

COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952

595964

APPLICATION FOR A STANDARD PATENT

Shell Internationale Research Maatschappij B.V., a Netherlands Company, of
Carel van Bylandtlaan 30, 2596 HR, The Hague, THE NETHERLANDS, hereby apply
for the grant of a standard patent for an invention entitled:

Process for Isomerization of a Hydrocarbon Feed Stream
which is described in the accompanying complete specification.

Details of basic application(s):-

Basic Applic. No: Country:

940,383

UNITED STATES OF AMERICA

Application Date:

10 December 1986

The address for service is:-

Spruson & Ferguson
Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia

DATED this SEVENTH day of DECEMBER 1987

Shell Internationale Research Maatschappij B.V.

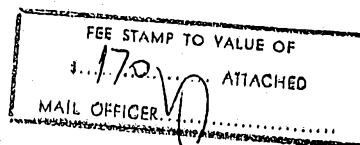
By: *M. J. Anderson*

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 7-2-90

Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 43992
S&F CODE: 61750



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SIXTY DOLLARS



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COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A
CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made for a patent for an invention entitled:

PROCESS FOR ISOMERIZATION OF A HYDROCARBON FEED STREAM

I, Onno Aalbers, of Carel van Bylandtlaan 30, 2596 HR The Hague, the Netherlands, do solemnly and sincerely declare as follows:-

1. I am authorised by SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., the applicant for the patent to make this declaration on its behalf.
2. The basic application~~(s)~~ as defined by Section 141 of the Act was/~~were~~ made in the U.S.A.
on 10th December, 1986
by STEPHEN CHARLES STEM and WAYNE EARL EVANS
3. Stephen Charles STEM, a U.S.-citizen of 3827 Redwood Falls, Houston, Texas 77082, U.S.A., and Wayne Earl EVANS, a U.S.-citizen of 8018 Addicks-Clodine, Houston, Texas 77083, U.S.A.

(~~respectively~~), ~~is~~ are the actual inventor(s) of the invention and the facts upon which the applicant is entitled to make the application are as follows:

The Applicant is the assignee of the actual inventor(s).

4. The basic application~~(s)~~ referred to in paragraph 2 of this Declaration was/~~were~~ the first application~~(s)~~ made in a Convention country in respect of the invention the subject of the application.

DECLARED at The Hague this

27th

day of

October 19 87

.....
Onno Aalbers

TO: THE COMMISSIONER OF PATENTS
AUSTRALIA

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PROCESS FOR ISOMERIZATION OF A HYDROCARBON FEED STREAM
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- (71) Applicant(s)
SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.
- (72) Inventor(s)
STEPHEN CHARLES STEM; WAYNE EARL EVANS
- (74) Attorney or Agent
SPRUSON & FERGUSON
- (57) Claim

1. A process for isomerization of a hydrocarbon feed stream comprising a normal paraffin having at least six carbon atoms per molecule which process comprises the following steps:

- a) passing said hydrocarbon feed stream to an isomerization zone maintained at isomerization conditions and containing an isomerization catalyst to produce an isomerization zone effluent stream comprising di-branched paraffins, mono-methyl-branched paraffins and unreacted normal paraffins;
- b) passing said isomerization zone effluent stream to a separatory tectosilicate sieve having a channel size sufficient to permit entry of said unreacted normal paraffins and said mono-methyl-branched paraffins but restrictive to prohibit entry of more highly-branched paraffins;
- c) separating with said tectosilicate sieve said more highly-branched paraffins as an isomerate product stream from said unreacted normal paraffins and

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from said mono-methyl-branched chain paraffins at separation conditions; and

- d) recycling at least a portion of said unreacted normal paraffin and mono-methyl-branched paraffin stream to said isomerization zone and/or to admixture with said hydrocarbon feed stream.

4. The process of claim 1 wherein said tectosilicate sieve comprises ferrierite.

FORM 10

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COMPLETE SPECIFICATION

(ORIGINAL)

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FOR OFFICE USE:

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Complete Specification Lodged:
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Name and Address
of Applicant:

Shell Internationale Research Maatschappij B.V.
Carel van Bylandtlaan 30
2596 HR
The Hague
THE NETHERLANDS

Address for Service: Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower, 31 Market Street
Sydney, New South Wales, 2000, Australia

Complete Specification for the invention entitled:

Process for Isomerization of a Hydrocarbon Feed Stream

The following statement is a full description of this invention, including the best method of performing it known to me/us

PROCESS FOR ISOMERIZATION OF A
HYDROCARBON FEED STREAM

The invention is concerned with a process for isomerization of a hydrocarbon feed stream comprising a normal paraffin having at least six carbon atoms per molecule.

5 It is desirable to produce gasoline with a relatively high octane number by methods other than lead addition. Two major techniques are currently available to acquire high octane gasoline pools without lead addition. First, hydrocarbons can be reformed in
10 the presence of a reforming catalyst, such as a platinum-rhenium catalyst, to a high octane gasoline. Second, normal paraffins can be isomerized to branched paraffins possessing high octane qualities. This invention concerns the latter of these two processes.

15 From the standpoint of increasing the octane number, it is desirable that hydrocarbons in gasoline have maximum branching. For example, methyl pentanes have lower octane ratings than do dimethylbutanes. Thus, in an isomerization process, it is beneficial to
20 maximize the content of the dimethylbutanes (di-branched paraffins) in the product at the expense of methylpentanes (mono-methyl-paraffins).

It has now been found that a means to accomplish this goal is to employ a specific separatory tecto-
25 silicate sieve which will enable recycle of not only normal paraffins to an isomerization zone, but also mono-methyl-branched hydrocarbons such as methyl-pentanes. Thus, the product stream of this type of isomerization process contains an increased proportion
30 of dimethylbutanes, the most highly branched (and highest octane) form of C_6 saturates. In refineries

which restrict production of gasoline due to octane limitations, the resultant octane enhancement could be used to increase gasoline production.

The invention therefore relates to
5 a process for isomerization of a hydrocarbon feed stream comprising a normal paraffin having at least six carbon atoms per molecule which process comprises the following steps:

- 10 a) passing said hydrocarbon feed stream to an isomerization zone maintained at isomerization conditions and containing an isomerization catalyst to produce an isomerization zone effluent stream comprising di-branched paraffins, mono-methyl-branched paraffins and unreacted normal
15 paraffins;
- b) passing said isomerization zone effluent stream to a separatory tectosilicate sieve having a channel size sufficient to permit entry of said unreacted normal paraffins and said mono-methyl-branched
20 paraffins but restrictive to prohibit entry of more highly-branched paraffins;
- c) separating with said tectosilicate sieve said more highly-branched paraffins as an isomerate product stream from said unreacted normal paraffins and
25 from said mono-methyl-branched chain paraffins at separation conditions; and
- d) recycling at least a portion of said unreacted normal paraffin and mono-methyl-branched paraffin stream to said isomerization zone and/or to
30 admixture with said hydrocarbon feed stream.

It should be noted that the zeolitic molecular
sieves employed in known isomerization processes are capable of selectively absorbing normal paraffins
employing the molecular size and configuration of the
35 normal paraffin molecules as a selection criteria. Particularly suitable zeolites of this type are Zeolite A and calcium exchanged Zeolite 5A. Other naturally

occurring zeolite molecular sieves include chabazite and erionite.

The isomerate produced with such processes will have a certain quantity of mono-methyl-branched hydrocarbons derived from the isomerization of normal paraffins in an upstream isomerization zone.

In contrast, in the process according to the present invention both normal paraffins and mono-methyl-branched chain hydrocarbons are recycled to increase and optimize the quantity of di-branched paraffins in the isomerate; mono-methyl-branched paraffins such as methylpentanes, are absorbed in the tectosilicate sieve and, after desorption, along with normal paraffins, are recycled to the feedstream and/or to the isomerization zone, wherein normal paraffins and mono-methyl-branched hydrocarbons are isomerized to multi-methyl-branched paraffins such as dimethylbutane. The present process increases the degree of branching existent within the isomerate, which increases the octane number.

A preferred embodiment of the invention resides in a process for the preparation of an isomerate gasoline stream which comprises: isomerizing normal hexane, and a hereinafter defined recycle stream, in the presence of an isomerization catalyst, to form an isomerization zone effluent stream comprising normal hexane, methylpentanes, and dimethyl butanes, passing said isomerization stream to a select tectosilicate having a channel size sufficient to permit entry of said normal hexane, and methylpentanes but restrictive to prohibit adsorption of said dimethylbutanes, recovering an isomerate gasoline stream comprising dimethylbutanes and a recycle stream comprising normal hexane, and methylpentanes and recycling at least a portion of said recycle stream to said isomerization zone.

The contemplated hydrocarbon feedstream to the process according to the invention is comprised mainly of isomeric forms of saturated hydrocarbons having six or more carbon atoms per molecule. These can comprise
5 C₆ normal paraffins, normal paraffins having more than six carbon atoms per molecule (C₇+) or mixtures thereof. Such feedstocks are usually derived from refinery operations and can contain quantities of C₅-, C₇+ and cyclic paraffins. Olefinic and aromatic hydro-
10 carbons may also be present. The preferred feedstock will contain more than 25 mol% normal hexane.

The paraffinic feed material is passed through an isomerization reactor having an isomerization catalyst therein. The isomerization catalyst preferably
15 comprises an aluminosilicate having Group VIII metal deposited therewith. Exemplary of such a catalyst is mordenite with platinum having a range of .005 wt% to 10.0 wt% with a preferred range being from .2 to .4 wt%. Other zeolite molecular sieves are also viable
20 which have a silicate to alumina molar ratio of greater than 3 and less than 60 and preferably less than 15. The zeolitic molecular sieves may have many polyvalent metal cations exchanged with the sieve, such as those of the alkali metals or alkaline earth metals. The
25 catalytic metals associated with the isomerization function are preferably noble metals from Group VIII of the Periodic Table of Elements. These can be exemplified by such metals as platinum, palladium, osmium, ruthenium, etc. The isomerization catalyst can
30 be present per se or it may be mixed with a binder material.

The isomerization conditions present in the isomerization zone are those selected to maximize the conversion of normal paraffins and mono-methyl-
35 paraffins to di-methyl-branched paraffins. This type of isomerization is favoured in the vapour phase with a

fixed bed of isomerization catalyst. Typical operating temperatures include from 200 to 400 °C with pressures of about 10 to 40 bar. The isomerization process, which is limited in octane upgrading by thermodynamic equilibria, is frequently measured at 10 points. Even at these select conditions, the effluent from the isomerization reactor will still contain substantial amounts (e.g. 20 to 30 wt%) of normal paraffins and mono-methyl-branched paraffins which are unreacted or partially reacted due to the afore-mentioned equilibrium.

After isomerization, it is preferred that the total isomerization zone effluent be transmitted to a separatory adsorption zone. This separatory zone will preferably comprise 3 to 8 adsorbent beds which can be modified to operate in an adsorption/desorption mode. A calcium-5A sieve as applied in known isomerization/-separation processes is capable of adsorbing virtually no methylpentane nor di-methylbutane while a sodium ZSM-5 molecular sieve will adsorb both methylpentane and dimethylbutane in substantial quantities; hence, neither of said molecular sieves is applicable in the process according to the invention.

The molecular sieve of the invention is a tecto-silicate having precise channel dimensions intermediate the channel dimensions present in either the calcium-5A sieve or the ZSM-5 sieve. The molecular sieve of this invention is capable of adsorbing not only normal hexane, but methylpentanes as well. A preferred molecular sieve of this invention is a tectosilicate having channel dimensions between 5.5 x 5.5 and 4.5 x 4.5, but excluding 4.5 x 4.5 (i.e. calcium-5A) Angstroms.

The most preferred molecular sieve is ferrierite, which exhibits greatly increased adsorption capacity toward methylpentane relative to a calcium-5A molecular sieve. It has been discovered that both the sodium and

hydrogen form of ferrierite are viable although it is preferred that the ferrierite be utilized with a cation of an alkali metal, alkaline earth metal or transition metal cations. The tectosilicates of this invention

5 include ferrierite and other analogous shape-selective materials with channel dimensions intermediate those of the calcium-5A and ZSM-5 molecular sieve which selectively adsorbs methylpentanes while dimethyl-

10 butanes are excluded. Other preferred tectosilicate sieves would be aluminophosphates, silicoaluminophosphates and borosilicates. It is also feasible that the instant tectosilicate could be a larger pore zeolite that has been ion exchanged with relatively

15 large cations so as to diminish the effective channel size of the tectosilicate to within the afore-mentioned range of dimensions. Thus, any tectosilicate having channel dimensions intermediate those of the calcium-5A and ZSM-5 is a candidate sieve with the potential to

20 differentiate between methylpentanes and dimethylbutanes.

As exemplary of the type of tectosilicates which are viable for this technique, the following list is given showing the channel size dimensions of various zeolites including those preferred for use in known isomerization processes such as chabazite, erionite,

25 calcium-5A, etc.

Table 1

Channel

<u>Zeolite</u>	<u>Dimensions (A)</u>	<u>Size</u>
chabazite	3.9 x 4.1	Too small
zeolite A	3.9 x 4.1	Too small
erionite	3.6 x 5.2	Too small
Ca-5A	4.5 x 4.5	Too small
ferrierite	4.5 x 5.5	Correct size
ZSM-5	5.4 x 5.6	Too large
offretite	6.0 x 6.0	Too large
mordenite	6.7 x 7.0	Too large
omega	7.4 x 7.4	Too large
Y zeolite	7.4 x 7.4	Too large

Zeolites that are too small in pore size do not discriminate between mono-methyl-branched C_6 (i.e. methylpentanes) and di-methyl-branched C_6 (i.e. dimethylbutanes). In fact, they exclude both. Zeolites that are listed as too large do not discriminate between mono-methyl-branched and di-methyl-branched C_6 . In fact, they adsorb both. Thus, only zeolites between, and not including, the sizes of the sieves of calcium-5A and ZSM-5 discriminate to accomodate mono-methyl-branched adsorption while excluding di-methyl-branched C_6 paraffins. While ferrierite is the best example of such a sieve, this invention should not be limited to ferrierite per se as the only species which is operable for this process.

The adsorption/desorption conditions typically utilized within the multiple tectosilicate sieves comprise a temperature of from 75 °C to 400 °C and a pressure of from 2 bar to 42 bar. Specific desorbents utilized in order to extract the desired trapped normal paraffin and mono-methyl-paraffins will preferably be hydrogen, which can be transferred with the normal paraffin and mono-methyl-paraffin recycle stream to the

isomerization zone.

The invention is illustrated by way of a schematic flow scheme of the present process.

In the Figure a hydrocarbon feed comprising C_6 paraffins and relatively small amounts of C_1-C_5 paraffins, C_7+ paraffins and aromatic compounds are passed through conduit 100 to isomerization zone 103 for the select isomerization of feed material to di-branched paraffins. An off gas stream may be removed in conduit 105 with an isomerization zone effluent stream in conduit 107 containing normal paraffins, mono-methyl-branched paraffins and more highly-branched paraffins. This effluent stream is passed to a multiple separatory zone 109 which contains particular tectosilicates useful in this invention having channel dimensions between 4.5 x 4.5 and 5.5 x 5.5 A. These tectosilicates may be prepared by any known ferrierite synthesis procedure. This separatory tectosilicate sieve is selective for adsorbing or trapping normal and mono-methyl-branched paraffins. Thus, the effluent in conduit 111 from separation zone 109 contains a substantial concentration of di-methyl-branched paraffins. As a result of this different separatory function versus known integrated isomerization-/- separation processes, recycle stream 113 will be very different. In fact, the difference is derivative of the presence of mono-methyl-branched paraffins in addition to the normal paraffins, all of which are recycled to feed paraffins 100 via conduit 113 and/or a portion of the same may be passed directly to the isomerization zone via conduit 115. A slip stream 117 may also be present to remove unwanted impurities or to extract normal paraffins and mono-methyl-branched paraffins which are not recyclable to exhaustion.

The invention is further illustrated by way of the following Examples.

EXAMPLE 1

In this example, sorption capacities of sodium ferrierite, calcium-5A and sodium ZSM-5 sieves were determined in regard to normal hexane, 3-methylpentane and 2,3-dimethylbutane. The particular denoted zeolite was placed on a pan in a Cahn balance, sample chamber was evacuated, and heated to 550 °C for one hour. The particular zeolite was thus dried and following drying was cooled to 105 °C. At this time, hydrocarbon vapours were admitted to the evacuated chamber to a level of 0.13 bar. Weight changes due to the adsorption of hydrocarbon into the zeolite were recorded. An exposure time of three hours was allowed for the branched hydrocarbons to approach equilibrium weight, whereas an exposure time of only one half hour was required for normal hexane. The results of this adsorption are shown in Table 2. Each combination of zeolite plus solvent was subjected to at least three separate determinations. Listed in the Table are results of individual determinations, as well as mean and standard deviation values for each set of determinations.

Table 2

Hydrocarbon	Weight of HC Adsorbed (mg/g)		
	Ca-5A	Na-Ferrierite	Na-ZSM-5
2,3-Dimethylbutane	1.6	2.1	59.4
	1.3	1.7	59.7
	1.9	1.9	61.1
	2.4	1.8	--
MEAN + STD DEV:	1.8 ± 0.4	1.9 ± 0.1	60.0 ± 0.9
3-Methylpentane	1.7	19.4	56.5
	1.9	19.6	63.9
	2.0	18.4	62.3
	1.5	--	--
	1.2	--	--
MEAN + STD DEV:	1.7 ± 0.3	19.2 ± 0.5	60.9 ± 3.8
n-Hexane	92.3	55.4	111.9
	90.1	54.5	105.4
	100.7	53.9	106.7
	99.3	56.7	--
MEAN + STD DEV:	95.6 ± 4.5	57.4 ± 1.0	107.9 ± 3.4

The sorption capacities are reported as weight gain in the sieve relative to the dry weight of the pure zeolite. As shown in Table 2, the calcium-5A zeolite adsorbed very little branched hydrocarbon and thus is a preferred adsorbent for the recycle of pure normal paraffins to exhaustion as exemplified in prior art processes. The ratio of 3-methylpentane/normal hexane sorption capacities is 0.018. In contrast, sodium ferrierite adsorbed little dimethylbutane but adsorbed a substantial amount of 3-methylpentane. The ratio of the 3-methylpentane/normal hexane sorption capacity is about 20 times greater for the sodium ferrierite than for calcium-5A zeolite. The sodium ZSM-5 sieve adsorbed virtually identical amounts of the mono- and di-branched isomers. Thus, the afore-described sodium ferrierite has the capability to effect a

separation between 3-methylpentane and 2,3-dimethylbutane.

EXAMPLE 2

5 The sorption capacities of a hydrogen ferrierite
towards the same three hydrocarbons were determined and
are presented in Table 3. These data clearly show the
comparison of the hydrogen ferrierite versus the
calcium-5A zeolite. The ratio of 3-methylpentane/normal
10 hexane sorption for the hydrogen ferrierite is about 25
times greater than that for the calcium-5A sieve. A
comparison of the sodium ferrierite and hydrogen
ferrierite, i.e. see Tables 2 and 3, underscores the
discovery that appropriately sized tectosilicates can
15 be tailored to modify the relative sieving
capabilities.

Table 3

Hydrocarbon	H-Ferrierite	Ca-5A
2,3-Dimethylbutane	3.6	1.6
	3.3	1.3
	3.2	1.9
	3.1	2.4
MEAN + STD DEV:	3.3 ± 0.2	1.8 ± 0.4
3-Methylpentane	28.8	1.7
	28.6	1.9
	27.1	2.0
	27.4	1.5
MEAN + STD DEV:	28.0 ± 0.8	1.7 ± 0.3
n-Hexane	56.5	92.3
		90.1
		100.7
		99.3
MEAN + STD DEV:	56.5	95.6 ± 4.5

EXAMPLE 3

A sample of ammonium ferrierite was tableted to particles having a size of 0.35-1.41 mm and placed in a glass tube. The glass tube was placed in a tube furnace under a flow of nitrogen and heated to 500 °C for 2 hours to expel ammonia and thus produce the hydrogen form of ferrierite. Under the same nitrogen flow, the molecular sieve was cooled to room temperature while the nitrogen flow was diverted through a gas saturation tower containing a mixture of normal hexane, 3-methylpentane and 2,3-dimethylbutane. The molecular sieves were exposed to hydrocarbon-containing streams of nitrogen for 1 hour. Samples of the hydrocarbon reservoir were taken at the beginning and at the end of the gas saturation period. The purpose of sampling both at the start and at the end of the experiment was to verify that the ratio of hydrocarbons remained essentially constant throughout the experiment. A portion of the hydrocarbon-containing vapour stream was diverted directly through a cold finger that was immersed in a dry ice/acetone bath to collect a sample of the actual hydrocarbon vapours.

Following exposure to these vapours, the hydrocarbon-saturated ferrierite sample was removed from the glass tube and placed on a vacuum line. The sample was evacuated to below 0.001 bar through a cold finger immersed in liquid nitrogen. The sample was heated to 40 °C and the sorbed hydrocarbon was quantitatively removed from the zeolite. It was experimentally determined that this first trapping was quantitative. The results of the adsorption were analyzed by gas chromatography and are shown in Table 4.

Table 4
Competitive Sorption of Hexane
Isomers By H-Ferrierite

<u>Sample</u>	wt% <u>2,3-DMB</u>	wt% <u>3-MP</u>	wt% <u>n-hexane</u>
Gas saturation tower contents at start of experiment	34.5	36.8	28.0
Gas saturation tower contents at end of experiment	36.5	36.6	26.3
Gaseous hydrocarbon stream	41.5	36.1	21.8
Hydrocarbon adsorbed by H-ferrierite	1.3	16.9	80.3

5 As shown in Table 4, very little dimethylbutane entered the hydrogen ferrierite. Because the adsorption capacity of normal hexane is greater than that of 3-methylpentane and because the rate of adsorption is faster for the unbranched molecules, the hydrocarbon recovered from the zeolite pores was enriched in normal hexane. A substantial amount of methylpentane was adsorbed along with the normal hexane.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for isomerization of a hydrocarbon feed stream comprising a normal paraffin having at least six carbon atoms per molecule which process comprises the following steps:

- 5 a) passing said hydrocarbon feed stream to an isomerization zone maintained at isomerization conditions and containing an isomerization catalyst to produce an isomerization zone effluent stream comprising di-branched paraffins, mono-methyl-branched paraffins and unreacted normal paraffins;
- 10 b) passing said isomerization zone effluent stream to a separatory tectosilicate sieve having a channel size sufficient to permit entry of said unreacted normal paraffins and said mono-methyl-branched paraffins but restrictive to prohibit entry of more highly-branched paraffins;
- 15 c) separating with said tectosilicate sieve said more highly-branched paraffins as an isomerate product stream from said unreacted normal paraffins and from said mono-methyl-branched chain paraffins at separation conditions; and
- 20 d) recycling at least a portion of said unreacted normal paraffin and mono-methyl-branched paraffin stream to said isomerization zone and/or to admixture with said hydrocarbon feed stream.
- 25

2. The process of claim 1 wherein said isomerization zone is maintained at a temperature of 200 °C to 400 °C and a pressure from 10 bar to 40 bar.

30 3. The process of claim 1 wherein said isomerization catalyst comprises an aluminosilicate having a Group VIII metal deposited therewith.

4. The process of claim 1 wherein said tectosilicate sieve comprises ferrierite.

5. The process of claim 4 wherein said ferrierite has cations exchanged therein selected from the group consisting of the alkali metal, alkali earth metal and transition metal cations.

6. The process of claim 1 wherein said tectosilicate sieve comprises an aluminophosphate.

7. The process of claim 1 wherein said tectosilicate sieve comprises a borosilicate.

8. The process of claim 1 wherein said tectosilicate sieve comprises silicoaluminophosphate.

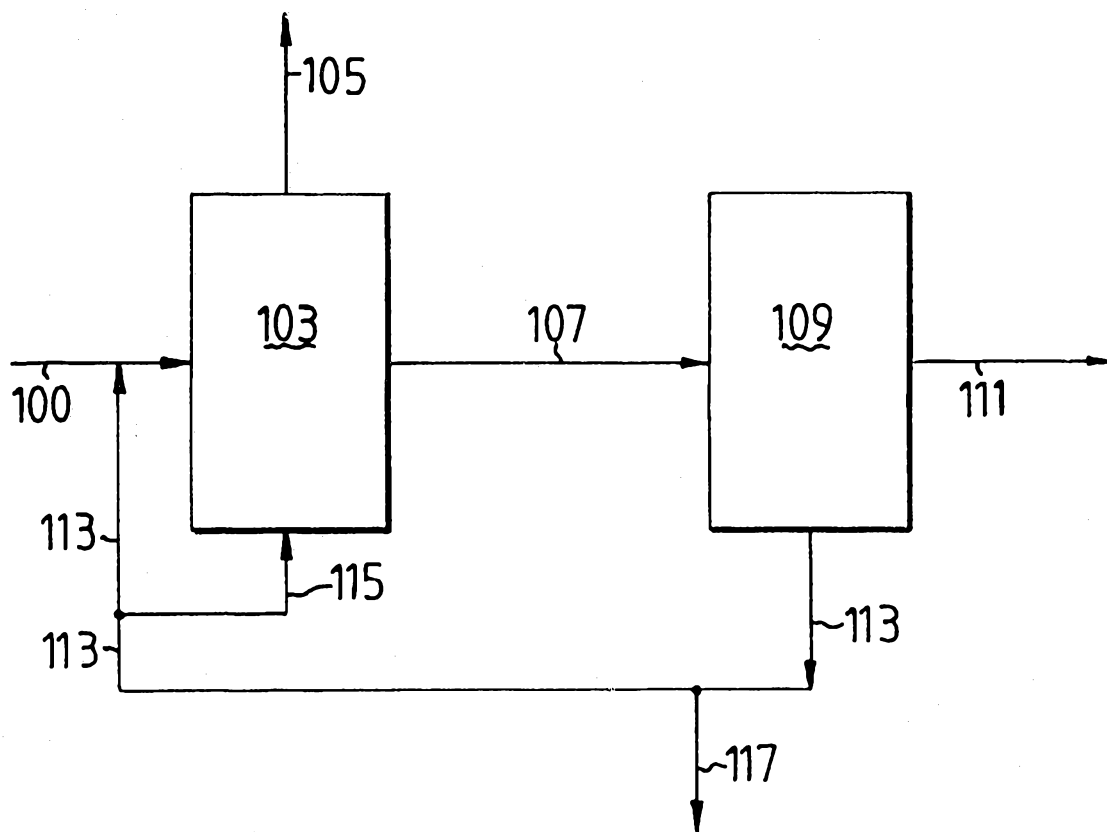
9. The process of claim 1 wherein said separation conditions include a temperature from 75 °C to 400 °C and a pressure of from 2 bar to 42 bar.

10. The product of the process of any one of claims 1 to 9.

11. The invention substantially as hereinbefore described with reference to any one of the Examples.

DATED this NINETEENTH day of NOVEMBER 1987
SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.

Patent Attorneys for the Applicant
SPRUSON & FERGUSON



FIGURE