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NL-2596 HR The Hague (NL)**(54) **Process for upgrading a hydrocarbonaceous feedstock.**

(57) Process for upgrading a hydrocarbonaceous feedstock substantially boiling in the gasoline range which comprises:

- a) subjecting the feedstock to a separation treatment and recovering therefrom a first hydrocarbon feed stream comprising C₆ and smaller hydrocarbons and a second hydrocarbon feed stream comprising C₆ and greater hydrocarbons;
- b) subjecting at least part of the second hydrocarbon feed stream to a separation treatment wherein normal paraffins and optionally mono-isoparaffins are separated from di-isoparaffins;
- c) recovering therefrom a first separation effluent stream comprising normal paraffins and optionally mono-isoparaffins and a second separation effluent stream comprising di-isoparaffins;
- d) subjecting at least part of the first separation effluent stream to a reforming step to produce a reformate;
- e) subjecting at least part of the reformate to a separation treatment and recovering therefrom a light fraction comprising C₆ and smaller hydrocarbons and a heavy fraction comprising C₆ and greater hydrocarbons; and
- f) subjecting at least part of the light fraction and the first hydrocarbon feed stream to an isomerisation step and recovering therefrom an isomerate.

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The present invention relates to a process for upgrading a hydrocarbonaceous feedstock substantially boiling in the gasoline range.

One of the main objects in nowadays oil refining is to produce gasolines fulfilling the increasing environmental demands on product quality and having a high octane number.

This means for gasoline that the octane specification has now to be established without lead-containing additives, less aromatics, in particular benzene, less olefins and lower gasoline vapour pressure.

Object of the present invention is to provide a process for the preparation of gasolines fulfilling both the increasing environmental demands on product quality and the high octane requirement.

It has now been found that gasolines can be produced having a high octane number and a reduced aromatics content, in particular benzene, when use is made of an upgrading process comprising a specific sequence of process steps.

Accordingly, the present invention relates to a process for upgrading a hydrocarbonaceous feedstock substantially boiling in the gasoline range, which process comprises:

- a) subjecting the feedstock to a separation treatment and recovering therefrom a first hydrocarbon feed stream comprising C_6 and smaller hydrocarbons and a second hydrocarbon feed stream comprising C_6 and greater hydrocarbons;
- b) subjecting at least part of the second hydrocarbon feed stream to a separation treatment wherein normal paraffins and optionally mono-isoparaffins are separated from di-isoparaffins;
- c) recovering therefrom a first separation effluent stream comprising normal paraffins and optionally mono-isoparaffins and a second separation effluent stream comprising di-isoparaffins;
- d) subjecting at least part of the first separation effluent stream to a reforming step to produce a reformat;
- e) subjecting at least part of the reformat to a separation treatment and recovering therefrom a light fraction comprising C_6 and smaller hydrocarbons and a heavy fraction comprising C_6 and greater hydrocarbons; and
- f) subjecting at least part of the light fraction and the first hydrocarbon feed stream to an isomerisation step and recovering therefrom an isomerate.

In this way a direct octane enhancement of the resultant gasoline blending pool is established whilst a substantial reduction of aromatics content, in particular benzene, is realized. In refineries with restriction on production of gasoline due to octane and/or capacity limitations, this octane enhancement can permit increased gasoline production.

The two hydrocarbon feed streams which are derived from the hydrocarbonaceous feedstock substantially boiling in the gasoline range in step a) can suitably be obtained by distillation. Suitably, the two hydrocarbon feed streams are adjacent fractions obtained by distillation. Depending, of course, on the sharpness of the cutting points of the fractions chosen in the distillation some overlap may occur among the adjacent fractions.

The hydrocarbonaceous feedstock boiling in the gasoline range can suitably be obtained by distillation of crude or by catalytic cracking although it may be obtained by other cracking processes such as thermal cracking, delayed coking, visbreaking and flexicoking. Such gasoline feedstocks usually contain unacceptable levels of sulphur and nitrogen and benefit from a hydrotreatment before they are subjected to the process according to the present invention.

Suitably, the process according to the present invention is carried out in such a way that in step b) both the normal paraffins and mono-isoparaffins (mono-branched paraffins) are separated from the di-isoparaffins (di-branched paraffins). This is suitably established by passing at least part of the second hydrocarbon feed stream to a separation zone comprising a shape-selective separatory molecular sieve having a pore size intermediate 5.5×5.5 to 4.5×4.5 Å, but excluding 4.5×4.5 Å, the pore size being sufficient to permit entry of normal paraffins and mono-isoparaffins but restrictive to prohibit entry of di-isoparaffins, other multi-branched paraffins, cyclic paraffins and aromatic hydrocarbons. In this way the normal paraffins and mono-isoparaffins can selectively be separated from the di-isoparaffins. Subsequently, the first separation effluent stream comprising both normal paraffins and mono-isoparaffins and the second separation effluent stream comprising di-isoparaffins can be recovered.

Subsequently, at least part of said first separation effluent stream is subjected to the reforming step. Preferably, substantially the entire first separation effluent stream is subjected to the reforming step.

Preferably, the normal paraffins are firstly separated from the mono-isoparaffins and di-isoparaffins, whereas the mono-isoparaffins are subsequently separated from the di-isoparaffins. To this end use can be made of a multiple select adsorbent molecular sieve system having particular separatory qualities. Preferably, the multiple separatory sieve system to be used comprises a first molecular sieve having a pore size of 4.5×4.5 Å or smaller and being shaped to permit adsorption of normal paraffins in a selective

manner vis-a-vis mono-isoparaffins, di-isoparaffins, other multi-branched paraffins, cyclic paraffins and aromatic hydrocarbons and a second molecular sieve having a pore size intermediate 5.5×5.5 to 4.5×4.5 Å, but excluding 4.5×4.5 Å, being selected to permit adsorption of mono-isoparaffins (and any remaining normal paraffins) in deference to di-isoparaffins, other multi-branched paraffins, cyclic paraffins and aromatic hydrocarbons which can be passed directly to a refinery gasoline blending pool. In operation, at least part of the second hydrocarbon feed stream is firstly contacted with the first shape-selective separatory molecular sieve as defined hereinabove to produce a first separation effluent stream comprising the normal paraffins and a second separation effluent stream comprising both mono- and di-isoparaffins. The latter separation effluent stream is subsequently contacted with the second shape-selective separatory molecular sieve as described hereinabove. Subsequently, a third separation effluent stream comprising mono-isoparaffins can be recovered and a fourth separation effluent stream comprising di-isoparaffins can be recovered. At least part of the first and third separation effluents is subjected to the reforming step. Preferably, substantially the entire first and third separation effluent streams are subjected to the reforming step. In another embodiment of the present invention at least part of the first and third separation effluent streams may suitably be used as a preferred chemical feedstock. For instance, as a feedstock for a highly selective (dehydro)cyclization process.

The multiple select adsorbent molecular sieve system as described hereinabove comprises at least two molecular sieves. These can be arranged in separate vessels, or they can be arranged in a stacked flow scheme within one vessel.

This first molecular sieve can be a calcium 5 Å zeolite or any other sieve of similar pore dimensions. It is not necessary to size the first sieve to adsorb all of the normal paraffins, but it is preferred so that the second molecular sieve does not have to function as a normal paraffin adsorption sieve.

The second molecular sieve in this process sequence is exemplified by a molecular sieve which has eight and ten member rings and pore dimensions intermediate 5.5×5.5 and 4.5×4.5 Å, but excluding 4.5×4.5 Å.

The preferred second molecular sieve of this invention is exemplified by a ferrierite molecular sieve. It is preferred that the ferrierite sieve be present in a hydrogen form, but it alternatively can be exchanged with a cation of an alkali metal, or alkaline earth metal or transition metal cation. The second molecular sieves of this invention include ferrierite and other analogous shape-selective materials with pore openings intermediate in dimensions to those of the calcium 5 Å zeolite and ZSM-5. Other examples of crystalline sieves include aluminophosphates, silicoaluminophosphates, and borosilicates.

The aluminophosphate, silicoaluminophosphate and borosilicate molecular sieves which can be used as a second molecular sieve will have a pore opening intermediate 5.5×5.5 and 4.5×4.5 Å, but excluding 4.5×4.5 Å.

It is feasible that the second molecular sieve comprises a large pore zeolite that has been ion exchanged with cations to diminish the effective pore size of the sieve to within the afore-mentioned range of dimensions.

When applying multiple select adsorbent molecular sieve systems, the sequence of the sieves, whether in discrete vessels or in a stacked variety, is very important. If the sieves are interchanged the process loses effectiveness because the larger sieve will rapidly fill with normal paraffins, prohibiting the efficient adsorption of mono-isoparaffins.

The respective sieves applied in a multiple select adsorbent molecular sieve system should be arranged in a process sequence to first provide adequate adsorption of the normal paraffin hydrocarbons, and then, adsorption of the mono-isoparaffins. Each of these respective sieves can be provided with a common desorbent stream or each sieve may have its own desorbent stream. The desorbent is preferably a gaseous material such as a hydrogen gas stream.

The light and heavy fraction which have been derived from the reformat in step e) can suitably be obtained by distillation. Suitably, the light and the heavy fraction are adjacent fractions obtained by distillation. Depending, of course, on the sharpness of the cutting points of the fractions chosen in the distillation some overlap may occur among the adjacent fractions. In another embodiment of the present invention at least part of the reformat is firstly subjected to a separation treatment wherein a gaseous fraction is separated from a liquid fraction, whereafter the liquid fraction is separated into the light fraction comprising C_6 and smaller hydrocarbons and the heavy fraction comprising C_6 and greater hydrocarbons. Suitably, at least part of the heavy fraction can directly be passed to a refinery gasoline blending pool and/or at least part of the heavy fraction can be co-processed with the second hydrocarbon feed stream.

The isomerisation in step f) is suitably carried out at a temperature between 100 and 320 °C and a pressure between 10 and 60 bar. The catalyst present in the isomerisation step is suitably catalytically active in isomerisation of hydrocarbons comprising 5 to 7 carbon atoms. The catalyst employed in the

isomerisation step is suitably a heterogeneous hydroisomerisation catalyst having an acid activity and a hydrogenation activity and comprising one or more metals from Group VIII of the Periodic Table of the Elements on a carrier material. The carrier material has acidic properties and may suitably consist of silica-alumina, in particular zeolites (e.g. mordenite, faujasite or zeolite Y) in the hydrogen form or exchanged with rare earth ions, or of alumina rendered acidic by combination of halogen (e.g. chlorine). Preferably, the employed catalyst comprises at least one noble metal from Group VIII (in particular platinum) on mordenite as carrier material. Most preferably, a catalyst is used containing H-mordenite which is prepared by treating mordenite one or more times with an aqueous solution of an ammonium compound (e.g. ammonium nitrate), followed by drying (e.g. at 100-200 °C and calcining (e.g. at 400-700 °C) of the treated mordenite.

The catalyst can comprise a binder material such as alumina, silica or silica-alumina.

In a preferred embodiment of the process according to the present invention at least part of the heavy fraction obtained in step e) is also subjected to a separation treatment as described hereinbefore wherein normal paraffins and optionally mono-isoparaffins are separated from di-isoparaffins, and whereby a first hydrocarbon product stream comprising normal paraffins and optionally mono-isoparaffins and a second hydrocarbon product stream comprising di-isoparaffins is recovered. At least part of the light fraction and/or at least part of the first hydrocarbon feed stream can also suitably be subjected to any of the separation treatments mentioned hereinbefore wherein normal paraffins and optionally mono-isoparaffins are separated from di-isoparaffins, prior to or after the isomerisation in step f. Before being subjected to such a separation treatment C₅ hydrocarbons are separated from the light fraction and/or first hydrocarbon feed stream or the isomerate obtained.

Suitably at least part of the first hydrocarbon product stream is co-processed in step d). In another embodiment of the process according to the present invention at least part of the first hydrocarbon product stream is used as a preferred chemical feedstock as indicated hereinbefore.

Suitably, the separation treatment downstream the reforming step is carried out in such a way that both the normal paraffins and mono-isoparaffins are separated from the di-isoparaffins. This is suitably established by passing the heavy fraction obtained in step e) to a separation zone comprising a shape-selective separatory molecular sieve having a pore size intermediate 5.5 x 5.5 to 4.5 x 4.5 Å but excluding 4.5 x 4.5 Å, the pore size being sufficient to permit entry of normal paraffins and mono-isoparaffins but restrictive to prohibit entry of di-isoparaffins. In this way the normal paraffins and mono-isoparaffins can selectively be separated from the di-isoparaffins, other multi-branched paraffins, cyclic paraffins and aromatic hydrocarbons. Subsequently, a first hydrocarbon product stream comprising both normal paraffins and mono-isoparaffins and a second hydrocarbon product stream comprising di-isoparaffins can be recovered.

Preferably, the separation treatment downstream the reforming step is carried out in such a way that the normal paraffins are firstly separated from the mono-isoparaffins and di-isoparaffins, whereas the mono-isoparaffins are subsequently separated from the di-isoparaffins. To this end use can be made of a multiple select adsorbent molecular sieve system as described hereinbefore.

When use is made of a multiple select adsorbent molecular sieve system both upstream and downstream of the reforming step, firstly the initially present normal paraffins and mono-isoparaffins are separated from di-isoparaffins, whereas subsequently normal paraffins and mono-isoparaffins, which have been produced in the reforming step are separated from di-isoparaffins.

The application of a multiple select adsorbent molecular sieve system both upstream and downstream of the reforming step is very attractive since it offers product flexibility together with product quality. Hence, in a preferred embodiment of the present invention a multiple select adsorbent molecular sieve system is applied both upstream and downstream of the reforming step. The separation treatments upstream and downstream the reforming step are preferably carried out in the same separation zone.

Suitably, at least part of the reformate obtained is passed to a hydrogenation unit before being subjected to any of the separation treatments described hereinbefore.

In the reforming step any conventional reforming catalyst can be applied. Preferably, in the reforming step a catalyst is applied having a substantial (dehydro)cyclization selectivity. Exemplary of such a catalyst is a platinum-containing catalyst with platinum present in for instance a range of 0.005 wt% to 10.0 wt%.

The catalytic metals associated with the reforming function are preferably noble metals from Group VIII of the Periodic Table of elements, such as platinum and palladium. The reforming catalyst can be present per se or it may be mixed with a binder material.

It is well appreciated that the application of noble metal(s)-containing reforming catalysts normally requires a pretreatment in the form of a catalytic hydrotreatment of the feedstock to be upgraded. In this way nitrogen-compounds and sulphur-compounds can be removed from the feedstock which compounds would otherwise reduce the performance of the reforming catalyst considerably.

The reforming step can suitably be carried out under conventional reforming conditions. Typically the process is carried out at a temperature from 450 to 550 °C and a pressure of 3 to 20 bar. The reaction section in which the reforming step is to be performed can suitably be separated into several stages or reactors.

5 The present invention will now be illustrated by means of the Example.

Example

10 A process according to the present invention is carried out in accordance with the flow diagram as schematically shown in Figure 1.

A hydrocarbonaceous feedstock substantially boiling in the gasoline range and having the properties as set out in Table 1 is introduced via a line 1 into a distillation column 2 in which the feedstock is separated into two hydrocarbon feed streams. A first hydrocarbon feed stream comprising hydrocarbons of the C₅-C₆ range is withdrawn via a line 3 and introduced into an isomerisation unit 4. The isomerate effluent obtained
15 therefrom is withdrawn via a line 5 and introduced into the gasoline blending pool 6, whereas a gaseous fraction is withdrawn via a line 7. A second hydrocarbon feed stream comprising C₆ and greater hydrocarbons is withdrawn via a line 8, and passed to a separation zone 9 which contains two molecular sieves 10 and 11. Molecular sieve #1 (10) is a commercial zeolite having a pore size from 4.5 to 4.5 Å or smaller. Molecular sieve 11, referred to as molecular sieve #2, has a pore size of 5.5 x 5.5 to 4.5 x 4.5 Å,
20 but excludes 4.5 x 4.5 Å. The first molecular sieve 10 selectively adsorbs normal paraffins in preference to mono-isoparaffins, di-isoparaffins, other multi-branched paraffins, cyclic paraffins and aromatic hydrocarbons. A fraction comprising normal paraffins is withdrawn via a line 12 and introduced into a reforming reactor 13. A first part of the separation effluent stream substantially freed from normal paraffins is withdrawn via a line 14 and introduced in the gasoline blending pool 6, whereas a second part of this
25 separation effluent stream is withdrawn via a line 15 and contacted with molecular sieve #2 (11). In this particular sieve, mono-isoparaffins are adsorbed while di-isoparaffins and other multi-branched paraffins, cyclic paraffins and aromatic hydrocarbons are passed through the sieve without adsorption. A fraction comprising mono-isoparaffins is withdrawn via a line 16 and introduced into the reforming reactor 13. The remaining separation effluent stream (di-isoparaffins fraction) which is now substantially freed from normal
30 paraffins and mono-isoparaffins is withdrawn via a line 17 and introduced in the gasoline blending pool 6. In the reforming step use is made of a commercially available highly selective (dehydro)cyclization catalyst under typical semi-regenerative reforming conditions. The reformate obtained is subsequently withdrawn via a line 18 and introduced into a distillation column 19. In the distillation column 19 the reformate is separated into a gaseous fraction, a light fraction comprising C₅-C₆ hydrocarbons and a heavy fraction comprising
35 gasoline. The gaseous fraction is withdrawn via a line 20, the light fraction is co-processed with the first hydrocarbon feed stream via a line 21 and the heavy fraction is withdrawn via a line 22 and recycled to the separation zone 9.

100 pbw of the feedstock in line 1 yields the various product fractions in the following quantities:

27.3 pbw first hydrocarbon feed stream (line 3)
40 72.7 pbw second hydrocarbon feed stream (line 8)
28.2 pbw isomerate fraction (line 5)
1.0 pbw gaseous fraction (line 7)
16.5 pbw normal paraffins fraction (line 12)
12.8 pbw a first part separation effluent stream (line 14)
45 67.4 pbw a second part separation effluent stream (line 15)
13.7 pbw a mono-isoparaffins fraction (line 16)
53.7 pbw a di-isoparaffins fraction (line 17)
30.2 pbw reformate fraction (line 18)
4.3 pbw gaseous fraction (line 20)
50 1.9 pbw light fraction (line 21)
24.0 pbw heavy fraction (line 22)

In the blending gasoline pool 6, 4.6 pbw of butane and 17.3 pbw of MTBE have been added to the gasoline obtained via a line 23. In this way 116.6 pbw of an overall gasoline is obtained having the maximum allowable RVP (Reid Vapour Pressure) specification. The overall gasoline obtained in the blending pool 6
55 has the properties as set out in Table 2.

From Table 2 it is clear that a very attractive gasoline, in terms of octane number and content of aromatics, in particular benzene, can be obtained by applying the present invention. In conventional upgrading processes gasolines are obtained having a considerable higher content of aromatics, in particular

benzene.

Table 1

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C (%wt)	:	85.2
H (%wt)	:	14.8
S (ppmw)	:	< 1
d (15/4)	:	0.731
I.B.P.	:	56
10% wt rec.	:	64
30% " "	:	92
50% " "	:	106
70% " "	:	127
90% " "	:	149
F.B.P.	:	197
RON	:	55.7
naphthenes "	:	27.2
aromatics "	:	10.3

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Table 2

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Gasoline properties:	
RON	95.0
total aromatics (%vol)	24.9
benzene (%vol)	1.0
naphthenes (%vol)	25.6
RVP (kPa)	60

Claims

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1. Process for upgrading a hydrocarbonaceous feedstock substantially boiling in the gasoline range which process comprises:

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a) subjecting the feedstock to a separation treatment and recovering therefrom a first hydrocarbon feed stream comprising C₆ and smaller hydrocarbons and a second hydrocarbon feed stream comprising C₆ and greater hydrocarbons;

b) subjecting at least part of the second hydrocarbon feed stream to a separation treatment wherein normal paraffins and optionally mono-isoparaffins are separated from di-isoparaffins;

c) recovering therefrom a first separation effluent stream comprising normal paraffins and optionally mono-isoparaffins and a second separation effluent stream comprising di-isoparaffins;

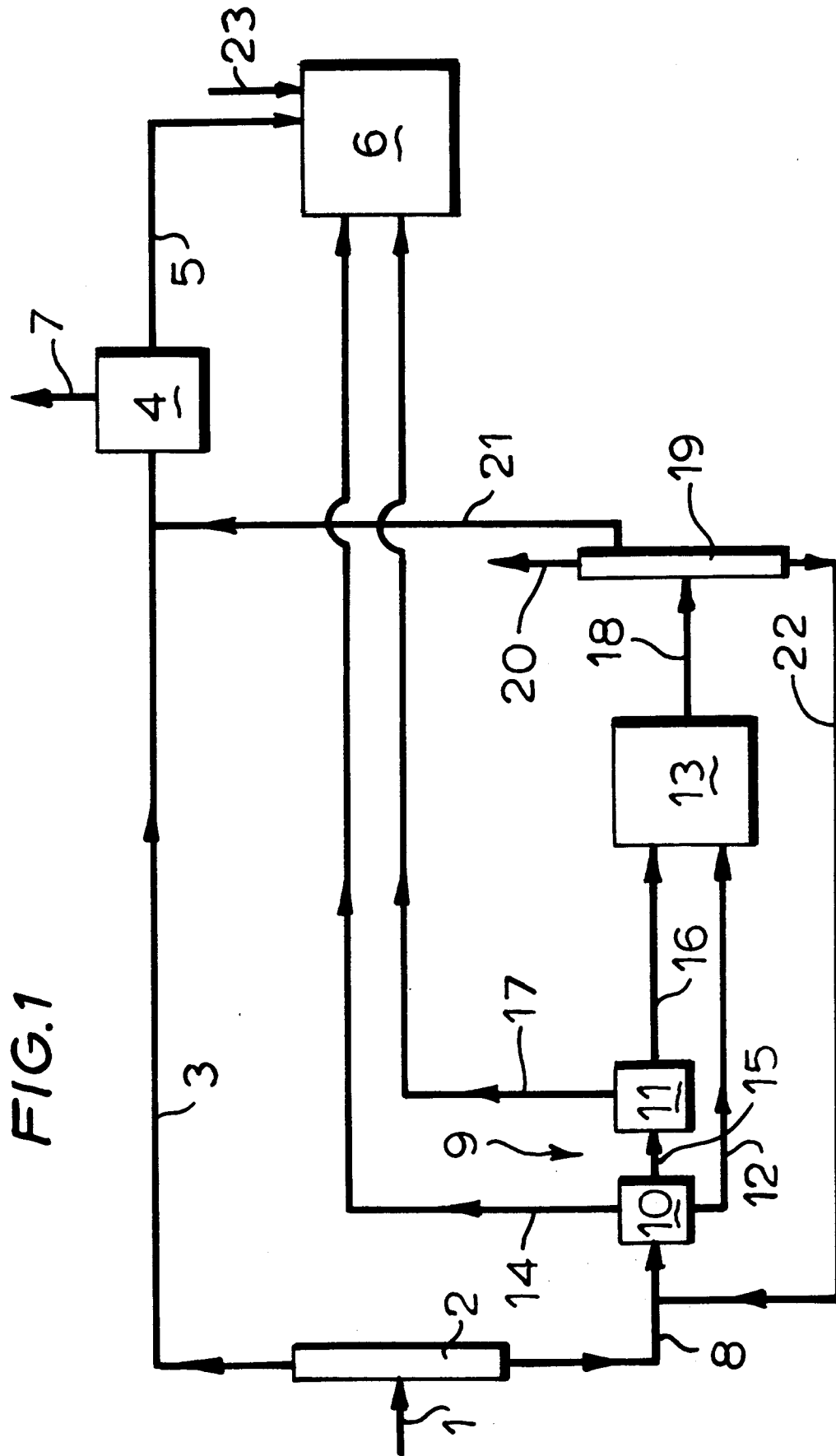
d) subjecting at least part of the first separation effluent stream to a reforming step to produce a reformate;

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e) subjecting at least part of the reformate to a separation treatment and recovering therefrom a light fraction comprising C₆ and smaller hydrocarbons and a heavy fraction comprising C₆ and greater hydrocarbons; and

f) subjecting at least part of the light fraction and the first hydrocarbon feed stream to an isomerisation step and recovering therefrom an isomerate.

- 5 2. Process according to claim 1, wherein in step b) both the normal paraffins and mono-isoparaffins are separated from the di-isoparaffins, and at least part of the normal paraffins and mono-isoparaffins so obtained is subjected to the reforming step.
- 10 3. Process according to claim 2, wherein firstly the normal paraffins are separated from the isoparaffins, and subsequently the mono-isoparaffins are separated from the di-isoparaffins.
- 15 4. Process according to any one of claims 1-3, wherein at least part of the heavy fraction obtained in step e) is subjected to a separation treatment wherein normal paraffins and optionally mono-isoparaffins are separated from di-isoparaffins, and recovering therefrom a first hydrocarbon product comprising normal paraffins and optionally mono-isoparaffins and a second hydrocarbon product stream comprising di-isoparaffins.
- 20 5. Process according to claim 6, wherein both the normal paraffins and mono-isoparaffins are separated from the di-isoparaffins.
- 25 6. Process according to claim 5, wherein firstly the normal paraffins are separated from the isoparaffins, and subsequently the mono-isoparaffins are separated from the di-isoparaffins.
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EUROPEAN SEARCH REPORT

Application Number
EP 94 20 1672

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
P,X	EP-A-0 553 931 (SHELL) * claims 1,3-7 * * example 1 * ---	1-6	C10G61/06
A	FR-A-1 208 231 (ESSO) * claims 1,3,5 * ---	1	
A	GB-A-1 106 044 (UOP) ---	1	
A	US-A-2 935 539 (ESSO) -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C10G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29 September 1994	Examiner De Herdt, O
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons & : member of the same patent family, corresponding document			