinic stream containing olefins and (ii) as bottoms an aromatic concentrate containing benzene, toluene, and paraffins;

(c) separating said aromatic concentrate thereby forming (i) a separated paraffin stream and (ii) a separated aromatic stream;

(d) combining said overhead unconverted paraffin stream and said separated paraffinic stream thereby forming a combined paraffin stream;

(e) thermally steam cracking said combined paraffin stream at 1100° F.–1700° F. thereby forming a thermally cracked combined paraffin stream containing olefins; and

(f) recovering said thermally cracked combined paraffin stream containing olefins.

10. The method of upgrading a charge light naphtha paraffinic hydrocarbon as claimed in Claim 9 including the further steps of

stripping said thermally cracked combined paraffin stream containing olefins thereby forming a stripped thermally cracked naphtha stream;

hydrogenating said stripped thermally cracked naphtha stream thereby forming a hydrogenated, thermally cracked naphtha stream; and

separating an aromatic concentrate from said hydrogenated, thermally cracked naphtha stream.

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