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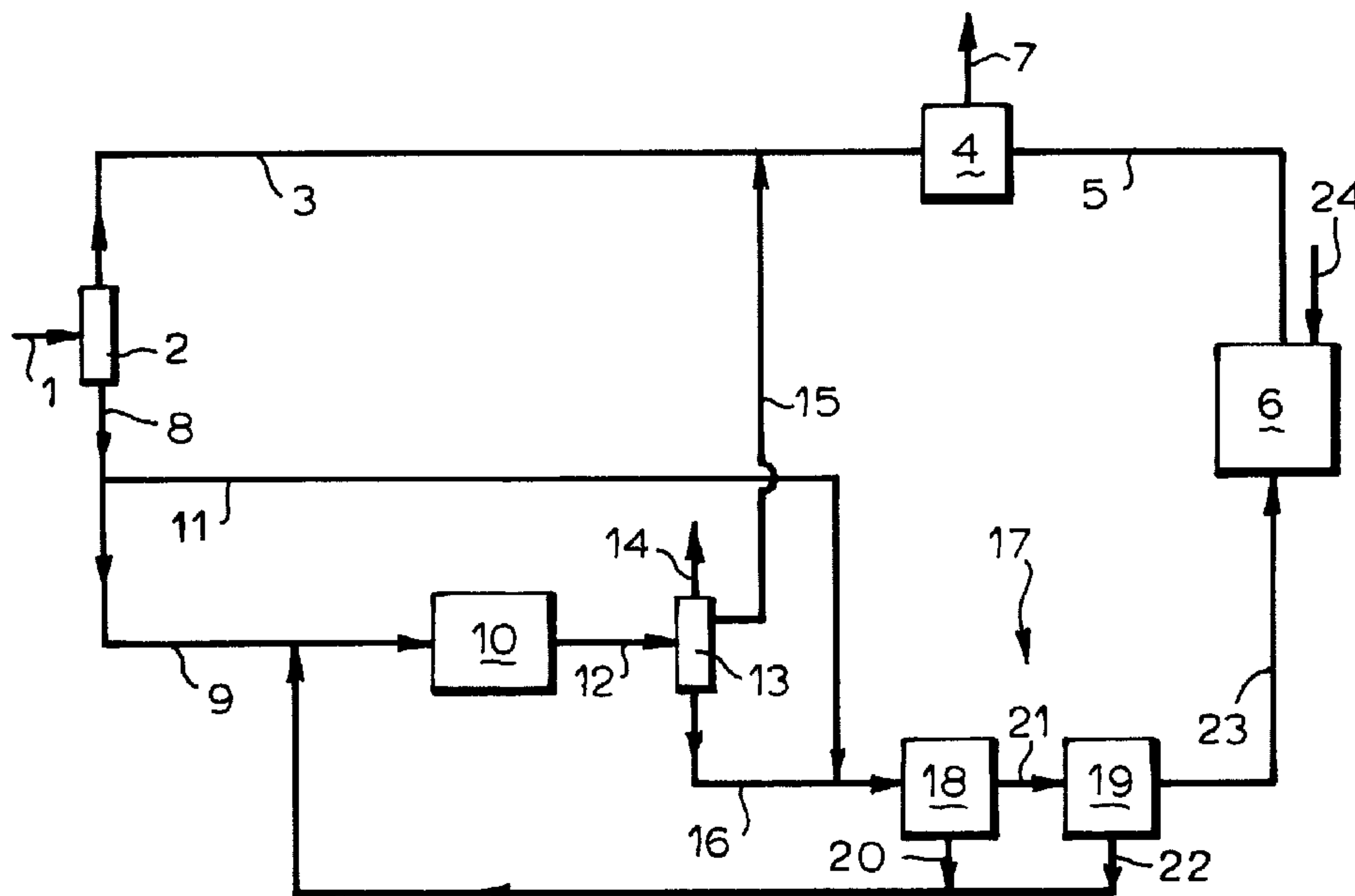
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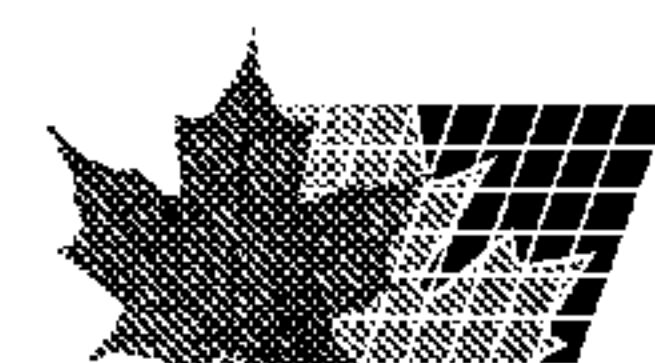
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(54) Title: PROCESS FOR UPGRADING A HYDROCARBONACEOUS FEEDSTOCK



(57) Abrégé/Abstract:

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 C₆ and smaller hydrocarbons and a second hydrocarbon feed stream comprising C₆ and greater hydrocarbons; b) dividing the second hydrocarbon feed stream in a first fraction and a second fraction; c) subjecting at least part of the first fraction to a reforming step to produce a reformat; d) subjecting at least part of the second fraction and at least part of the reformat to a separation treatment wherein normal paraffins and optionally mono-isoparaffins are separated from di-isoparaffins; and e) recovering therefrom a first hydrocarbon product stream comprising normal paraffins and optionally mono-isoparaffins and a second hydrocarbon product stream comprising di-isoparaffins.



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TS 8508

A B S T R A C T

PROCESS FOR UPGRADING A HYDROCARBONACEOUS FEEDSTOCK

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) dividing the second hydrocarbon feed stream in a first fraction and a second fraction;
- c) subjecting at least part of the first fraction to a reforming step to produce a reformate;
- d) subjecting at least part of the second fraction and at least part of the reformate to a separation treatment wherein normal paraffins and optionally mono-isoparaffins are separated from di-isoparaffins; and
- e) recovering therefrom a first hydrocarbon product stream comprising normal paraffins and optionally mono-isoparaffins and a second hydrocarbon product stream comprising di-isoparaffins.

C20/TS8508FF

PROCESS FOR UPGRADING A HYDROCARBONACEOUS FEEDSTOCK

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

5 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
10 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.

15 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.

20 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
25 comprising C_6 and greater hydrocarbons;
- b) dividing the second hydrocarbon feed stream in a first fraction and a second fraction;
- c) subjecting at least part of the first fraction to a reforming step to produce a reformate;

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d) subjecting at least part of the second fraction and at least part of the reformate to a separation treatment wherein normal paraffins and optionally mono-isoparaffins are separated from di-isoparaffins; and

5 e) recovering therefrom a first hydrocarbon product stream comprising normal paraffins and optionally mono-isoparaffins and a second hydrocarbon product stream comprising di-isoparaffins.

According to one aspect of the present invention,
10 there is provided 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 C₆ and smaller
15 hydrocarbons and a second hydrocarbon feed stream comprising C₆ and greater hydrocarbons; b) dividing the second hydrocarbon feed stream in a first fraction and a second fraction; c) subjecting at least part of the first fraction to a reforming step to produce a reformate; d) subjecting at
20 least part of the second fraction and at least part of the reformate to a separation treatment wherein normal paraffins and optionally mono-isoparaffins are separated from di-isoparaffins; and e) recovering therefrom a first hydrocarbon product stream comprising normal paraffins and
25 optionally mono-isoparaffins and a second hydrocarbon product stream comprising di-isoparaffins; and f) passing the second hydrocarbon product stream from step e) to a gasoline blending pool.

In this way a direct octane enhancement of the
30 resultant gasoline blending pool is established whilst a

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substantial reduction of aromatics content, in particular of the benzene content, is realized. In refineries with restriction on production of gasoline due to octane and/or capacity limitations, this octane enhancement can permit
5 increased gasoline production.

The two hydrocarbon feed streams which are derived from the hydrocarbonaceous feedstock substantially boiling in the gasoline range can suitably be obtained by distillation. Suitably, the two hydrocarbon feed streams
10 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
15 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
20 and nitrogen and benefit from a hydrotreatment before they are subjected to the process according to the present invention.

Suitably, in step b) the first fraction comprises 90-10 %v and the second fraction comprises 10-90 %v of the
25 second hydrocarbon feed stream. Conveniently, the first fraction comprises 75-25 %v and the second fraction 25-75 %v of the second hydrocarbon feed stream.

Suitably, the process according to the present invention is carried out in such a way that both the normal
30 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 both the second fraction and the reformat stream to a separation zone comprising a shape-selective 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, 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 hydrocarbon product stream comprising both normal paraffins and mono-isoparaffins and the second hydrocarbon product stream comprising di-isoparaffins can be recovered.

Suitably, in step c) at least part of the first hydrocarbon product stream obtained in step e) is co-processed with the first fraction. At least part of this first hydrocarbon product stream can also suitably be used as a preferred chemical feedstock. For instance, as a feedstock for a highly selective (dehydro)cyclization process.

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 molecular sieve system to be used comprises a first molecular sieve having a pore size of 4.5 x 4.5 Å or smaller and being shaped to permit adsorption of normal paraffins in a selective manner vis-à-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 x 5.5 to 4.5 x 4.5 Å, but excluding 4.5 x 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 fraction and at least part of the reformat stream is
5 firstly contacted with the first shape-selective separatory molecular sieve as defined hereinabove to produce a hydrocarbon product stream comprising both mono- and di-isoparaffins. The latter hydrocarbon product stream is subsequently contacted with the second shape-selective separatory molecular sieve as described
10 hereinabove.

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.

15 The 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 the normal paraffins, but it is preferred so that the second molecular sieve does not have to function as a normal paraffin adsorption sieve.

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

The preferred second molecular sieve of this invention is
25 exemplified by a ferrierite molecular sieve. It is preferred that the ferrierite sieve is 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 molecular sieves of this invention include ferrierite and other analogous
30 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
35 molecular sieves which can be used as the 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 molecular sieve comprises a large pore zeolite that been ion exchanged with cations to diminish the effective pore size of the sieve to within the aforementioned 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.

In a preferred embodiment of the process according to the present invention the first fraction is, prior to the reforming step, also subjected to a separation treatment wherein normal paraffins and optionally mono-isoparaffins are separated from di-isoparaffins, and whereby a first separation effluent stream comprising normal paraffins and optionally mono-isoparaffins is recovered and a second separation effluent stream comprising di-isoparaffins is subjected to the reforming step.

In this way it is established that the amount of gas make and the production of hydrocarbons having a low octane rating can substantially be reduced in the reforming step.

Suitably, the separation treatment upstream 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 first fraction 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. 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, the first separation effluent stream comprising both normal paraffins and mono-isoparaffins can be recovered and the second separation effluent stream comprising di-isoparaffins can be subjected to the reforming step. At least part of the first separation effluent stream can suitably be used as a preferred chemical feedstock as indicated hereinbefore.

Preferably, the separation treatment upstream the reforming step is carried out in such a way that the normal paraffins are firstly separated from the isoparaffins and subsequently the mono-isoparaffins are 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 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 were still present in the second separation effluent stream or 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 of the reforming step can suitably be carried out in the same separation zone.

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

5 Suitably, at least part of the reformat stream is separated, e.g. by means of distillation, in a gaseous fraction, a light fraction comprising C_6 and smaller hydrocarbons and a gasoline fraction. The light fraction can suitably be subjected, for instance together with at least part of the first hydrocarbon feed stream, to an isomerisation step.

10 The isomerisation step can 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 atoms. The catalyst employed in the isomerisation step is
15 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
20 (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
25 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
30 such as alumina, silica or silica-alumina.

The isomerate effluent stream obtained can subsequently passed to a refinery gasoline blending pool.

At least part of the gasoline fraction is subjected to the separation treatment wherein normal paraffins and optionally
35 mono-isoparaffins are separated from di-isoparaffins. At least part

of the light fraction may also be subjected to such a separation treatment.

In the reforming step any conventional reforming catalyst can be applied. Preferably, in the reforming step a catalyst is applied
5 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
10 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
15 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
20 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 reactor section in which the reforming step is to be performed can suitably be separated into several stages or reactors.

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

Example

A process according to the present invention is carried out in accordance with the flow diagram as schematically shown in
30 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
35 hydrocarbon feed stream comprising hydrocarbons of the C₅-C₆ range

is withdrawn via a line 3 and introduced into an isomerisation unit 4. The isomerase effluent obtained 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 C_6 and greater hydrocarbons is withdrawn via a line 8. The second hydrocarbon feed stream is divided in a first fraction (40 %v) and a second fraction (60 %v). The first fraction is withdrawn via a line 9 and introduced into a reforming reactor 10, whereas the second fraction is withdrawn via a line 11. The reforming is carried out at a temperature of 510 °C, a pressure of 10.6 bar, a weight hourly space velocity of 1.8 kg/(kg.hr) and a hydrogen/feed ratio of 510 Nl/kg. The commercially available reforming catalyst comprises platinum and tin on alumina. The reformate obtained is withdrawn via a line 12 and introduced into a distillation column 13. In the distillation column 13 the reformate is separated in a gaseous fraction, a light fraction comprising C_5 - C_6 hydrocarbons and a gasoline fraction. The gaseous fraction is withdrawn via a line 14, the light fraction is co-processed with the first hydrocarbon feed stream via a line 15 and the gasoline fraction is withdrawn via a line 16. The second fraction is introduced via the line 11 into the line 16 and together with the gasoline fraction passed to a separation zone 17 containing molecular sieves 18 and 19. Molecular sieve #1 (18) is a commercial zeolite having a pore size of from 4.5 to 4.5 Å or smaller. Molecular sieve 19, referred to as molecular sieve #2, has a pore size between 5.5 x 5.5 to 4.5 x 4.5 Å, but excludes 4.5 x 4.5 Å.

The first molecular sieve 18 selectively adsorbs normal paraffins in preference to mono-isoparaffins, di-isoparaffins and other multi-branched paraffins, cyclic paraffins and aromatic hydrocarbons. A fraction comprising the normal paraffins is withdrawn via a line 20. The separation effluent substantially freed from normal paraffins is withdrawn via a line 21 and contacted with molecular sieve #2 (19). 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 22, and the remaining separation effluent (di-isoparaffins fraction) which is now substantially freed from normal paraffins and

5 mono-isoparaffins is withdrawn via a line 23 and introduced into the gasoline blending pool 6. The fractions withdrawn via the lines 20 and 22 are co-processed in the reforming step.

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

10	28.2 pbw first hydrocarbon feed stream (line 3)
	71.8 pbw second hydrocarbon feed stream (line 8)
	28.9 pbw first fraction (line 9)
	42.9 pbw second fraction (line 11)
	51.7 pbw reformate fraction (line 12)
15	11.2 pbw gaseous fraction (line 14)
	6.1 pbw light fraction (line 15)
	34.4 pbw gasoline fraction (line 16)
	33.3 pbw isomerate (line 5)
	1.0 pbw gaseous fraction (line 7)
20	10.7 pbw normal paraffins fraction (line 20)
	66.6 pbw separation effluent stream (line 21)
	12.1 pbw mono-isoparaffins fraction (line 22)
	54.5 pbw di-isoparaffins fraction (line 23)

In the gasoline blending pool 6, 3.5 pbw of butane has been

25 added to the gasoline obtained via a line 24. In this way 91.3 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 has the properties as set out in Table 2.

From Table 2 it is clear that a very attractive gasoline, in

30 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.

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Table 1

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 (%v)	:	27.2
aromatics "	:	10.3

Table 2

Gasoline properties:

RON	:	95
total aromatics (%v)	:	33.5
benzene (%v)	:	1.0
naphthenes (%v)	:	22.8
RVP (kPa)	:	60

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CLAIMS:

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

5 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;

10 b) dividing the second hydrocarbon feed stream in a first fraction and a second fraction;

c) subjecting at least part of the first fraction to a reforming step to produce a reformate;

15 d) subjecting at least part of the second fraction and at least part of the reformate to a separation treatment wherein normal paraffins and optionally mono-isoparaffins are separated from di-isoparaffins; and

20 e) recovering therefrom a first hydrocarbon product stream comprising normal paraffins and optionally mono-isoparaffins and a second hydrocarbon product stream comprising di-isoparaffins; and

f) passing the second hydrocarbon product stream from step e) to a gasoline blending pool.

25 2. Process according to claim 1, wherein in step d) both the normal paraffins and mono-isoparaffins are separated from the di-isoparaffins.

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.

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4. Process according to any one of claims 1-3, wherein in step c) at least part of the first hydrocarbon product stream is co-processed with the first fraction.

5. Process according to any one of claims 1-4, wherein the first fraction is, prior to the reforming step,

firstly subjected to a separation treatment wherein normal paraffins and optionally mono-isoparaffins are separated from di-isoparaffins, and whereby a first separation effluent stream comprising normal paraffins and optionally mono-isoparaffins is recovered and a second separation effluent stream comprising di-isoparaffins is subjected to the reforming step.

6. Process according to claim 5, wherein both the normal paraffins and mono-isoparaffins are separated from the di-isoparaffins.

7. Process according to claim 6, wherein firstly the normal paraffins are separated from the isoparaffins, and subsequently the mono-isoparaffins are separated from the di-isoparaffins.

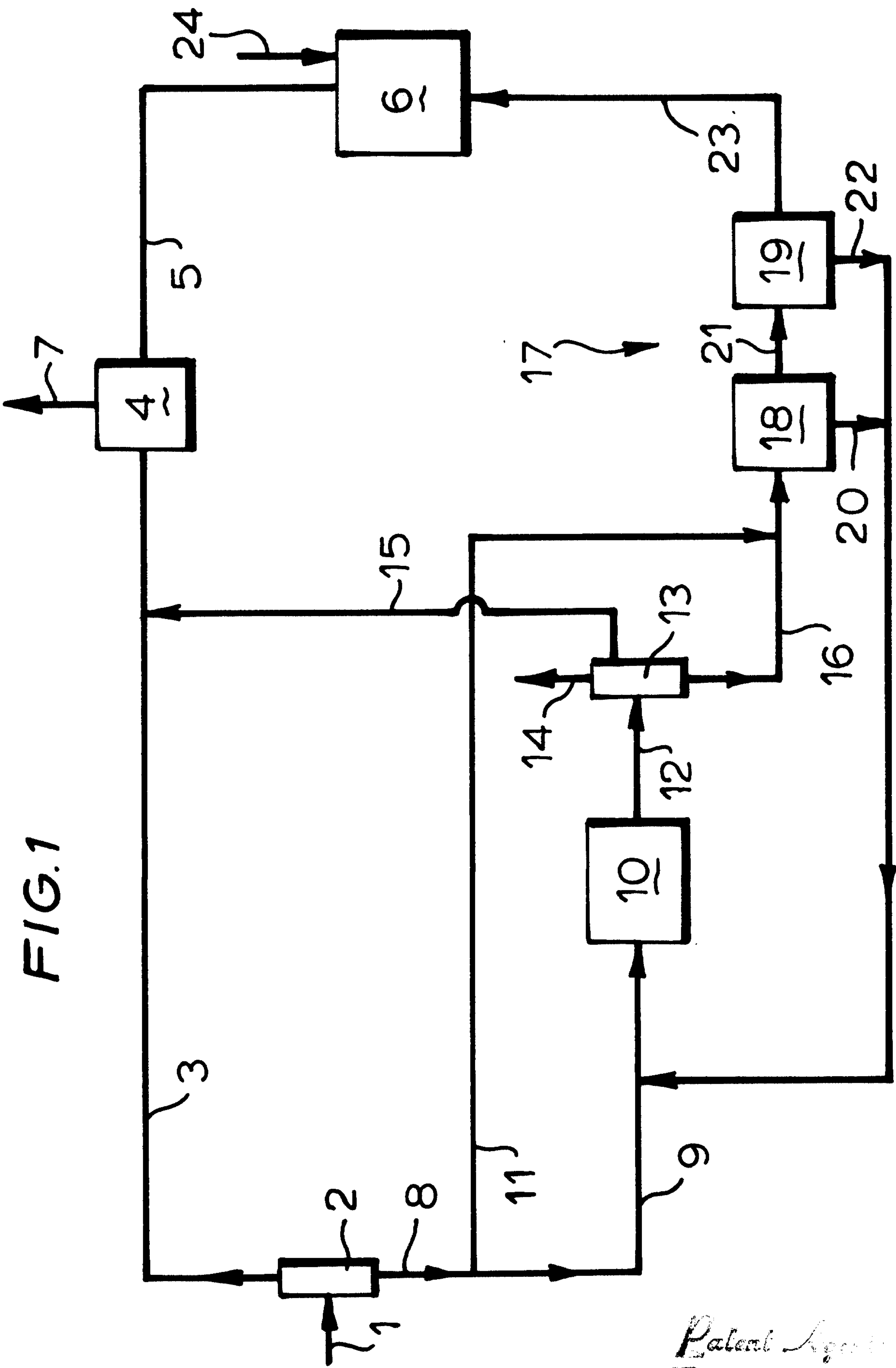


FIG. 1

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