

(11) EP 2 243 814 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

27.10.2010 Bulletin 2010/43

(21) Application number: 09158607.3

(22) Date of filing: 23.04.2009

(51) Int Cl.:

C10G 9/00 (2006.01) C10G 45/62 (2006.01) C10G 69/06 (2006.01) C10G 45/58 (2006.01) C10G 45/64 (2006.01) C10G 69/14 (2006.01)

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK TR

Designated Extension States:

AL BA RS

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(54) Upgrading light naphtas for increased olefins production

- (57) The present invention is a process to upgrade light naphthas comprising branched paraffins and their use as a feedstock in a steam cracking unit, said light naphthas consisting essentially of 90 to 100% by weight of hydrocarbons having at least 5 and up to 8 carbon atoms, said process comprising,
- a) providing an isomerization zone recovered from the gasoline unit of an oil refinery,
- b) providing a separation zone capable to treat an hydrocarbon stream comprising branched paraffins and normal paraffins to produce a first hydrocarbon stream having a reduced branched paraffins content and an enhanced normal paraffins content and a second hydrocarbon stream having an enhanced branched paraffins content and a reduced normal paraffins content,
- c) sending the light naphtha to the isomerization zone and operating said zone at conditions effective to produce a light naphtha having a reduced branched paraffins content and an enhanced normal paraffins content,
- d) sending the withdrawn light naphtha from step c) to the separation zone to recover a first and a second hydrocarbon streams,
- e) sending the first hydrocarbon stream recovered from step d) to the steam cracking unit,
- f) recycling at least a part of the second hydrocarbon stream recovered from step d) at the inlet of the isomer-

ization zone,

or

- c) sending the light naphtha to the separation zone to recover a first and a second hydrocarbon streams,
- d) sending the second hydrocarbon stream recovered from step c) to the isomerization zone and operating said zone at conditions effective to produce a light naphtha having a reduced branched paraffins content and an enhanced normal paraffins content,
- e) mixing the outlet stream of step d) with the first hydrocarbon stream recovered from step c) and sending said mixed stream to the steam cracking unit.

or

- c) sending the light naphtha to the separation zone to recover a first and a second hydrocarbon streams,
- d) sending the first hydrocarbon stream recovered from step c) to the steam cracking unit,
- e) sending at least a part of the second hydrocarbon stream recovered from step d) to the isomerization zone and operating said zone at conditions effective to produce a light naphtha having a reduced branched paraffins content and an enhanced normal paraffins content,
- f) recycling the outlet stream from step e) to the inlet of the separation zone.

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Description

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[Field of the invention]

[0001] The present invention relates to the upgrading of light naphthas for increased olefins production. Light naphthas are becoming widely available as feedstocks for steam crackers due to the difficulties in its valorization as components of the gasoline pool in refineries. The quality of these naphthas as feeds to steam crackers could be improved by increasing the amount of normal paraffins at the expense of iso-paraffins, which would increase the yield of ethylene while reducing yields of fuel gas, C4s and pygas. The isomerization reaction between normal and iso-paraffins is essentially limited by thermodynamic equilibrium. This has led to consider whether it would be feasible to operate the refinery isomerization units driving the reaction in a reverse mode, namely transforming iso-paraffins into normal paraffins.

[Background of the invention]

[0002] GB 2 018 815 A1 describes a process for converting unsaturated C4 hydrocarbons into normal butane and more particularly to the conversion of normal butenes and isobutene into normal butane. The normal butane can thereafter be either recovered, or advantageously, recycled to the ethylene process as a premium cracking feedstock to increase the overall yield of ethylene. In a preferred embodiment the feed stream of normal butenes and isobutene is obtained from unsaturated C4 hydrocarbons generated in the recovery zone of a conventional ethylene production facility. The crude unsaturated C4 hydrocarbon by-product stream separated in the recovery zone of a naphtha steam cracker is usually directed to a butadiene recovery facility where high purity 1,3-butadiene is separated from the remaining C4 hydrocarbons. The remaining C4 hydrocarbons are withdrawn from the butadiene recovery facility primarily as a mixture known in the art as "butene raffinate." This mixture is generally comprised of normal butenes and isobutene. The process comprises passing a stream of unsaturated C4 hydrocarbons in contact with hydrogen through a hydrogenation zone to react the hydrogen and the unsaturated C4 hydrocarbons to form normal butane and isobutane. The normal butane and isobutane are discharged from the hydrogenation zone and are introduced into a separation zone to separate the normal butane from the isobutane. The normal butane is discharged and recovered from the separation zone. The isobutane from the separation zone is passed into an isomerization zone to convert a portion of the isobutane into normal butane to form a stream of normal butane and isobutane. Thereafter, the normal butane and isobutane stream formed in the isomerization zone is withdrawn from the isomerization zone. This stream can thereafter be directed to the same separation zone which separates the normal butane and isobutane introduced from the hydrogenation zone to recover additional amounts of normal butane.

[0003] US 5019661 provides a single-stage process for the shape-selective hydroisomerization of a branched olefin of at least 4 carbon atoms to produce a less branched paraffin product, said process comprising contacting said olefin and a hydrogen-containing gas with a zeolite or zeolite-like catalyst containing at least one metal of Group VIII and in which a major portion of said at least one of these metals is supported within the molecular channels and cavities of the said catalyst, said process being conducted under conditions such that hydroisomerization predominates over both simple hydrogenation and cracking. It is an object of the present invention to provide a process whereby olefinic feedstocks may be hydroisomerised to paraffinic feedstocks and specific catalysts therefor. By way of example, 2-methylpent-1-ene or 3,3-dimethylbut-1-ene may be hydroisomerised to a product containing large amounts of n-hexane. There is no mention of the use of said process (i) to enhance the normal paraffin content of a paraffin fraction and further (ii) use said enhanced normal paraffin fraction as a feedstock in a steam cracker to make olefins.

[0004] US 2005 101814 relates to a process for the production of light olefins from a naphtha feed stream. The naphtha is sent to an adsorptive separation unit which produces a first process stream comprising primarily n-paraffins, and a second process stream comprising non-normal hydrocarbons. The second process stream is processed through a ring opening reactor that hydrogenates and converts the aromatics and naphthenes to paraffins. The paraffins from the adsorptive separation unit and from the hydrogenation ring opening reactor are then passed through a steam cracking unit to produce light olefins. This process increases the yield of light olefins from a naphtha feedstream. The process may optionally include the passing of a py-gas stream generated in the steam cracking unit to the ring opening reactor to further increase the light olefin production. In an alternate process the paraffins from the hydrogenation ring opening reactor are then passed through an isomerization unit for the conversion of a portion of the iso-paraffins to normal paraffins, and the resulting mixture is recycled to the adsorption unit. The isomerization unit increases light olefin production by increasing the amount of normal paraffins recovered from the naphtha feed stream. This process concerns only the treatment of the conventional naphtha feedstock to be used in a steam cracker.

[0005] The present invention relates to the use of an existing isomerization zone of an oil refinery to increase the normal paraffins content of a light naphtha which is further cracked in a steam cracking unit to produce olefins.

[Brief summary of the invention]

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[0006] In a first embodiment the present invention is a process to upgrade light naphthas comprising branched paraffins and their use as a feedstock in a steam cracking unit, said light naphthas consisting essentially of 90 to 100% by weight of hydrocarbons having at least 5 and up to 8 carbon atoms, said process comprising,

- a) providing an isomerization zone recovered from the gasoline unit of an oil refinery,
- b) providing a separation zone capable to treat an hydrocarbon stream comprising branched paraffins and normal paraffins to produce a first hydrocarbon stream having a reduced branched paraffins content and an enhanced normal paraffins content and a second hydrocarbon stream having an enhanced branched paraffins content and a reduced normal paraffins content,
- c) optionally providing a depentanizer,
- d) sending the light naphtha to the isomerization zone and operating said zone at conditions effective to produce a light naphtha having a reduced branched paraffins content and an enhanced normal paraffins content,
- e) sending the withdrawn light naphta from step d) to the separation zone to recover a first and a second hydrocarbon streams,
 - f) sending the first hydrocarbon stream recovered from step e) to the steam cracking unit,
 - g) recycling at least a part of the second hydrocarbon stream recovered from step e) at the inlet of the isomerization zone.
 - h) optionally, before the recycling of step g), sending the second hydrocarbon stream recovered at step e) to a depentanizer to recover a stream comprising essentially pentane and a stream having a reduced pentane content and sending at least a part of said stream comprising essentially pentane at the inlet of the isomerization zone.

[0007] In a second embodiment the present invention is a process to upgrade light naphthas comprising branched paraffins and their use as a feedstock in a steam cracking unit, said light naphthas consisting essentially of 90 to 100% by weight of hydrocarbons having at least 5 and up to 8 carbon atoms, said process comprising,

- a) providing an isomerization zone recovered from the gasoline unit of an oil refinery,
- b) providing a separation zone capable to treat an hydrocarbon stream comprising branched paraffins and normal paraffins to produce a first hydrocarbon stream having a reduced branched paraffins content and an enhanced normal paraffins content and a second hydrocarbon stream having an enhanced branched paraffins content and a reduced normal paraffins content,
- c) sending the light naphtha to the separation zone to recover a first and a second hydrocarbon streams,
- d) sending the second hydrocarbon stream recovered from step c) to the isomerization zone and operating said zone at conditions effective to produce a light naphtha having a reduced branched paraffins content and an enhanced normal paraffins content,
- e) mixing the outlet stream of step d) with the first hydrocarbon stream recovered from step c) and sending said mixed stream to the steam cracking unit.
- [0008] In a third embodiment the present invention is a process to upgrade light naphthas comprising branched paraffins and their use as a feedstock in a steam cracking unit, said light naphthas consisting essentially of 90 to 100% by weight of hydrocarbons having at least 5 and up to 8 carbon atoms, said process comprising,
 - a) providing an isomerization zone recovered from the gasoline unit of an oil refinery,
 - b) providing a separation zone capable to treat an hydrocarbon stream comprising branched paraffins and normal paraffins to produce a first hydrocarbon stream having a reduced branched paraffins content and an enhanced normal paraffins content and a second hydrocarbon stream having an enhanced branched paraffins content and a reduced normal paraffins content,
 - c) optionally providing a depentanizer,
 - d) sending the light naphtha to the separation zone to recover a first and a second hydrocarbon streams,
 - e) sending the first hydrocarbon stream recovered from step d) to the steam cracking unit,
 - f) sending at least a part of the second hydrocarbon stream recovered from step d) to the isomerization zone and operating said zone at conditions effective to produce a light naphtha having a reduced branched paraffins content and an enhanced normal paraffins content,
 - g) optionally, before sending the second hydrocarbon recovered from step d) to the isomerization zone, sending said hydrocarbon stream to a depentanizer to recover a stream comprising essentially iso-pentane and a stream having a reduced pentane content and sending said stream comprising essentially iso-pentane to the isomerization zone,

i) recycling the outlet stream from step f) to the inlet of the separation zone.

[0009] In a fourth embodiment the present invention is a process to upgrade light naphthas comprising branched paraffins and their use as a feedstock in a steam cracking unit, said light naphthas consisting essentially of 90 to 100% by weight of hydrocarbons having at least 5 and up to 8 carbon atoms, said process comprising,

- a) providing an isomerization zone recovered from the gasoline unit of an oil refinery,
- b) providing a deisopentanizer,
- c) sending the light naphtha to a deisopentanizer to recover a stream comprising essentially isopentane and a stream having a reduced isopentane content,
- d) sending the stream having a reduced isopentane content recovered from step c) to the steam cracking unit,
- e) sending the stream comprising essentially isopentane recovered from step c) to the isomerization zone and operating said zone at conditions effective to produce a light naphtha having a reduced branched paraffins content and an enhanced normal paraffins content,
- f) recycling the outlet of step e) to the inlet of the deisopentanizer.

[0010] The fourth embodiment is of particular interest when the light naphtha to be upgraded is a C5 cut comprising, the total being 100w%,

0 to 10 % of C7+,

20 0 to 10% of C4,

80 to 100% of C5, advantageously said C5 is essentially a mixture of iC5 and nC5.

[0011] Advantageously the isomerization zone operates in the presence of hydrogen.

[Detailed description of the invention]

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[0012] As regards the light naphtha to be upgraded, one can cite by way of example a C5 and a C5/C6 naphtha. The light naphtha to be upgraded can be a C5 cut comprising, the total being 100w%, 100 to 95% of a mixture of pentane and isopentane and 0 to 5% of cyclopentane.

The light naphtha to be upgraded can be a C5/C6 cut comprising, the total being 100w%,

30 0 to 10 % of C7+,

0 to 10% of C4,

80 to 100% of a mixture of normal and branched C5 and C6.

[0013] In an embodiment the light naphtha to be upgraded can be a C5/C6 cut comprising, the total being 100w%, 0 to 10 % of C7+,

35 0 to 10% of C4,

20 to 60% of a mixture of normal and branched C5,

20 to 60% of a mixture of normal and branched C6.

[0014] As regards the isomerization zone, Figure 1 shows the equilibrium between the C5 and C6 normal and branched paraffins as function of the reaction temperature. It can be seen that the formation of iso-paraffins is more favorable at higher temperatures although in the considered range it is always found a larger proportion of iso-paraffins. Equilibrium is more favorable for the production of n-C5 than n-C6. The figure also indicates that at higher temperatures other catalytic concepts could be used. It appears clearly from Figure 1 that high reaction temperatures should be preferred for driving the reverse reaction towards n-paraffins and at those conditions a zeolite catalyst could be more advisable. However since existing isomerization units in refineries were designed mainly at low temperature, this case could be also interesting as a minimum investing option.

[0015] Any catalyst known in the art to be suitable for the isomerization of paraffin-rich hydrocarbon streams may be used as an isomerization catalyst in the isomerization zone. One suitable isomerization catalyst comprises a platinum-group metal, hydrogen-form crystalline aluminosilicate zeolite and a refractory inorganic oxide, and the composition preferably has a surface area of at least 580 m2 /g. The preferred noble metal is platinum, which is present in an amount of from about 0.01 to 5 mass % of the composition, and optimally from about 0.15 to 0.5 mass %. Catalytically effective amounts of one or more promoter metals preferably selected from Groups VIB(6), VIII(8-10), IB(11), IIB(12), IVA(14), rhenium, iron, cobalt, nickel, gallium and indium also may be present. The crystalline aluminosilicate zeolite may be synthetic or naturally occurring, and preferably is selected from the group consisting of FAU, LTL, MAZ and MOR with mordenite having a silica-to-alumina ratio of from 16:1 to 60:1 being especially preferred. The zeolite generally comprises from about 50 to 99.5 mass % of the composition, with the balance being the refractory inorganic oxide. Alumina, and preferably one or more of gamma-alumina and eta-alumina, is the preferred inorganic oxide. Further details of the composition are disclosed in U.S. Pat. No. 4,735,929, incorporated herein in its entirety by reference thereto. A preferred isomerization catalyst composition comprises one or more platinum-group metals, a halogen, and an inorganic-oxide

binder. Preferably the catalyst contains a Friedel-Crafts metal halide, with aluminum chloride being especially preferred. The optimal platinum-group metal is platinum which is present in an amount of from about 0.1 to 5 mass %. The inorganic oxide preferably comprises alumina, with one or more of gamma-alumina and eta-alumina providing best results. Optimally, the carrier material is in the form of a calcined cylindrical extrudate. The inlet stream of the isomerization zone may also contain an organic polyhalo component, with carbon tetrachloride being preferred, and the total chloride content is from about 2 to 15 mass %. An organic-chloride promoter, preferably carbon tetrachloride, is added during operation to maintain a concentration of 30 to 300 mass ppm of promoter in the combined feed. Other details and alternatives of preparation steps and operation of the preferred isomerization catalyst are as disclosed in U.S. Pat. Nos. 2,999,074 and 3,031,419 which are incorporated herein by reference.

[0016] Hydrogen is advantageously mixed with the inlet stream of the isomerization zone to provide a mole ratio of hydrogen to hydrocarbon feed of about 0.01 to 5. The hydrogen may be supplied totally from outside the process or supplemented by hydrogen recycled to the feed after separation from reactor effluent. Light hydrocarbons and small amounts of inserts such as nitrogen and argon may be present in the hydrogen. Water should be removed from hydrogen supplied from outside the process, preferably by an adsorption system as is known in the art. In a preferred embodiment the hydrogen to hydrocarbon mol ratio in the reactor effluent is equal to or less than 0.05, generally obviating the need to recycle hydrogen from the reactor effluent to the feed.

[0017] Water and sulfur are catalyst poisons especially for the chlorided platinum-alumina catalyst composition described herein below. Water can act to permanently deactivate the catalyst by removing high-activity chloride from the catalyst, and sulfur temporarily deactivates the catalyst by platinum poisoning. A hydrotreating or hydrodesulfurization step usually reduces water-generating oxygenates to the preferred required 0.1 ppm or less and sulfur to 0.5 ppm or less. Other means such as adsorption systems for the removal of sulfur and water from hydrocarbon streams are well known to those skilled in the art.

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[0018] Isomerization conditions in the isomerization zone include reactor temperatures usually ranging from about 50 to 350°C. Higher reaction temperatures are generally preferred in order to favour equilibrium mixtures having the highest concentration of normal alkanes. Temperatures in the range of about 150 to about 250°C are preferred in the present invention. Reactor operating pressures generally range from about 100 kPa to 10 MPa absolute, preferably between about 0.5 and 4 MPa. Liquid hourly space velocities range from about 0.2 to about 15 volumes of isomerizable hydrocarbon feed per hour per volume of catalyst, with a range of about 0.5 to 5 hr-1 being preferred.

[0019] Contacting within the isomerization zone may be effected using the catalyst in a fixed-bed system, a moving-bed system, a fluidized-bed system, or in a batch-type operation. A fixed-bed system is preferred. The reactants may be contacted with the bed of catalyst particles in either upward, downward, or radial-flow fashion. The reactants may be in the liquid phase, a mixed liquid-vapour phase, or a vapour phase when contacted with the catalyst particles, with excellent results being obtained by application of the present invention to a primarily liquid-phase operation. The isomerization zone may be in a single reactor or in two or more separate reactors with suitable means there between to insure that the desired isomerization temperature is maintained at the entrance to each zone. Two or more reactors in sequence are preferred to enable improved isomerization through control of individual reactor temperatures and for partial catalyst replacement without a process shutdown.

[0020] The isomerization of light naphthas is typically performed in a fixed bed reactor operated at temperatures around about 200°C to about 250°C in order to favour the formation of normal compounds. Under these conditions it is usually preferred to use a catalyst containing a noble metal supported on a chlorated-alumina.

[0021] Cooling or heating of the stream at the inlet of the isomerization zone may be appropriate for temperature flexibility or for the start-up of the process.

[0022] Separation of normal from iso paraffins can be done using an adsorption process that separates both types of species by using a shape selective zeolite. These separation processes could be also useful to enhance the reverse reaction by recycling iso-paraffins instead of n-paraffins as in the conventional process.

[0023] As regards the deisopentanizer and the depentanizer, this is known in the art. The depentanizer is a conventional fractionation to separate the C5 from the C6 and above. The deisopentanizer is known as a super fractionation and separates the iC5 from the C5 cut.

[0024] As regards the separation zone, This is known in the art. The adsorption separation unit may be of any suitable type that is appropriate for the specific situation of the process. The adsorption unit is comprised of a bed of adsorbent comprised of a molecular sieve or other appropriate adsorbent for adsorbing hydrocarbons. Examples of suitable adsorption separation units include, but are not limited to, swing bed or simulated moving bed adsorption units. The inlet stream is separated in the adsorption unit by the selective adsorption and retention of normal paraffins in the adsorption bed. The adsorption separation process undergoes an adsorption step, wherein selected components of the inlet stream are adsorbed onto the adsorbent, and followed by a desorption step wherein the selected components are desorbed from the adsorbent. In this case, the selected components are the normal paraffins. The normal paraffins remain on the adsorbent until a desorbent is passed through the adsorption unit.

[0025] During the adsorption step, the normal paraffins are separated from the inlet stream by adsorption onto the

adsorbent. The remaining components of the inlet stream are non-normal (branched) hydrocarbons and pass through the adsorption bed unaffected. The non-normal hydrocarbons pass out of the adsorption unit as a raffinate stream containing a portion of the desorbent (remaining in the adsorbent bed further to the desorption step). Said raffinate is fractionated to separate the desorbent and recover the second hydrocarbon stream having an enhanced branched paraffins content and a reduced normal paraffins content.

[0026] During the desorption step, a desorbent is delivered to the adsorption unit and passes through the adsorbent bed. The desorbent has properties which enable it to displace the heavier normal paraffins from the adsorbent, resulting in the formation of an extract stream. The extract stream comprises normal hydrocarbons and a portion of the desorbent material. The extract stream is fractionated to recycle the desorbent and recover the second hydrocarbon stream having an enhanced branched paraffins content and a reduced normal paraffins content.

[0027] One can cite the Molex® process of UOP and process described in US 3392113 and US 3455815.

[0028] Fig 2 depicts a process according to the first embodiment of the invention. The light naphtha is sent via line 1 and 2 to the isomerization zone to produce a light naphtha having a reduced branched paraffins content and an enhanced normal paraffins content. The effluent is withdrawn via line 3 and sent to the separation zone to recover a first hydrocarbon stream 4 having a reduced branched paraffins content and an enhanced normal paraffins content and a second hydrocarbon stream 5 having an enhanced branched paraffins content and a reduced normal paraffins content. The first hydrocarbon stream 4 is sent to the steam cracking unit (not shown). A part of the second hydrocarbon stream 5 is recycled via line 7 to the isomerization zone and the other part is purge via line 6.

[0029] Fig 2-a derives from fig 2, a dependanizer is inserted after the separation zone to recycle the pentane at the isomerization zone via line 7 and purge the C6.

[0030] Fig 3 depicts a process according to the second embodiment of the invention. The light naphtha is sent via line 1 to the separation zone to recover a first hydrocarbon stream 4 having a reduced branched paraffins content and an enhanced normal paraffins content and a second hydrocarbon stream 3 having an enhanced branched paraffins content and a reduced normal paraffins content. The second hydrocarbon stream 3 is sent to the isomerization zone operating at conditions effective to produce a light naphtha 5 having a reduced branched paraffins content and an enhanced normal paraffins content. The outlet stream 5 is mixed with the first hydrocarbon stream 4 and said mixed stream 7 is sent to the steam cracking unit (not shown).

[0031] Fig 4 depicts a process according to the third embodiment of the invention. The light naphtha is sent via lines 1 and 2 to the separation zone to recover a first hydrocarbon stream 4 having a reduced branched paraffins content and an enhanced normal paraffins content and a second hydrocarbon stream 3 having an enhanced branched paraffins content and a reduced normal paraffins content. The first hydrocarbon stream 4 is sent to the steam cracking unit (not shown). The second hydrocarbon stream 3 is sent to the isomerization zone via line 6 after a purge 5. The isomerization zone is operated at conditions effective to produce a light naphtha having a reduced branched paraffins content and an enhanced normal paraffins content 7 recycled at the inlet of the separation zone.

[0032] Fig 4-a derives from fig 4 by insertion of a depentanizer. Hydrocarbon stream 3 is sent to a depentanizer to recover a stream 6 comprising essentially pentane and a stream 5 having a reduced pentane content. The stream 6 comprising essentially isopentane is sent to the isomerization zone.

[0033] Fig 5 depicts a process according to the fourth embodiment of the invention. The light naphtha is sent via line 1 and 2 to a deisopentanizer to recover a stream 5 comprising essentially isopentane and a stream 4 having a reduced isopentane content. The stream 4 having a reduced isopentane content is sent to the steam cracking unit (not shown). The stream 5 comprising essentially isopentane is sent to the isomerization zone operated at conditions effective to produce a light naphtha 6 having a reduced branched paraffins content and an enhanced normal paraffins content recycled to the inlet of the deisopentanizer.

45 [Examples]

Example 1

[0034] This ex is made according to fig 2. This is a simulation, the isomerization temperature is 300°C, the recovery of normal paraffins is 99%, the recovery of others is 10% and the purge 20%. In the following table "str 1" corresponds to line 1 on the fig.

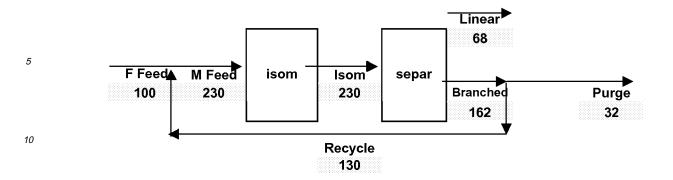
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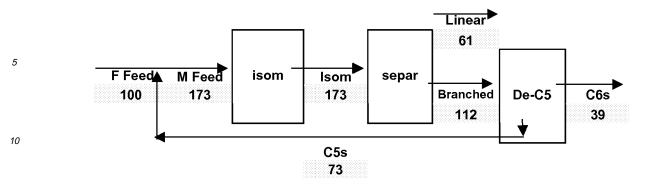
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| | Str1 | Str2 | Str3 | Str4 | Str5 | Str6 | Str7 |
|------------------|------------|------------|-----------|--------|----------|-------|---------|
| Stream | Fresh Feed | Mixed Feed | Isomerate | Linear | Branched | Purge | Recycle |
| | wt% | wt% | wt% | wt% | wt% | wt% | wt% |
| i-C4 | 0.2 | 0.4 | 0.4 | 0.1 | 0.5 | 0.5 | 0.5 |
| n-C4 | 4.1 | 1.8 | 1.8 | 6.0 | 0.0 | 0.0 | 0.0 |
| i-C5 | 17.2 | 26.6 | 26.5 | 9.0 | 33.8 | 33.8 | 33.8 |
| n-C5 | 27.7 | 12.2 | 12.2 | 41.2 | 0.2 | 0.2 | 0.2 |
| NaftC5 | 1.6 | 2.5 | 2.5 | 0.8 | 3.2 | 3.2 | 3.2 |
| 2-Me-C5 | 14.2 | 17.4 | 15.5 | 5.3 | 19.8 | 19.8 | 19.8 |
| 3-Me-C5 | 10.2 | 12.5 | 11.2 | 3.8 | 14.3 | 14.3 | 14.3 |
| 22DM-C4 | 2.1 | 7.0 | 8.5 | 2.9 | 10.9 | 10.9 | 10.9 |
| 23-DM-C4 | 2.6 | 4.0 | 3.9 | 1.3 | 5.0 | 5.0 | 5.0 |
| n-C6 | 13.9 | 6.1 | 7.8 | 26.3 | 0.1 | 0.1 | 0.1 |
| NaftC6 | 3.3 | 5.1 | 5.1 | 1.7 | 6.5 | 6.5 | 6.5 |
| AroC6 | 1.0 | 1.5 | 1.5 | 0.5 | 1.9 | 1.9 | 1.9 |
| C7+ | 1.9 | 3.0 | 3.0 | 1.0 | 3.8 | 3.8 | 3.8 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| | | | | | | | |
| Flowrate (ton/h) | 100.0 | 229.6 | 229.6 | 67.6 | 162.0 | 32.4 | 129.6 |

45 Example 2

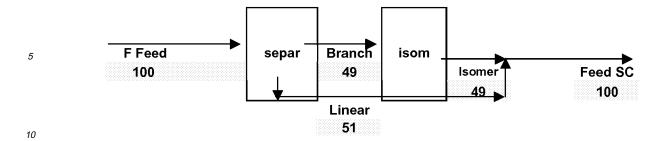
[0035] This ex is made according to fig 2-a. This is a simulation, the isomerization temperature is 300°C, the recovery of normal paraffins is 99%, the recovery of others is 10%.



| | Str1 | Str2 | Str3 | Str4 | Str5 | Str6 | Str7 |
|------------------|------------|------------|-----------|--------|----------|-------|-------|
| Stream | Fresh Feed | Mixed Feed | Isomerate | Linear | Branched | C6s | C5s |
| | wt% | wt% | wt% | wt% | wt% | wt% | wt% |
| i-C4 | 0.2 | 0.1 | 0.1 | 0.4 | 0.0 | 0.0 | 0.0 |
| n-C4 | 4.1 | 2.3 | 2.3 | 6.7 | 0.0 | 0.0 | 0.0 |
| i-C5 | 17.2 | 51.9 | 46.6 | 13.3 | 64.6 | 0.0 | 99.5 |
| n-C5 | 27.7 | 16.2 | 21.5 | 60.8 | 0.3 | 0.0 | 0.5 |
| NaftC5 | 1.6 | 0.9 | 0.9 | 0.3 | 1.3 | 3.7 | 0.0 |
| 2-Me-C5 | 14.2 | 8.2 | 8.2 | 2.3 | 11.4 | 32.5 | 0.0 |
| 3-Me-C5 | 10.2 | 5.9 | 5.9 | 1.7 | 8.2 | 23.4 | 0.0 |
| 22DM-C4 | 2.1 | 1.2 | 4.5 | 1.3 | 6.3 | 17.8 | 0.0 |
| 23-DM-C4 | 2.6 | 1.5 | 2.1 | 0.6 | 2.9 | 8.3 | 0.0 |
| n-C6 | 13.9 | 8.1 | 4.1 | 11.7 | 0.1 | 0.2 | 0.0 |
| NaftC6 | 3.3 | 1.9 | 1.9 | 0.5 | 2.6 | 7.6 | 0.0 |
| AroC6 | 1.0 | 0.5 | 0.5 | 0.2 | 0.8 | 2.2 | 0.0 |
| C7+ | 1.9 | 1.1 | 1.1 | 0.3 | 1.5 | 4.4 | 0.0 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| | | | | | | | |
| Flowrate (ton/h) | 100.0 | 172.9 | 172.9 | 60.7 | 112.2 | 39.3 | 72.9 |

45 Example 3

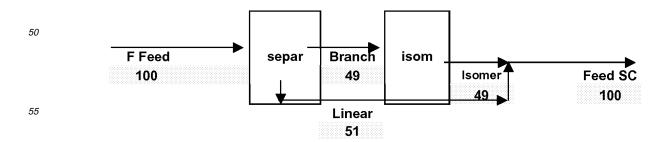
[0036] This ex is made according to fig 3. This is a simulation, the isomerization temperature is 300°C, the recovery of normal paraffins is 99%, the recovery of others is 10%. In the following table "str 1" corresponds to line 1 on the fig.



| | Str1 | Str3 | Str4 | Str5 | Str7 |
|------------------|------------|--------|--------|-----------|---------|
| Stream | Fresh Feed | Branch | Linear | Isomerate | Feed SC |
| | wt% | wt% | wt% | wt% | wt% |
| i-C4 | 0.2 | 0.4 | 0.0 | 0.4 | 0.2 |
| n-C4 | 4.1 | 0.1 | 7.9 | 0.1 | 4.1 |
| i-C5 | 17.2 | 31.4 | 3.4 | 21.9 | 12.5 |
| n-C5 | 27.7 | 0.6 | 54.2 | 10.1 | 32.4 |
| NaftC5 | 1.6 | 2.9 | 0.3 | 2.9 | 1.6 |
| 2-Me-C5 | 14.2 | 25.9 | 2.8 | 17.6 | 10.1 |
| 3-Me-C5 | 10.2 | 18.5 | 2.0 | 12.7 | 7.3 |
| 22DM-C4 | 2.1 | 3.8 | 0.4 | 9.7 | 5.0 |
| 23-DM-C4 | 2.6 | 4.8 | 0.5 | 4.5 | 2.5 |
| n-C6 | 13.9 | 0.3 | 27.2 | 8.9 | 18.2 |
| NaftC6 | 3.3 | 6.0 | 0.7 | 6.0 | 3.3 |
| AroC6 | 1.0 | 1.7 | 0.2 | 1.7 | 0.9 |
| C7+ | 1.9 | 3.5 | 0.4 | 3.5 | 1.9 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| | | | | | |
| Flowrate (ton/h) | 100.0 | 49.3 | 50.7 | 49.3 | 100.0 |

Example 4

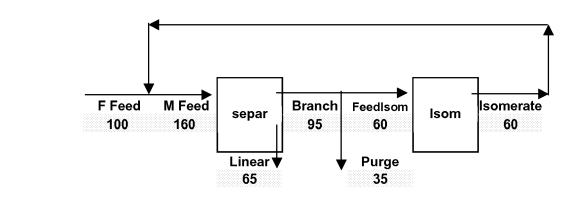
[0037] This ex is made according to fig 3. This is a simulation, the isomerization temperature is 150°C, the recovery of normal paraffins is 99%, the recovery of others is 10%. In the following table "str 1" corresponds to line 1 on the fig.



| | Str1 | Str3 | Str4 | Str5 | Str7 |
|------------------|------------|--------|--------|-----------|---------|
| Stream | Fresh Feed | Branch | Linear | Isomerate | Feed SC |
| | wt% | wt% | wt% | wt% | wt% |
| i-C4 | 0.2 | 0.4 | 0.0 | 0.4 | 0.2 |
| n-C4 | 4.1 | 0.1 | 7.9 | 0.1 | 4.1 |
| i-C5 | 17.2 | 31.4 | 3.4 | 25.0 | 14.0 |
| n-C5 | 27.7 | 0.6 | 54.2 | 7.0 | 30.9 |
| NaftC5 | 1.6 | 2.9 | 0.3 | 2.9 | 1.6 |
| 2-Me-C5 | 14.2 | 25.9 | 2.8 | 15.8 | 9.2 |
| 3-Me-C5 | 10.2 | 18.5 | 2.0 | 9.7 | 5.8 |
| 22DM-C4 | 2.1 | 3.8 | 0.4 | 18.3 | 9.2 |
| 23-DM-C4 | 2.6 | 4.8 | 0.5 | 4.8 | 2.7 |
| n-C6 | 13.9 | 0.3 | 27.2 | 4.7 | 16.1 |
| NaftC6 | 3.3 | 6.0 | 0.7 | 6.0 | 3.3 |
| AroC6 | 1.0 | 1.7 | 0.2 | 1.7 | 0.9 |
| C7+ | 1.9 | 3.5 | 0.4 | 3.5 | 1.9 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| | | | | | |
| Flowrate (ton/h) | 100.0 | 49.3 | 50.7 | 49.3 | 100.0 |

Example 5

[0038] This ex is made according to fig 4. This is a simulation, the isomerization temperature is 250°C, the recovery of normal paraffins is 99%, the recovery of others is 10% and the purge 37%. In the following table "str 1" corresponds to line 1 on the fig.



Str2 Str1 Str3 Str4 Str5 Str6 Str7 Fresh Feed Mixed Feed Stream Branch FeedIsom Isomerate Linear Purge 55 wt% wt% wt% wt% wt% wt% wt% 0.2 i-C4 0.3 0.5 0.1 0.5 0.5 0.5

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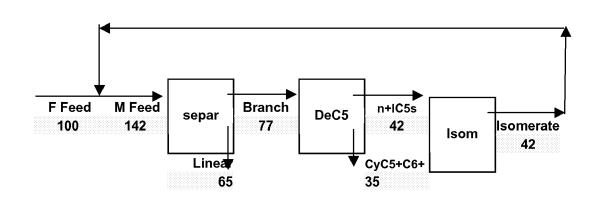
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(continued)

| | Str1 | Str2 | Str3 | Str4 | Str5 | Str6 | Str7 |
|------------------|------------|------------|--------|--------|-------|----------|-----------|
| Stream | Fresh Feed | Mixed Feed | Branch | Linear | Purge | Feedlsom | Isomerate |
| | wt% | wt% | wt% | wt% | wt% | wt% | wt% |
| n-C4 | 4.1 | 2.6 | 0.0 | 6.2 | 0.0 | 0.0 | 0.0 |
| i-C5 | 17.2 | 18.3 | 27.7 | 4.5 | 27.7 | 27.7 | 20.0 |
| n-C5 | 27.7 | 20.4 | 0.3 | 49.5 | 0.3 | 0.3 | 8.1 |
| NaftC5 | 1.6 | 2.3 | 3.5 | 0.6 | 3.5 | 3.5 | 3.5 |
| 2-Me-C5 | 14.2 | 15.5 | 23.6 | 3.8 | 23.6 | 23.6 | 17.7 |
| 3-Me-C5 | 10.2 | 10.9 | 16.6 | 2.7 | 16.6 | 16.6 | 12.3 |
| 22DM-C4 | 2.1 | 5.7 | 8.7 | 1.4 | 8.7 | 8.7 | 11.9 |
| 23-DM-C4 | 2.6 | 3.4 | 5.2 | 0.8 | 5.2 | 5.2 | 4.7 |
| n-C6 | 13.9 | 11.6 | 0.2 | 28.2 | 0.2 | 0.2 | 7.7 |
| NaftC6 | 3.3 | 4.8 | 7.3 | 1.2 | 7.3 | 7.3 | 7.3 |
| AroC6 | 1.0 | 1.4 | 2.1 | 0.3 | 2.1 | 2.1 | 2.1 |
| C7+ | 1.9 | 2.8 | 4.2 | 0.7 | 4.2 | 4.2 | 4.2 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| | | | | | | | |
| Flowrate (ton/h) | 100.0 | 159.5 | 94.5 | 65.0 | 35.0 | 59.5 | 59.5 |

Example 6

[0039] This ex is made according to fig 4-a. This is a simulation, the isomerization temperature is 250°C, the recovery of normal paraffins is 99%, the recovery of others is 10%. In the following table "str 1" corresponds to line 1 on the fig.



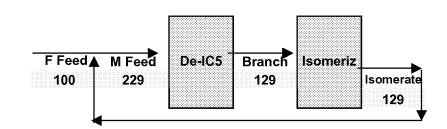
| | Str1 | Str2 | Str3 | Str4 | Str5 | Str6 | Str7 |
|--------|------------|------------|--------|--------|------|------|-----------|
| Stream | Fresh Feed | Mixed Feed | Branch | Linear | C6+ | IC5s | Isomerate |
| | wt% | wt% | wt% | wt% | wt% | wt% | wt% |
| i-C4 | 0.2 | 1.7 | 2.8 | 0.4 | 0.0 | 5.1 | 5.1 |
| n-C4 | 4.1 | 2.9 | 0.1 | 6.2 | 0.0 | 0.1 | 0.1 |

(continued)

| | Str1 | Str2 | Str3 | Str4 | Str5 | Str6 | Str7 |
|------------------|-------------|------------|--------|--------|-------|-------|-----------|
| Stream | Fresh Feed | Mixed Feed | Branch | Linear | C6+ | IC5s | Isomerate |
| | wt% | wt% | wt% | wt% | wt% | wt% | wt% |
| i-C5 | 17.2 | 31.4 | 52.0 | 6.9 | 5.7 | 90.2 | 64.9 |
| n-C5 | 27.7 | 27.3 | 0.5 | 59.1 | 0.1 | 0.9 | 26.2 |
| NaftC5 | 1.6 | 1.2 | 1.9 | 0.3 | 4.1 | 0.2 | 0.2 |
| 2-Me-C5 | 14.2 | 10.3 | 17.1 | 2.3 | 35.8 | 1.6 | 1.1 |
| 3-Me-C5 | 10.2 | 7.4 | 12.2 | 1.6 | 25.6 | 1.1 | 0.7 |
| 22DM-C4 | 2.1 | 1.7 | 2.8 | 0.4 | 5.8 | 0.3 | 0.7 |
| 23-DM-C4 | 2.6 | 1.9 | 3.2 | 0.4 | 6.7 | 0.3 | 0.3 |
| n-C6 | 13.9 | 9.9 | 0.2 | 21.5 | 0.4 | 0.0 | 0.5 |
| NaftC6 | 3.3 | 2.4 | 4.0 | 0.5 | 8.4 | 0.4 | 0.4 |
| AroC6 | 1.0 | 0.7 | 1.1 | 0.1 | 2.4 | 0.0 | 0.0 |
| C7+ | 1.9 | 1.3 | 2.2 | 0.3 | 4.9 | 0.0 | 0.0 |
| Total | Total 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| | | | | | | | |
| Flowrate (ton/h) | 100.0 | 142.4 | 77.4 | 65.0 | 35.0 | 42.4 | 42.4 |

Example 7

[0040] This ex is made according to fig 5. This is a simulation, the isomerization temperature is 250°C; In the following table "str 1" corresponds to line 1 on the fig.



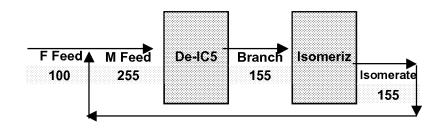
| | Str1 | Str2 | Str4 | Str5 | Str6 |
|---------|------------|------------|--------|----------|-----------|
| Stream | Fresh Feed | Mixed Feed | Linear | Branched | Isomerate |
| | wt% | wt% | wt% | wt% | wt% |
| i-C4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| n-C4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| i-C5 | 37.0 | 56.3 | 0.0 | 100.0 | 71.3 |
| n-C5 | 59.6 | 42.2 | 96.6 | 0.0 | 28.7 |
| NaftC5 | 3.4 | 1.4 | 3.4 | 0.0 | 0.0 |
| 2-Me-C5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3-Me-C5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

(continued)

| | Str1 | Str2 | Str4 | Str5 | Str6 |
|------------------|------------|------------|--------|----------|-----------|
| Stream | Fresh Feed | Mixed Feed | Linear | Branched | Isomerate |
| | wt% | wt% | wt% | wt% | wt% |
| 22DM-C4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 23-DM-C4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| n-C6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| NaftC6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| AroC6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| C7+ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| | | | | | |
| Flowrate (ton/h) | 100.0 | 254.8 | 100.0 | 154.8 | 154.8 |

Example 8

[0041] This ex is made according to fig 5. This is a simulation, the isomerization temperature is 150°C. In the following table "str 1" corresponds to line 1 on the fig.



| | Str1 | Str2 | Str4 | Str5 | Str6 |
|----------|------------|------------|--------|----------|-----------|
| Stream | Fresh Feed | Mixed Feed | Linear | Branched | Isomerate |
| | wt% | wt% | wt% | wt% | wt% |
| i-C4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| n-C4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| i-C5 | 37.0 | 62.0 | 7.9 | 97.0 | 78.2 |
| n-C5 | 59.6 | 36.6 | 88.7 | 3.0 | 21.8 |
| NaftC5 | 3.4 | 1.4 | 3.4 | 0.0 | 0.0 |
| 2-Me-C5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3-Me-C5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 22DM-C4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 23-DM-C4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| n-C6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| NaftC6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| AroC6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

(continued)

| | Str1 | Str2 | Str4 | Str5 | Str6 |
|------------------|------------|------------|--------|----------|-----------|
| Stream | Fresh Feed | Mixed Feed | Linear | Branched | Isomerate |
| | wt% | wt% | wt% | wt% | wt% |
| C7+ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| | | | | | |
| Flowrate (ton/h) | 100.0 | 254.8 | 100.0 | 154.8 | 154.8 |

Example 9

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Working conditions

[0042] The following working conditions were used:

- 20 g of catalyst loaded without diluents.
- Pressure = 30 bar
- The reactor adiabatic and up flow.
- A model charge feed was used: 90 % iC5 + 10 % nC5 + 300 ppm C₂Cl₄ bought from Air Product ®
- H2/Hydrocarbon = 0.5 mol/mol (about 90 NI/I) constant over the test
- WH = 1 and 2 h⁻¹
- T = 140 °C, 150°C then 160 °C
- Catalyst :chlorinated alumina (ATIS-2L from Albemarle)
- The dew point was maintained between 47°C and 56°C to avoid catalyst deactivation
- The quantity of iC5 converted into nC5 were calculated from the online analyses. The feed was also analyzed to determine eventual presence of sulfur. No sulfur compounds were detected.

 Conversion is calculated with the following formula:

$$conversion = \frac{iC5converted}{iC5initial}$$

40 Results of the test

[0043] From the test performed, the following results were obtained:

Maximum of conversion obtained in comparison with the thermodynamic equilibrium

[0044]

| Temperature (°C) | Ratio iC5/nC5 at the thermodynamic equilibrium | Maximum conversion (thermodynamic) | Conversion measured (VVH in h ⁻¹) |
|---------------------|--|------------------------------------|--|
| 140 | 77 / 23 | 14% | 7% (1 h ⁻¹) |
| 150 | 76 / 24 | 15% | 13% (2 h ⁻¹) |
| 160 | 75 / 25 | 16% | 14% (2 h ⁻¹) |

[0045] Even at an elevated VVH, conversions close to the thermodynamic equilibrium were obtained.

Claims

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- 1. Process to upgrade light naphthas comprising branched paraffins and their use as a feedstock in a steam cracking unit, said light naphthas consisting essentially of 90 to 100% by weight of hydrocarbons having at least 5 and up to 8 carbon atoms, said process comprising,
 - a) providing an isomerization zone recovered from the gasoline unit of an oil refinery,
 - b) providing a separation zone capable to treat an hydrocarbon stream comprising branched paraffins and normal paraffins to produce a first hydrocarbon stream having a reduced branched paraffins content and an enhanced normal paraffins content and a second hydrocarbon stream having an enhanced branched paraffins content and a reduced normal paraffins content,
 - c) optionally providing a depentanizer,
 - d) sending the light naphtha to the isomerization zone and operating said zone at conditions effective to produce a light naphtha having a reduced branched paraffins content and an enhanced normal paraffins content,
 - e) sending the withdrawn light naphtha from step d) to the separation zone to recover a first and a second hydrocarbon streams,
 - f) sending the first hydrocarbon stream recovered from step e) to the steam cracking unit,
 - g) recycling at least a part of the second hydrocarbon stream recovered from step e) at the inlet of the isomerization zone.
 - h) optionally, before the recycling of step g), sending the second hydrocarbon stream recovered at step e) to a depentanizer to recover a stream comprising essentially pentane and a stream having a reduced pentane content and sending at least a part of said stream comprising essentially pentane at the inlet of the isomerization zone.
- 25 2. Process to upgrade light naphthas comprising branched paraffins and their use as a feedstock in a steam cracking unit, said light naphthas consisting essentially of 90 to 100% by weight of hydrocarbons having at least 5 and up to 8 carbon atoms, said process comprising,
 - a) providing an isomerization zone recovered from the gasoline unit of an oil refinery,
 - b) providing a separation zone capable to treat an hydrocarbon stream comprising branched paraffins and normal paraffins to produce a first hydrocarbon stream having a reduced branched paraffins content and an enhanced normal paraffins content and a second hydrocarbon stream having an enhanced branched paraffins content and a reduced normal paraffins content,
 - c) sending the light naphtha to the separation zone to recover a first and a second hydrocarbon streams,
 - d) sending the second hydrocarbon stream recovered from step c) to the isomerization zone and operating said zone at conditions effective to produce a light naphtha having a reduced branched paraffins content and an enhanced normal paraffins content,
 - e) mixing the outlet stream of step d) with the first hydrocarbon stream recovered from step c) and sending said mixed stream to the steam cracking unit.
 - 3. Process to upgrade light naphthas comprising branched paraffins and their use as a feedstock in a steam cracking unit, said light naphthas consisting essentially of 90 to 100% by weight of hydrocarbons having at least 5 and up to 8 carbon atoms, said process comprising,
 - a) providing an isomerization zone recovered from the gasoline unit of an oil refinery,
 - b) providing a separation zone capable to treat an hydrocarbon stream comprising branched paraffins and normal paraffins to produce a first hydrocarbon stream having a reduced branched paraffins content and an enhanced normal paraffins content and a second hydrocarbon stream having an enhanced branched paraffins content and a reduced normal paraffins content,
 - c) optionally providing a depentanizer,
 - d) sending the light naphtha to the separation zone to recover a first and a second hydrocarbon streams,
 - e) sending the first hydrocarbon stream recovered from step d) to the steam cracking unit,
 - f) sending at least a part of the second hydrocarbon stream recovered from step d) to the isomerization zone and operating said zone at conditions effective to produce a light naphtha having a reduced branched paraffins content and an enhanced normal paraffins content,
 - g) optionally, before sending the second hydrocarbon recovered from step
 - h) to the isomerization zone, sending said hydrocarbon stream to a depentanizer to recover a stream comprising essentially pentane and a stream having a reduced pentane content and sending said stream comprising

essentially isopentane to the isomerization zone,

- i) recycling the outlet stream from step f) to the inlet of the separation zone.
- 4. Process to upgrade light naphthas comprising branched paraffins and their use as a feedstock in a steam cracking unit, said light naphthas consisting essentially of 90 to 100% by weight of hydrocarbons having at least 5 and up to 8 carbon atoms, said process comprising,
 - a) providing an isomerization zone recovered from the gasoline unit of an oil refinery,
 - b) providing a deisopentanizer,
 - c) sending the light naphtha to a deisopentanizer to recover a stream comprising essentially isopentane and a stream having a reduced isopentane content,
 - d) sending the stream having a reduced isopentane content recovered from step c) to the steam cracking unit,
 - e) sending the stream comprising essentially isopentane recovered from step c) to the isomerization zone and operating said zone at conditions effective to produce a light naphtha having a reduced branched paraffins content and an enhanced normal paraffins content,
 - f) recycling the outlet of step e) to the inlet of the deisopentanizer.
 - **5.** Process according to any one of the preceding claims wherein the isomerization zone operates under the presence of hydrogen.
 - **6.** Process according to any one of the preceding claims wherein the light naphtha to be upgraded is a C5 cut comprising, the total being 100w%, 100 to 95% of a mixture of pentane and isopentane and 0 to 5% of cyclopentane.
 - 7. Process according to any one of the preceding claims wherein the light naphtha to be upgraded is a C5/C6 cut comprising, the total being 100w%,

0 to 10 % of C7+,

0 to 10% of C4,

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80 to 100% of a mixture of normal and branched C5 and C6.

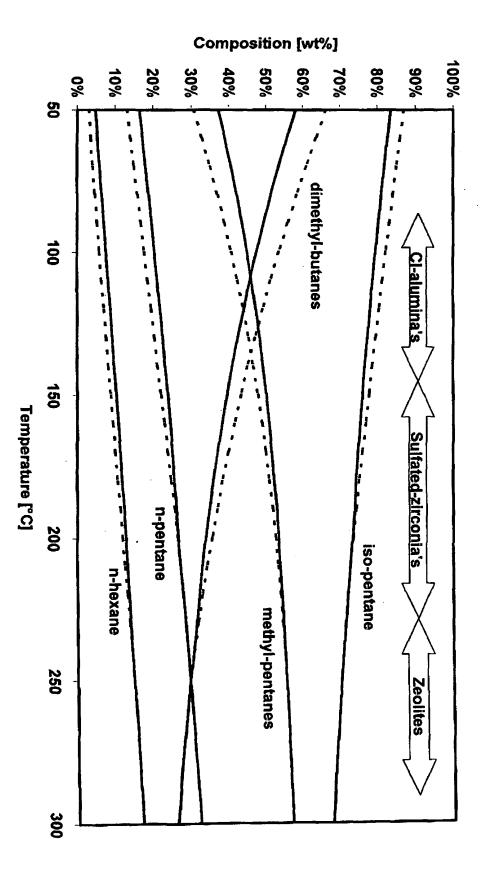
8. Process according to any one of the preceding claims wherein the light naphtha to be upgraded is a C5/C6 cut comprising, the total being 100w%,

0 to 10 % of C7+,

0 to 10% of C4,

20 to 60% of a mixture of normal and branched C5,

20 to 60% of a mixture of normal and branched C6.



... <u>....</u> -

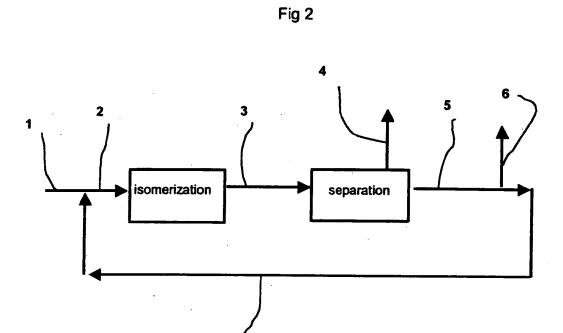


Fig 2-a

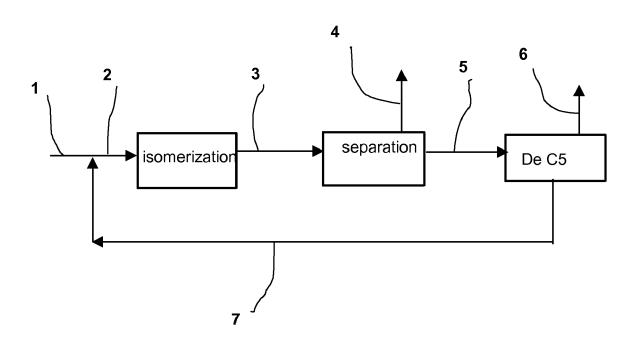


Fig 3

Separation

separation

isomerization

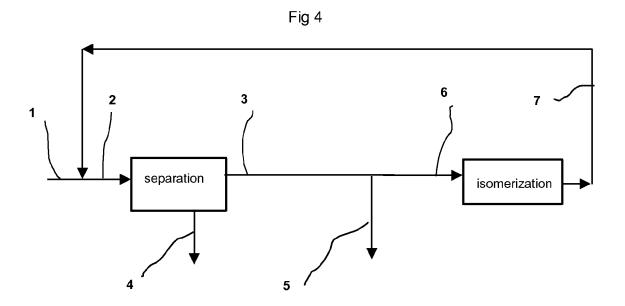
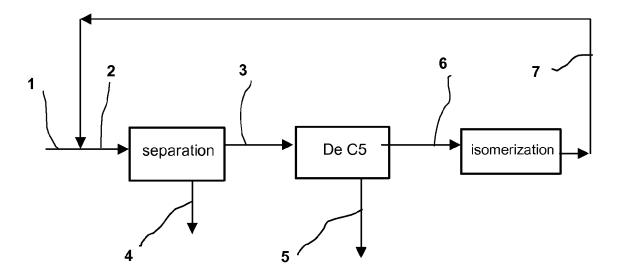
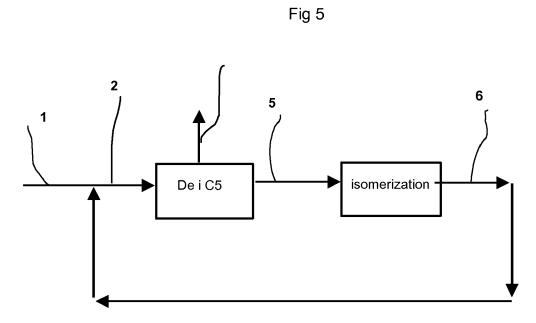


Fig 4-a







EUROPEAN SEARCH REPORT

Application Number

EP 09 15 8607

| | DOCUMENTS CONSID | ERED TO BE RELEVANT | | |
|---|--|---|---|---|
| Category | Citation of document with i of relevant pass | ndication, where appropriate, ages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (IPC) |
| D,X A | US 2005/101814 A1 (AL) 12 May 2005 (20 constant) to claims 4-6; figur page 3, paragraph page 4, paragraph page 9, paragraph page 10, paragraph | res 2,3 * [*] ns 26,27,30,31 * n 34 * n 80-85 * | 1-3,5-8 | INV. C10G9/00 C10G45/58 C10G45/62 C10G45/64 C10G69/06 C10G69/14 |
| Х | US 7 485 768 B1 (R) 3 February 2009 (20 * claims 1,2,13 * * column 3, lines 3 * column 5, lines 5 * column 7, lines 5 * column 8, lines 2 | 33-40 * 18,19 * 55-60 * | 3-8 | |
| Α | US 2002/043480 A1 (AL) 18 April 2002 (* claim 1 * | DUCREUX OLIVIER [FR] ET (2002-04-18) | 1-8 | |
| A,D | US 5 019 661 A (MOI 28 May 1991 (1991-6 * claim 1 * | | 1-8 | TECHNICAL FIELDS SEARCHED (IPC) |
| | The present search report has | • | | |
| | Place of search | Date of completion of the search | | Examiner |
| | Munich | 15 December 2009 | Har | f, Julien |
| X : parti Y : parti docu A : tech O : non | ATEGORY OF CITED DOCUMENTS icularly relevant if taken alone icularly relevant if combined with anot iment of the same category inological background-written disclosure mediate document | L : document cited for | ument, but publise the application rother reasons | shed on, or |



Application Number

EP 09 15 8607

| CLAIMS INCURRING FEES | | | | | | | | | |
|--|--|--|--|--|--|--|--|--|--|
| The present European patent application comprised at the time of filing claims for which payment was due. | | | | | | | | | |
| Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s): | | | | | | | | | |
| No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due. | | | | | | | | | |
| LACK OF UNITY OF INVENTION | | | | | | | | | |
| The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely: | | | | | | | | | |
| see sheet B | | | | | | | | | |
| All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims. | | | | | | | | | |
| As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee. | | | | | | | | | |
| Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims: | | | | | | | | | |
| None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims: | | | | | | | | | |
| The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC). | | | | | | | | | |



LACK OF UNITY OF INVENTION SHEET B

Application Number

EP 09 15 8607

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1-3,5-8

process to upgrade light naphthas comprising branched paraffins comprising isomerisation of the light naphtha to produce a light naphtha with reduced branched paraffins content, sending the isomerised light naphtha to a separation zone to recover a first and a second hydrocarbon stream, steam cracking the first hydrocarbon stream with reduced branched paraffins content and recycling the second hydrocarbon stream with reduced normal paraffins content to the isomerisation zone (claim 1) or comprising sending the light naphtha to a separation zone to recover a first and a second hydrocarbon stream, sending the second hydrocarbon stream with reduced normal paraffins content to the isomerisation zone to produce a light naphtha with reduced branched paraffins content, mixing the isomerised second hydrocarbon stream with the first hydrocarbon stream with reduced branched paraffins content and steam cracking the mixed stream (claim 2) or comprising sending the light naphtha to a separation zone to recover a first and a second hydrocarbon stream, steam cracking the first hydrocarbon stream with reduced branched paraffins content, sending the second hydrocarbon stream with reduced normal paraffins content to the isomerisation zone to produce a light naphtha with reduced branched paraffins content and recycling the isomerised second hydrocarbon stream to the separation zone (claim 3)

2. claim: 4

process to upgrade light naphthas comprising branched paraffins comprising sending the light naphtha to a deisopentaniser, sending the stream with reduced isopentane content to the steam cracking unit, sending the isopentane stream to the isomerisation zone to produce a light naphtha with reduced branched paraffins content and recycling the isomerised stream to the deisopentaniser

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 09 15 8607

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15-12-2009

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

FORM P0459

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