

[54] **PRODUCTION OF LIGHT ENDS**

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208/130, 67; 260/683 R

[56] **References Cited****UNITED STATES PATENTS**

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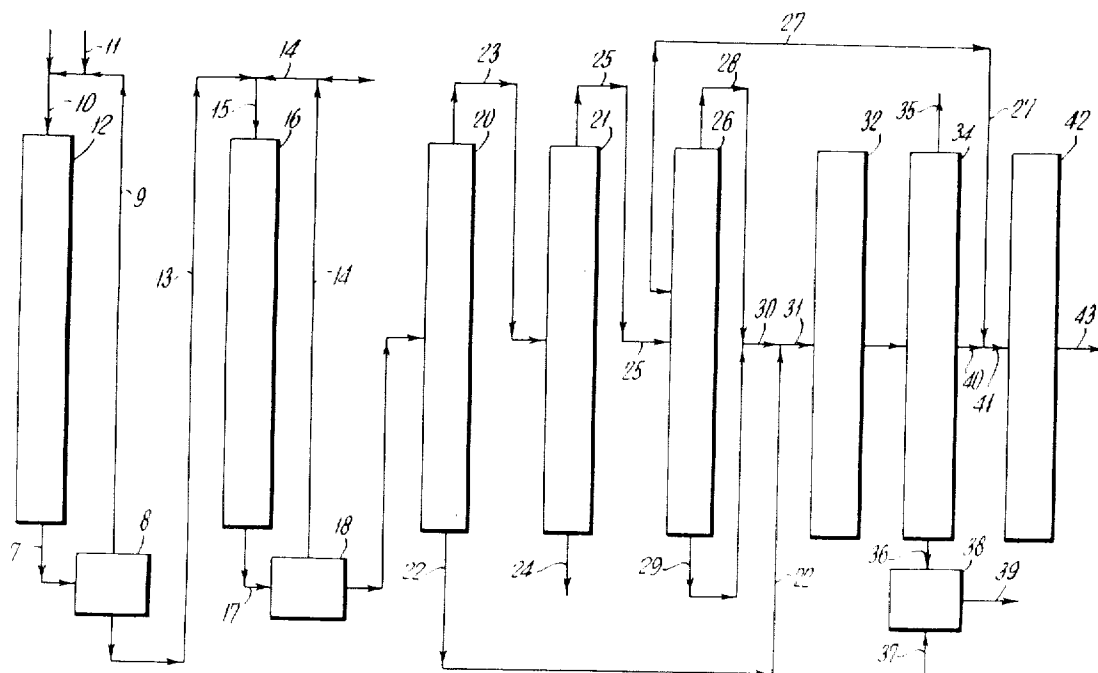
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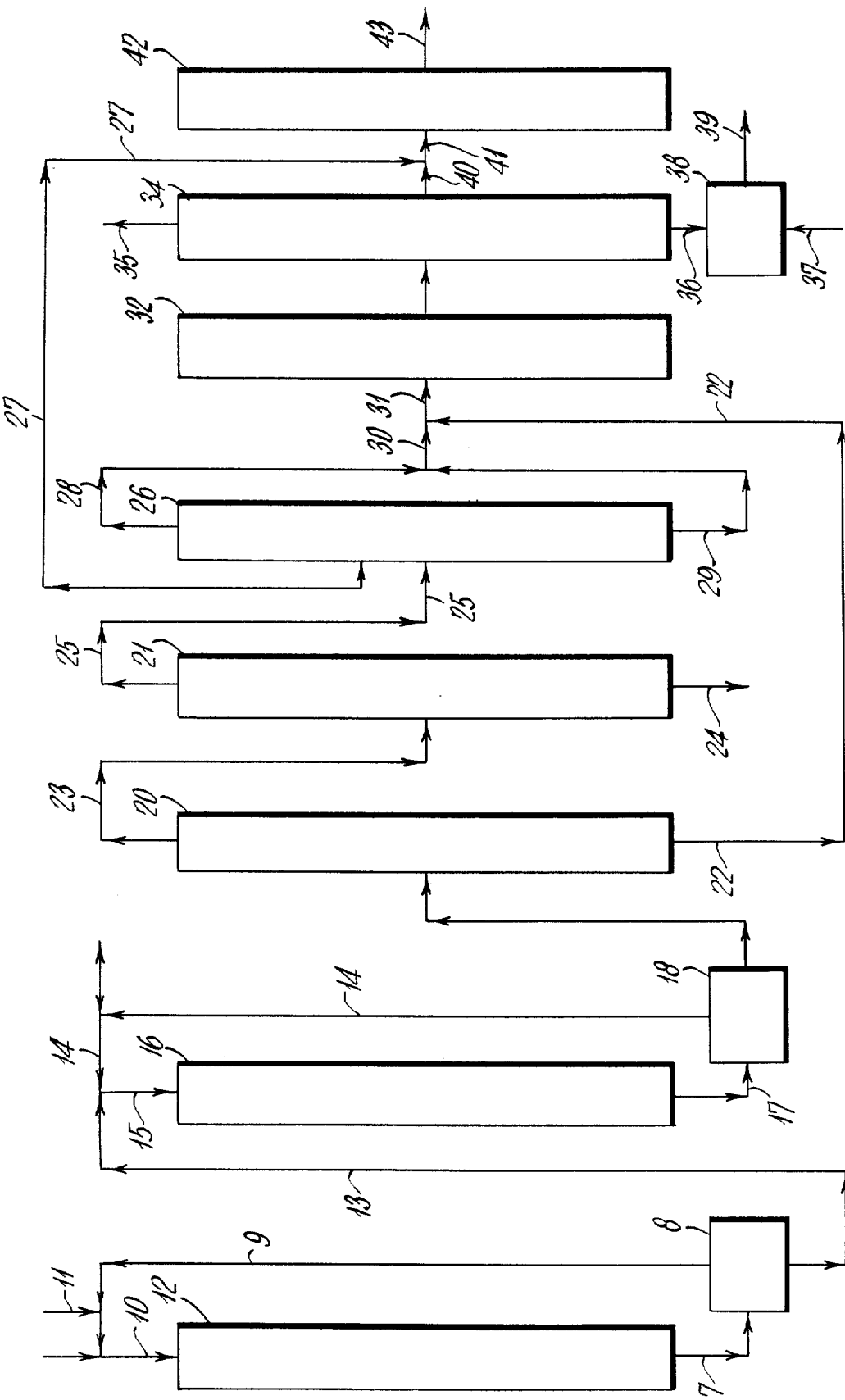
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[57] **ABSTRACT**

Petrochemical feedstocks such as ethylene may be prepared from heavier hydrocarbon stock such as gas oils with simultaneous production of alkylate gasolines.

19 Claims, 1 Drawing Figure



PRODUCTION OF LIGHT ENDS

This invention relates to the production of light ends. More specifically it relates to a process for treating hydrocarbon feedstock to convert it to petrochemical charge stock and alkylate gasoline.

BACKGROUND OF THE INVENTION

As is well known to those skilled in the art, there is an increasing demand for charge stock for petrochemical operations. In particular it has become increasingly more desirable to prepare (and thus to have sources of raw materials which may be converted to) e.g. lower olefins or aromatics. One petrochemical which is particularly desirable is ethylene; this material is used in a wide variety of processes.

It is an object of this invention to provide a process for preparing ethylene. It is a further object of this invention in a preferred embodiment, to provide a process which gives substantial production of ethylene together with desired alkylate gasoline as by-product. Other objects will be apparent to those skilled in the art.

STATEMENT OF THE INVENTION

In accordance with certain of its aspects, the method of this invention comprises

thermally steam cracking, in the presence of steam at thermal steam cracking conditions, a hydrocarbon thermal steam cracking charge stream including (i) a hydrocarbon component containing at least about 9 carbon atoms and (ii) deisobutanized C_3 to C_5 paraffin stream thereby forming a product stream containing (i) an ethylene fraction and (ii) a C_3 to C_4 olefin fraction; and recovering said product stream.

DESCRIPTION OF THE INVENTION

The charge which may be treated by the process of this invention may be a petroleum hydrocarbon containing at least about 9 carbon atoms. Typical of such charge materials may be those recovered during atmospheric crude distillation and having a boiling point above the gasoline range. Included in the fractions obtained at atmospheric pressure may be middle distillates including kerosenes (typically having a boiling range of 400°F–500°F when obtained from U.S. source or a boiling range of 320°F–450°F when obtained from sources outside the U.S.), furnace oils (typically having a boiling range of 500°F–650°F), diesel oils (typically having a boiling range of 550°F–650°F), or straight run atmospheric gas oils (typically having a boiling range of 575°F–700°F) commonly containing at least about C_9 and predominantly C_{10} to C_{14} hydrocarbons.

Other typical charge hydrocarbons may include fractions obtained during vacuum distillation of topped crudes. Typical of these may be vacuum gas oils having a boiling range of 700°F–1,050°F and predominantly containing hydrocarbons having 12–22 carbon atoms.

Recycle gas oils, containing substantial proportions of aromatic components may be employed as less preferred charge to the process of this invention.

The preferred among these petroleum hydrocarbons containing at least about 9 carbon atoms may be gas oils characterized by the following properties:

Property	Broad	Typical
API Gravity	20–45	30
IBP °F	500–650	550
EBP °F	650–1050	1000
Aromatics vol. %	25–60	40
Naphthenes vol. %	40–75	60
Paraffins vol. %		
Olefins vol. %		

The specific preferred charge may be an atmospheric gas oil. When the charge gas oil is an atmospheric gas oil, it may be characterized by the following properties:

Property	Broad	Typical
API Gravity	25–45	35
IBP °F	500–600	550
EBP °F	650–750	675
Aromatics vol. %	20–90	30
Naphthenes vol. %	40–80	70
Paraffins vol. %		

Where the charge gas oil is a vacuum gas oil, it may be characterized by the following properties:

Property	Broad	Typical
API Gravity	15–30	22
IBP °F	550–650	600
EBP °F	950–1050	1000
Aromatics vol. %	30–70	50
Naphthenes vol. %	30–70	50
Paraffins vol. %		

The charge hydrocarbon, eg gas oil, may contain sulfur (expressed as elemental sulfur) in amount of 0.1–2.5 percent by weight. Desulfurization may preferably be effected by passing 100 parts by volume of charge oil in liquid phase together with hydrogen (in amount of 1,000–3,000 SCFB of charge oil) at 650°F–750°F, say 675°F and 500–1,500 psig, say 800 psig into contact with a dehydrosulfurizing catalyst at LHSV of 1–4 say 2. Typical catalyst may be 3% cobalt oxide and 10% molybdenum oxide on alumina.

Desulfurized oil may contain 0.1–0.3 percent, preferably say 0.2 percent by weight of sulfur (expressed as elemental sulfur).

The desulfurized oil may be passed to an isomerizing-cracking operation wherein it is subjected to isomerizing-cracking conditions in the presence of an isomerizing-cracking catalyst to form an isomerized-cracked stream containing a maximum of isobutane and gasoline.

The isomerizing-cracking catalyst is a catalyst which is characterized by its ability to crack the hydrocarbon charge gas oil to form a product containing (per 100 parts by volume of charge gas oil) 5–15 parts, say 10 parts of gasoline — and, by simultaneous isomerization of the C_4 fraction, 5–15 parts, say 10 parts of isobutane.

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 $S_m X_2$ 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 %) 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 1 of U.S. Pat. No. 3,689,434 — a chlorided platinum on alumina catalyst.

Isomerization-cracking of the charge gas oil, 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 at 250°F–400°F, preferably 275°F–375°F., say 325°F., and pressure of 100–1,000 psig, preferably 200–700 psig, say 300 psig to an isomerization-cracking operation.

There is also passed to said isomerizing-cracking operation, hydrogen (including recycle 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 90 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 zone, the charge, preferably desulfurized gas oil, may be converted to an isomerized-cracked stream containing (i) an uncracked oil fraction and (ii) a light fraction containing isobutane. The product stream may be withdrawn and passed to a high pressure separator wherein 50–100 parts, preferably 70–98, say 90 parts by volume of hydrogen may be flashed off at 200–700 psig, say 290 psig and recirculated to the isomerization-cracking operation.

The product stream from which hydrogen has been separated may contain (i) light paraffins i.e. paraffins having boiling points lower than that of isobutane and including typically C_4 and C_3 and C_2 ; (ii) isobutane; (iii) medium paraffins i.e. paraffins having boiling points higher than that of isobutane and below that of gasolines i.e. 100°F–150°F; (iv) gasoline fraction, including C_6 to C_8 components, typically boiling at 200°F–400°F; (v) heavy paraffins having a boiling point above the gasoline range (typically C_9 and above i.e. boiling above about 300°F and commonly in the range of 300°F–500°F) and below the starting point of the gas oil range eg about 500°F; and (vi) uncracked charge eg gas oil, typically having a boiling point of above about 500°F. Any aromatics or naphthenes or olefins which are present are also contained in the fractions which have comparable boiling points.

This isomerized-cracked product stream, (less the hydrogen) may be passed to a distilling operation wherein the charge is separated into (a) a stream containing hydrocarbons having less than 6 carbon atoms; (b) a stream containing a gasoline cut — nominally a C_6 to C_8 fraction; and (c) an uncracked oil fraction which is a stream containing both (i) the fraction iden-

tified supra as heavy paraffins and (ii) uncracked charge oil.

Although it may be possible to effect the distilling operation in a single distillation tower, in one preferred embodiment, it may be carried out in two steps. In a first, or stripping operation in this embodiment, the charge may be admitted to the tower at 250°F–400°F, preferably 275°F–375°F, say 325°F.

Stripped bottoms recovered in amount of 15–55 parts, preferably 20–50 parts, say 40 parts by volume in the preferred embodiment be essentially an uncracked or "recycle" gas oil plus the C_9 and heavier components in the charge to the stripping operation. This stream typically has the following characteristics:

Property	Broad	Typical
API Gravity	30–50	40
IBP °F	300–500	400
EBP °F	500–650	550
Aromatics vol. %	40–60	50
Naphthenes vol. %	40–60	50
Paraffins vol. %		

Stripped overhead, recovered in amount of 30–85 parts, preferably 40–80 parts, say 60 parts by volume may include the light paraffins, isobutane, medium paraffins, and the gasoline fraction. This overhead may typically be characterized as containing about 90 parts liquid lighter than nonane.

The stripped overhead, containing hydrocarbons having less than about 9 carbon atoms, may be passed to a rectifying operation wherein it is separated into an overhead containing hydrocarbons having less than about 6 carbon atoms and a bottoms containing a gasoline fraction typically including hydrocarbons having about 6–8 carbon atoms.

Typically 30–85 parts, preferably 40–80 parts, say 60 parts by volume of stripped overhead may be passed to the rectification operation. Bottoms, removed from the rectification operation may include 1–15 parts, say 10 parts of a C_6 to C_8 gasoline fraction which is passed to gasoline collection. Typically it may be characterized by:

Property	Broad	Typical
API Gravity	50–70	60
IBP °F	100–250	200
EBP °F	250–450	400
Aromatics vol. %	5–35	25
Naphthenes vol. %	65–95	75
Paraffins vol. %		

Overhead, recovered from the rectification operation may include 30–70 parts, preferably 50 parts of a fraction containing hydrocarbons having less than 6 carbon atoms and particularly containing isobutane. This less than C_6 fraction may contain mostly propane, isobutane, n-butane, pentane and isopentane; and it is substantially free from other products. Typically it may be characterized by:

Property	Volume %	
	Broad	Typical
Ethane	0–10	0
Propane	10–60	25
n-butane	10–40	15
i-butane	10–90	20
n-pentane	0–20	5
i-pentane	15–70	35
C_8 and heavier	0–20	0

The less than C_4 overhead fraction from the rectification portion of the distilling operation may be separated in a third step or deisobutanizing operation into (i) an isobutane-containing stream, (ii) a C_4 and lighter stream, and (iii) a C_5 and heavier stream.

As will be apparent to those skilled in the art, the mode of separation in the deisobutanizing operation may depend upon the relative proportions of the various components. It may for example be desirable, where no gasoline is separated, 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 of the deisobutanizing operation, 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 of the deisobutanizing operation, separation may be carried out in a single fractionating tower yielding light paraffins as overhead, heavy paraffins as bottoms, and a gasoline fraction and an isobutane fraction as side-cuts which latter is preferably stripped to yield a clean isobutane fraction.

The product streams, as recovered from separation (or deisobutanizing) may include the following:

C ₄ and Lighter Stream — Volume %		
Property	Broad	Typical
Ethane	0-15	0
Propane	20-80	65
n-butane	20-70	35
i-butane	0-15	5

This stream may typically be recovered in amount of 5-40 parts, preferably 10-30 parts, say 20 parts.

Isobutane-Containing Stream — Volume %		
Property	Broad	Typical
n-butane	0-10	5
i-butane	80-100	90
n-pentane	0-5	0
i-pentane	0-10	5

This stream may typically be recovered in amount of 5-45 parts, preferably 10-30 parts, say 10 parts.

C ₅ and Heavier Stream — Volume %		
Property	Broad	Typical
n-butane	0-15	7
i-butane	0-15	3
n-pentane	5-30	10
i-pentane	30-90	75
hexanes	0-25	5

This stream may typically be recovered in amount of 10-50 parts, preferably 15-35 parts, say 20 parts.

In practice of the process of this invention, the (a) C_4 and lighter stream and (b) the C_5 and heavier stream recovered from the de-isobutanizing operation may be

combined to yield a de-isobutanized stream (a charge stream for thermal steam cracking as hereinafter set forth) in amount of 15-90 parts, preferably 25-65 parts, say 40 parts, having the following characteristics:

Property	Volume %	
	Broad	Typical
Ethane	0-10	0
Propane	10-50	30
n-butane	5-40	20
i-butane	0-30	2
n-pentane	0-25	5
i-pentane	15-60	40
heavier	0-30	3

It will be apparent that the so-called C_3 to C_5 deisobutanized stream may typically contain primarily pentane, propane and butane with some ethane. Depending on the mode of operation it might contain greater or lesser amounts of these and other components. Most efficient operation may be achieved when it contains a minimum of isobutane (which component is passed to alkylation) and a minimum of hydrocarbons having more than about 6 carbon atoms (which components may be effectively recovered as by-products).

It will be apparent to those skilled in the art that the deisobutanized stream may be obtained by techniques other than those set forth. For example, it may be possible to mix (i) a stream containing propane and n-butane with (ii) a hydrocarbon stream containing C_5 where both streams are derived from independent sources.

In practice of the process of the preferred embodiment of this invention, the so-formed deisobutanized stream, preferably a C_3 to C_5 deisobutanized stream, is combined with a hydrocarbon component containing at least about 9 carbon atoms, most preferably the uncracked oil fraction (e.g. bottoms) from isomerizing-cracking, to form a hydrocarbon stream to be thermally steam cracked. Typically 0.2-4.0 parts say 1 part of the "bottoms" may be combined with say 1.0 part of the de-isobutanized stream. In the preferred embodiment, the molar ratio of the bottoms to the de-isobutanized stream may be above about 0.1:1. Typically it may be 0.1:1-1:1, preferably say 0.2:1.

It is a feature of the process of this invention, that the ratio of "bottoms" or "greater than about C_9 " or "recycle gas oil from isomerization-cracking" to the deisobutanized stream may be controlled to yield most effective operation of thermal steam cracking; and thus to permit attainment of maximum production of (i) ethylene and (ii) C_3 to C_4 olefin.

It may be desirable, in one embodiment, to increase the ratio of heavy to light components in the charge to thermal steam cracking by adding to the charge 20-100 parts, preferably 25-60 parts, say 30 parts of gas oil (eg virgin or recycle, atmospheric or vacuum) to the charge.

In another embodiment, it may be desirable to withdraw a portion of the distilled "bottoms" from stripping. Optionally a portion of this withdrawn bottoms could be recycled to the isomerization-cracking operation.

tion to permit production of additional isobutanes therein.

In still another embodiment, where the ultimate isobutane requirements were less, it might be desirable to operate the deisobutanizer at less than maximum efficiency. In this instance, only the desired portion of isobutane would be separated; and the remaining portion of the isobutane might be recovered (either as overhead or as bottoms) and be a component of the "deisobutanized" paraffin stream.

It is a feature of the process of this invention that the thermal steam cracking charge stream (because of inter alia the ratio of the component uncracked eg gas oil and deisobutanized streams) may be cracked to give substantially high yield of ethylene.

Thermal cracking is preferably carried out in a non-catalytic tubular furnace or oil heater in the presence of steam. The temperature of thermal 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.

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 50 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
methane	10–40	28.5
acetylene	0–5	0.4
ethylene	20–70	27.6
ethane	2–12	5.7

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 10 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 10 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% 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 20 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 20 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 100–1,000 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 Cyanamid 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 10 parts, may be characterized by the following:

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

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. It will be apparent to those skilled in the art that the drawing is schematic and is not intended to show details including eg the number of distillation towers, etc., and also that various pieces of auxiliary equipment such as pumps, feed heaters, condensers, reboilers, storage vessels etc. may be present in commercial operation.

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 in this specific embodiment include 10,000 BPD of virgin atmospheric gas oil having an API gravity of 35, an IBP of 550°F, an EBP of 675°F and a sulfur content of 1–2 percent. This charge, together with pure and recycle hydrogen admitted through line 11 in amount of 1.5 moles of hydrogen per mole of hydrocarbon in the gas oil, is desulfurized in desulfurizing operation 12 which is schematically shown.

Desulfurization occurs in liquid phase at inlet temperature of 700°F at 800 psig. LHSV is 1–2. The catalyst is 3% cobalt oxide and 10% molybdenum oxide on alumina.

Effluent from operation 12 is withdrawn through line 7. Hydrogen is separated in separation operation 8 and after removal of hydrogen sulfide (not shown) is returned through line 9 to line 11. Desulfurized gas oil is

passed through line 13 to isomerization-cracking 16.

Desulfurized gas oil containing 1,000 ppm sulfur is withdrawn through line 13, mixed with 5,000 SCFB of pure and recycle hydrogen admitted through line 14, and the mixture passed to isomerizing-cracking operation 16 through line 15. Isomerizing-cracking operation 16 is preferably carried out to maximize the production of gasoline and isobutane.

The catalyst in operation 16 is that prepared in accordance with the experimental catalyst of Example 1 of U.S. Pat. No. 3,689,434 - a chloride-activated platinumized alumina catalyst. Conditions in operation 16 include average temperature of 325°F, a pressure of 300 psig, and an LHSV of 2. Effluent leaving through line 17 is passed through separation operation 18 at 325°F and 280 psig to yield a recycle stream of hydrogen which is withdrawn through line 14.

Also withdrawn from separation operation 18 is the hydrogen-free stream in line 19; and this stream is passed to distillation which in this embodiment includes stripping operation 20 and rectifying operation 21. In this embodiment, the stream in line 19 is passed at 300°F and 14.7 psia to stripping operation 20. Withdrawn from stripping operation 20, as bottoms in line 22 at 400°F and 14.7 psia are 3330 BPD of stripped bottoms.

The stripped bottoms in line 22 include a heavier-than-gasoline fraction, typically containing hydrocarbons having more than about 9 carbon atoms. It includes (i) refractory portions of the charge to isomerization-cracking operation 16 which have not been cracked and (ii) hydrocarbons having more than about 9 carbon atoms which have been formed in operation 16 by the cracking of heavier hydrocarbons.

In this embodiment, the stripped bottoms in line 22 may have the following composition:

Property	Value
API Gravity	40
IBP °F	400
EBP °F	550
Aromatics vol. %	50
Naphthenes vol. %	50
Paraffins vol. %	
Olefins vol. %	

Overhead in line 23 recovered at 100°F in amount of 6660 BPD is a stream containing hydrocarbons having less than 9 carbon atoms including less than about 30 percent pentanes and about 90 percent of liquids below C₉.

Expressed alternatively, this stripped overhead stream may be said to contain 2,000 BPD of light paraffins (boiling below isobutane), 1330 BPD of isobutane, 2,220 BPD of medium paraffins (boiling above isobutane but below the gasoline cut), and 1110 BPD of a gasoline fraction (predominantly C₆ to C₈).

Stripped overhead in line 23 is passed at 100°F and 14.7 psia to rectifying operation 21, bottoms withdrawn through line 24 in amount of 1,110 BPD from rectifying operation 21 include a gasoline fraction, predominantly a C₆ to C₈ fraction characterized as follows:

Property	Range	Value
IBP °F	80-180°F	100°F
EBP °F	200-380°F	250°F
less than C ₆ vol. %	0-15	0

-continued

Property	Range	Value
C ₈	10-80	65
C ₇	5-50	20
C ₆	0-40	10
greater than C ₈	0-25	5

The C₅ and lighter rectifier overhead, withdrawn through line 25 in amount of 5,550 BPD may have the following characteristics:

Property	Range	Value
EBP °F	150-350°F	250°F
Ethane vol. %	0-10	0
Propane vol. %	10-60	25
n-butane vol. %	10-40	15
i-butane vol. %	20-90	20
n-pentane vol. %	0-20	5
i-pentane vol. %	15-70	35
C ₆ and heavier	0-20	0
normal paraffins vol. %	10-60	40
isoparaffins vol. %	40-90	60

The C₅ and lighter overhead from the rectification operation is admitted to de-isobutanizing operation 26. It will be apparent to those skilled in the art that de-isobutanizing may be carried out in one or in several towers. In one embodiment for example, the operation may be carried out in a single tower in which isobutane is removed as a sidestream which is stripped prior to further processing. In a second embodiment, isobutane and lighter cuts may be recovered as overhead from a first tower which is distilled in a second tower to recover isobutane as bottoms. In a third embodiment, isobutane and heavier may be recovered as bottoms from a first tower, these bottoms being distilled in a second tower from which isobutane is recovered as overhead.

In the drawing, deisobutanizing is schematically shown as a single tower. Isobutane is withdrawn in amount of 1,330 BPD through line 27 in purity greater than 90 percent.

Overhead, recovered through line 28 in amount of 2,000 BPD is a C₄ and lighter stream:

Property	Range	Value
ethane vol. %	0-15	0
propane vol. %	20-80	60
n-butane vol. %	20-70	35
i-butane vol. %	0-15	5
C ₅ and greater vol. %	0-15	0
isoparaffins vol. %	less than 15	5

Deisobutanizer bottoms, a C₅ stream, recovered in amount of 2,220 BPD in line 29 may have a composition as follows:

Property	Value
IBP °F	83
EBP °F	155
C ₅ vol. % greater than	85

In practice of the process of this invention, the 2,000 BPD of C₄ and lighter, deisobutanizer overhead in line 28 are combined with 2,220 BPD of the C₅ stream in line 29 to form in line 30, a deisobutanized stream (which contains the components admitted to

deisobutanizing in line 25 except for those removed through line 27 having the following composition:

Property	Volume % Range	Value
ethane	0-10	0
propane	10-50	30
n-butane	5-40	20
isobutane	0-30	2
n-pentane	0-25	5
i-pentanes	15-60	40
heavier	0-30	3
EBP °F		255°F

In this embodiment, the deisobutanized stream in line 30 (in amount of 4,220 BPD) is mixed with the stripped bottoms, C₄ and greater fraction, from the stripping operation, in line 22 to form in line 31 a thermal steam cracking charge stream having the following composition:

Component	Volume % Range	Value
C ₃	0-40	17
C ₄	0-40	12
C ₅	10-50	25
C ₆ plus	10-70	46

In the preferred embodiment, the molar ratio of the C₄ and heavier fraction to the deisobutanized fraction is about 0.3:1. If the fraction in line 22 is greater than is called for by this ratio, then a portion thereof may be withdrawn; if the fraction in line 22 is less than is called for by the ratio, then additional comparable material may be added from an outside source. It is however a feature of the process of this invention that the system may be controlled to balance these quantities and to obtain the desired ratio.

For example, if with a particular charge, it is found that there is too much material in line 22, then it may be possible to operate the isomerization-cracking operation 16 at more severe conditions of time and/or temperature thus producing less C₄ and heavier and more lights; and mutatis mutandis.

Thermal steam cracking of the charge in line 31 may be effected at 1,400°F and 25 psig with a steam to hydrocarbon mole ratio of about 5.

During thermal steam cracking in operation 32, the charge stream is converted to a thermally cracked product stream containing an olefin fraction. This stream withdrawn through line 33 is characterized by the following composition:

Component	Range	Volume %
hydrogen	5-15	11.0
methane	20-30	25.1
acetylene	0-2	0.4
ethylene	20-30	24.4
ethane	0-10	5.0
propylene	5-15	11.1
propane	0-5	1.6
butadiene	0-5	2.0
butene	0-5	4.7
n-butane	0-5	2.8
i-butane	0-5	0.02
C ₅ +	10-15	12.2

The thermally cracked product stream containing an olefin fraction is fractionally distilled in operation 34 to yield a light olefinic overhead, containing ethylene as

the main olefin, in amount of 4,975 BPD (withdrawn through line 35) and a heavier thermal naphtha or dripolene withdrawn through line 36 in amount of 920 BPD. This latter pentane plus stream is partially hydrogenated (with 1,000 SCFB of hydrogen admitted through line 37 to operation 38) at 650°F and 500 psig in the presence of nickel-molybdenum on alumina (American Cyanamid HDS-3) hydrogenation catalyst; and the hydrogenated naphtha, in amount of 1,000 BPD, is passed through line 39 to the gasoline pool. The product in line 39 has an octane (RON Clear) number of 98.0.

The olefin cut recovered in fractional distillation operation 34, containing 500 BPD of C₄ olefins, 210 BPD of n-butane, and 840 BPD of propylene is passed through line 40 and, together with 1,330 BPD of isobutane from line 27, is then passed through line 41 to alkylation operation 42.

Alkylation is effected at 55°F in the presence of 95% 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 43 in amount of 2,000 BPD is characterized by an octane (RON Clear) number of 95.

It will be apparent to those skilled in the art that the novel process of this invention permits attainment of outstanding results. Specifically the novel process makes it possible to convert a charge stream containing hydrocarbons having more than about 9 carbon atoms into maximum amounts of petrochemical charge stock; and it is particularly desirable to be able to obtain as the major by-product a desired alkylate gasoline.

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 which comprises

thermally steam cracking, in the presence of steam at thermal steam cracking conditions, a hydrocarbon thermal steam cracking charge stream including (i) a hydrocarbon component containing at least about 9 carbon atoms and (ii) deisobutanized C₃ to C₅ paraffin stream thereby forming a product stream containing (i) an ethylene fraction and (ii) a C₃ to C₄ olefin fraction; and

recovering said product stream.

2. The method of claim 1 wherein said hydrocarbon component containing at least about 9 carbon atoms comprises a gas oil.

3. The method of claim 1, wherein said hydrocarbon component containing at least about 9 carbon atoms comprises a gas oil which has been contacted with isomerizing-cracking catalyst at isomerizing-cracking conditions.

4. The method of claim 1, wherein said hydrocarbon component containing at least about 9 carbon atoms comprises a gas oil which has been contacted with isomerizing-cracking catalyst at isomerizing-cracking conditions and stripped of hydrocarbon components having less than about 9 carbon atoms.

5. The method of claim 1 wherein the molar ratio of (i) said hydrocarbon stream containing at least about 9 carbon atoms to (ii) said deisobutanized C₃ to C₅ stream is 0.1 - 5:1.

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6. The method of claim 1 wherein the molar ratio of (i) said hydrocarbon stream containing at least about 9 carbon atoms to (ii) said deisobutanized C₃ to C₅ stream is 0.2 - 2:1.

7. The method of claim 1 wherein said C₃ to C₄ olefin fraction is alkylated with an isobutane-containing stream thereby forming alkylate; and said alkylate is recovered.

8. The method which comprises

deisobutanizing a hydrocarbon fraction containing less than six carbon atoms thereby forming (i) an isobutane-containing stream, (ii) a C₄ and lighter stream, and (iii) a C₅ and heavier stream; combining said C₄ and lighter stream and said C₅ and heavier stream thereby forming a deisobutanized stream;

combining said deisobutanized stream and a hydrocarbon component stream containing at least about 9 carbon atoms thereby forming a thermal steam cracking charge stream;

thermally steam cracking in the presence of steam at thermal steam cracking conditions, said thermal steam cracking charge stream thereby forming (i) an ethylene fraction and (ii) a C₃ to C₄ olefin fraction; and

recovering said ethylene fraction.

9. The method of claim 8 wherein said thermal steam cracking conditions include temperature of 1,200°F-1,600°F.

10. The method of claim 8 wherein said C₃ to C₄ olefin fraction is alkylated with an isobutane-containing stream thereby forming alkylate; and said alkylate is recovered.

11. The method of claim 8 wherein said C₃ to C₆ olefin fraction is alkylated with said isobutane-containing stream thereby forming alkylate; and recovering said alkylate.

12. The method which comprises

passing a charge petroleum hydrocarbon containing at least about 9 carbon atoms into contact with an isomerizing-cracking catalyst at isomerizing-cracking conditions in the presence of hydrogen thereby forming an isomerized-cracked stream containing (i) an uncracked oil fraction and (ii) a light fraction containing isobutane;

distilling said isomerized-cracked stream thereby recovering (i) an uncracked oil fraction (ii) fraction containing less than 6 carbon atoms, and (iii) a gasoline fraction;

separating said fraction containing less than 6 carbon atoms into (i) an isobutane-containing stream, (ii) a C₄ and lighter stream, and (iii) a C₅ and heavier stream;

combining said C₄ and lighter stream and said C₅ and heavier stream thereby forming a deisobutanized stream;

combining said deisobutanized stream and said uncracked oil fraction thereby forming a thermal steam cracking charge stream;

thermally steam cracking said thermal steam cracking charge stream in the presence of steam thereby forming a thermally steam cracked product stream

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containing (i) an ethylene fraction and (ii) a C₃ to C₄ olefin fraction;

withdrawing said ethylene fraction;

alkylating said C₃ to C₄ olefin fraction with said isobutane-containing stream thereby forming alkylate; and

withdrawing said alkylate.

13. The method of claim 12 wherein the molar ratio of said deisobutanized stream and said uncracked oil fraction in said thermal steam cracking charge stream is 0.1- 5:1.

14. The method of claim 12 wherein the molar ratio of said deisobutanized stream and said uncracked oil fraction in said thermal steam cracking charge stream is 0.5 - 3:1.

15. The method of claim 12 wherein said thermal steam cracking is carried out at 1,200°F-1,600°F.

16. The method of claim 12 wherein said isomerizing-cracking is carried out at 2,75°F-375°F.

17. The method of claim 12 wherein said charge petroleum hydrocarbon to isomerizing-cracking is a gas oil.

18. The method of claim 12 wherein said charge petroleum hydrocarbon to isomerizing-cracking is a desulfurized gas oil.

19. The method which comprises

passing a charge gas oil into contact with an isomerizing-cracking catalyst at isomerizing-cracking conditions including temperature of 275°F-375°F in the presence of hydrogen thereby forming an isomerized-cracked stream containing (i) a light fraction containing isobutane, (ii) a C₆ to C₈ gasoline fraction, and (iii) a heavier than gasoline fraction including uncracked charge gas oil;

distilling said isomerized-cracked stream thereby recovering (i) a light fraction containing isobutane, (ii) a C₆ to C₈ gasoline fraction, and (iii) a heavier than gasoline fraction including uncracked gas oil; separating said fraction containing less than 6 carbon atoms into (i) an isobutane-containing stream, (ii) a C₄ and lighter stream, and (iii) a C₅ and heavier stream;

combining said C₄ and lighter stream and said C₅ and heavier stream thereby forming a deisobutanized stream;

combining said heavier than gasoline fraction and said deisobutanized stream in mole ratio of 0.1 -10:1 thereby forming a thermal steam cracking charge stream;

thermally steam cracking said thermal steam cracking charge in the presence of steam at 1,200°F-1,600°F thereby forming a thermally steam cracked product stream containing (i) an ethylene fraction and (ii) a C₃ to C₄ olefin fraction; withdrawing said ethylene fraction;

alkylating said C₃ to C₄ olefin fraction with said isobutane-containing stream thereby forming alkylate; and

withdrawing said alkylate.

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