637163

FORM 1

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

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 Upgrading a Sulphur-Containing Feedstock

which is described in the accompanying complete specification.

Details of basic application(s):-

Basic Applic. No:	Country:	Application Date:
8926555.7	GB	24 November 1989

The address for service is:-

Spruson & Ferguson
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Level 33 St Martins Tower
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Sydney New South Wales Australia

DATED this TWENTY FIRST day of NOVEMBER 1990

Shell Internationale Research Maatschappij B.V.

By:

Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 145564
S&F CODE: 61750

SO18603 5845/22/11/90

SPRUSON & FERGUSON

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 upgrading a sulphur-containing feedstock

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 Great Britain
on 24th November, 1989
by Shell Internationale Research Maatschappij B.V.

3. Ian Ernest MAXWELL, a New Zealand citizen; Frederik MULLER, a Netherlands citizen, both of Badhuisweg 3, 1031 CM Amsterdam, the Netherlands; Frank Hsian Hok KHOUW, a Netherlands citizen; Kim Heong KHOR, a Malaysian citizen and Jacques LUCIEN, a French citizen, all of Carel van Bylandtlaan 30, 2596 HR The Hague, the Netherlands

(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 13th day of August 1990

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TO: THE COMMISSIONER OF PATENTS
AUSTRALIA

Onno Aalbers

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PROCESS FOR UPGRADING A SULPHUR-CONTAINING FEEDSTOCK

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(56) Prior Art Documents
US 4627909

(57) Claim

1. A process for upgrading a sulphur-containing feedstock comprising a hydrocarbon mixture substantially boiling in the gasoline range which process comprises subjecting the feedstock to a reforming step and subsequently to a hydrotreating step, and recovering therefrom a product substantially boiling in the gasoline range and having increased aromaticity and decreased sulphur content, wherein in the reforming step a catalyst is applied which comprises a metal(M)-containing crystalline silicate having an X-ray diffraction pattern containing the four strongest lines at interplanar spacings (d), expressed in Å, of 11.1 $\pm$ 0.2, 10.0 $\pm$ 0.2, 3.84 $\pm$ 0.07 and 3.72 $\pm$ 0.06, wherein M represents at least one of Al, Fe, Ga, W, Mo or Zn, and wherein the metal(M)-containing crystalline silicate comprises either a crystalline aluminosilicate having a SiO_2/Al_2O_3 molar ratio of at least 20 or an iron-containing crystalline (alumino)silicate having a SiO_2/Fe_2O_3 molar ratio of 25 to 1000, and in case alumina is present a SiO_2/Al_2O_3 molar ratio of 20 to 2000.

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FORM 10

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COMPLETE SPECIFICATION

(ORIGINAL)

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Priority:

Related Art:

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Complete Specification for the invention entitled:

Process for Upgrading a Sulphur-Containing Feedstock

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

5845/3

T 5421

A B S T R A C T

PROCESS FOR UPGRADING A SULPHUR-CONTAINING FEEDSTOCK

Process for upgrading a sulphur-containing feedstock comprising a hydrocarbon mixture substantially boiling in the gasoline range which process comprises subjecting the feedstock to a reforming step and subsequently to a hydrotreating step, and recovering therefrom a product substantially boiling in the gasoline range and having increased aromaticity and decreased sulphur content.

T 5421

PROCESS FOR UPGRADING A SULPHUR-CONTAINING FEEDSTOCK

The present invention relates to a process for upgrading a sulphur-containing feedstock and is particularly concerned with improving the quality of a feedstock which comprises hydrocarbons boiling in the gasoline range obtained by catalytic cracking.

Gasoline obtained by catalytic cracking requires further processing before it can satisfactorily meet the present day stringent requirements for high octane and low sulphur content. Thus catalytically cracked gasoline has a comparatively high olefin content, a low aromatics content and if there has been no initial treatment of the feedstock, an unacceptable high sulphur content. Quality improvement may be carried out by catalytic reforming with, for instance platinum-containing reforming catalysts. However, the presence of sulphur- and nitrogen-containing compounds in the reformer feedstock reduces the performance of such catalysts and removal of these compounds by catalytic hydrotreatment is thus considered necessary prior to reforming in order to ensure sufficient catalyst life time, with consequent increase in cost.

Surprisingly, it has been found that a (mixed) feedstock containing an unacceptable high portion of sulphur and substantially boiling in the gasoline range, can very attractively be upgraded in respect of aromatics and sulphur content in a two-stage process wherein the sulphur-containing feedstock is firstly subjected to a specific reforming step and subsequently to a hydrotreating step.

According to a first embodiment of the present invention there is provided a process for upgrading a sulphur-containing feedstock comprising a hydrocarbon mixture substantially boiling in the gasoline range which process comprises subjecting the feedstock to a reforming step and subsequently to a hydrotreating step, and recovering therefrom a product substantially boiling in the gasoline range and having increased aromaticity and decreased sulphur content, wherein in the reforming step a catalyst is applied which comprises a metal(M)-containing crystalline silicate having an X-ray diffraction pattern containing the four strongest lines at interplanar spacings (d), expressed in Å, of 11.1 ± 0.2, 10.0 ± 0.2, 3.84 ± 0.07 and 3.72 ± 0.06, wherein M represents at least one of Al, Fe, Ga, W, Mo or Zn, and wherein the metal(M)-containing crystalline silicate comprises either a crystalline aluminosilicate having a SiO_2/Al_2O_3 molar ratio of at least 20 or an iron-containing crystalline (alumino)silicate having a SiO_2/Fe_2O_3 molar ratio of 25 to 1000, and in case alumina is present a SiO_2/Al_2O_3 molar ratio of 20 to 2000.

It has further been found that in the present process, the hydrotreatment can be carried out at far milder conditions than is customary whilst still obtaining a product of good quality substantially boiling in the gasoline range. Consequently, the present invention constitutes an attractive novel (less complicated) process which can overall suitably be carried out under milder conditions. Moreover, in the process according to the present invention a high yield of liquid products can be obtained, whilst the hydrotreating step is moreover advantageously controlled and controllable.

Preferably use is made of a hydrocarbon mixture substantially boiling in the gasoline range which can be obtained 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, usually more than 500ppmw, often above 100ppmw or even more than 500ppmw.

Other suitable feedstocks to be processed in accordance with the present invention comprise substantially naphthenes-containing hydrocarbon mixtures, for instance straight-run naphthas, or mixtures of hydrocarbonaceous materials which may be

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derived from a cracking process and substantially naphthenes-containing hydrocarbonaceous materials.

The feedstock to be processed is suitably obtained by the application of catalytic cracking, usually fluid catalytic cracking of heavy hydrocarbon oils, such as vacuum gas oils, flashed distillates, long residues, deasphalted vacuum residues and mixtures thereof. Fluid catalytic cracking on a commercial scale is usually carried out in a continuous process using an arrangement which consists substantially of a vertically arranged cracking reactor and a catalyst regenerator. The oil to be cracked is brought in contact with hot regenerated catalyst coming from the regenerator. The mixture of oil and catalyst is passed through the reactor section in an upward direction. In the reactor section coke is deposited on the catalyst as a result of which the catalyst is deactivated. The deactivated catalyst is separated from the product and, after stripping, transported to the regenerator. The cracked product is separated into a light fraction having a high content of C_3 to C_4 olefins, a gasoline fraction and several heavy fractions, such as a light cycle oil, a heavy cycle oil and a slurry oil.

The sulphur-containing feedstock may consist entirely of a fraction substantially boiling in the gasoline range, i.e. substantially boiling in the range C_4 - 220°C. However, other light components, capable of benefitting from aromatization, may be included in the feedstock and coprocessed therewith in the reforming step, for example a mixture substantially comprising normally gaseous olefins and/or paraffins such as C_{2-4} olefins and/or C_7 paraffins.

While the full gasoline boiling range fraction from the cracking reactor may be included in the feedstock, it may be preferred to employ as hydrocarbon mixture a cut

thereof substantially boiling in the range of 70 to 220°C, preferably in the range of 70 to 180°C. Preferably, the sulphur-containing feedstock consists essentially of a hydrocarbon mixture substantially boiling in the gasoline range.

A sulphur-containing feedstock which comprises a hydrocarbon mixture substantially boiling in the range of 140 to 220°C, preferably in the range of 160 to 220°C, can advantageously be coprocessed with the product from the reforming step in the hydrotreating step. Suitably the sulphur-containing feedstock comprising a hydrocarbon mixture substantially boiling in the gasoline range can be derived from a (catalytic) cracking process. Suitably, additional hydrogen can be coprocessed with the product from the reforming step in the hydrotreating step.

Although not preferred it will be understood that part of the effluent from the reforming step can be subjected to a separation treatment.

It has been found that in the reforming step a catalyst can suitably be applied which increases the aromatics content of the feedstock, such as stable (sulphur tolerant) metal-containing crystalline silicates showing a high selectivity towards aromatization. Suitably, in the reforming step a catalyst is applied which effects aromatization of at least 50 % of olefins and/or naphthenes initially present in the sulphur-containing feedstock.

Suitably in the reforming step a catalyst is applied which comprises metal(M)-containing crystalline silicates having an X-ray diffraction pattern containing the four strongest lines at interplanar spacings (d), expressed in Å, of 11.1 ± 0.2, 10.0 ± 0.2, 3.84 ± 0.07 and 3.72 ± 0.06, and wherein M represents at least one of Al, Fe, Ga, W, Mo or Zn.

The metal(s) M can either be incorporated in the matrix of the zeolite or can be present in the pores of the catalyst. The metal(s) are preferably present in the pores of the catalyst.

The X-ray data quoted above can be obtained by diffraction of the Cu K_α X-rays as well known in the art.

Preferably the catalyst to be used in the reforming step comprises metal-containing crystalline silicates such as ZSM-5, crystalline iron-containing crystalline (alumino)silicates or crystalline metallo silicates having the X-ray diffraction pattern as indicated hereinabove.

Suitably the catalyst applied in the reforming step comprises a crystalline aluminosilicate having a SiO_2/Al_2O_3 molar ratio of at least 20, preferably of at least 100, and the X-ray diffraction pattern as described hereinbefore.

Suitably a catalyst can be applied in the reforming step which comprises an iron-containing crystalline silicate. Preference is given to iron-containing crystalline silicates having a SiO_2/Fe_2O_3 molar ratio of 25 to 1000. In case the reforming step is carried out using an iron-containing crystalline aluminosilicate, the catalyst preferably has a SiO_2/Fe_2O_3 molar ratio of 25 to 1000 and a SiO_2/Al_2O_3 molar ratio of 20 to 2000.

Suitably, the reforming step is carried out using a catalyst as described hereinbefore which comprises at least one of the metals Ga, Mo, W or Zn, preferably Ga. Suitably, such a catalyst comprises from 0.01 to 10% by weight, more preferably from 0.1 to 5% by weight, of the above metal.

Further, the reforming step can suitably be carried out using a catalyst which comprises a metal-

containing crystalline silicate having a Si/M molar ratio of 25 to 250, and wherein M is at least one of the metals Ga, Mo, W, or Zn, preferably Ga.

The metal-containing crystalline silicates may be prepared by methods known in the art, for example from aqueous solution containing the following compounds: one or more compounds of an alkali metal, one or more organic nitrogen compounds (RN) containing an organic cation or from which an organic cation is formed during the preparation of the silicate, one or more silicon compounds and one or more aluminium compounds. Preparation is effected by maintaining the mixture at an elevated temperature until the silicate has been formed and then separating the silicate crystals from the mother liquor and washing, drying and calcining the crystals.

Many synthetic routes exist to prepare these zeolitic catalysts. An extensive discussion can be found in " Hydrothermal Chemistry of Zeolites " by R.M. Barrer, Academic Press, New York, 1982.

The metal-containing silicates as prepared often contain alkali metal ions. By means of suitable exchange techniques these can be replaced by other cations, such as hydrogen ions or ammonium ions. The metal-containing crystalline silicates employed in the process according to the present invention preferably have an alkali metal content of less than 0.05% by weight. In the process according to the present invention the metal-containing crystalline silicates can be used as such or in combination with an inert binding material, such as kaolin or bentonite.

The metals can be incorporated by well-known techniques such as, for example, impregnation and ion-exchange. The metals are preferably introduced

after crystallization of the silicate, for instance by post-impregnation.

Suitably, in the hydrotreating step use is made of an alumina-containing catalyst, for instance a silica-alumina-containing catalyst having both desulphurization and denitrogenation activity. Preferably, use is made in the hydrotreating step of a metal-containing alumina catalyst, whereby the metal is at least one of the group VIB and/or Group VIII metals, preferably at least one of the metals Ni, Co or Mo.

The catalysts which can suitably be applied in the hydrotreating step comprise commercially available catalysts and can be prepared by methods known in the art.

In the process according to the present invention the reforming step can suitably be carried out at a temperature of 350 to 600°C, a pressure of from 1 to 40 bar and a space velocity of from 0.5 to 10 g/g/h, and the hydrotreating step can suitably be carried out at a temperature of 230 to 370°C, a hydrogen partial pressure of 2 to 30 bar and a space velocity of 0.5 to 15 g/g/h. Preferably, the reforming step is carried out at a temperature of 400 to 550 °C, a pressure of from 10 to 30 bar and a space velocity of from 0.5 to 5 g/g/h, and the hydrotreating step is carried out at a temperature of 250 to 350 °C, a hydrogen partial pressure of from 3 to 15 bar and a space velocity of from 2.0 to 10 g/g/h.

The process according to the present invention can be carried out using a series of reactors or in a stacked-bed configuration. Use of a series of reactors containing the respective catalysts is preferred. It will be understood that the catalyst applied in the reforming step can be subjected to a regeneration treatment, preferably a semi-continuous regeneration.

The desired gasoline boiling range product of reduced sulphur content and increased aromaticity may be recovered by any suitable means, usually by fractionation.

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

Example

a) Composition of catalysts A and B.

Reforming catalyst A comprises a commercially available ZSM-5 type crystalline zeolite having a SiO_2/Al_2O_3 molar ratio of 250 and containing 130 ppm Na. Catalyst A was ion exchanged in its H^+ form with gallium as follows:

80 g of zeolite were refluxed for 1 hour in a 0.05 M solution of gallium nitrate. The sample was washed with distilled water, dried (120°C, 16 h) and then calcined at 540°C for 2 h.

The resulting gallium-containing aluminosilicate contained 1 %wt of gallium.

Hydrotreating catalyst B comprises 84.1 %wt of amorphous alumina and 2.7 %wt of nickel and 13.2 %wt of molybdenum.

b) Catalysts A and B were employed during 25 hours in an experiment carried out in accordance with the present invention. Catalyst B was firstly subjected to a presulphiding treatment. As feedstock a catalytically cracked gasoline was used having the following properties:

Boiling range	: 85 - 210°C
Olefins in C_5^+ (%wt)	: 28.6
Saturates in C_5^+ (%wt)	: 24.9
Aromatics in C_5^+ (%wt)	: 46.5
Sulphur in C_5^+ (ppmw)	: 2420
RON-0 of C_5^+	: 94

The operation conditions under which the experiment was carried out and the results obtained are given in Table 1 as shown hereinafter.

Table 1

Catalyst	A	B
Conditions		
Temperature (°C)	499	285
Pressure (bar)	20	16
WHSV (g/g/h)	2	7.5
H_2 partial pressure	-	7
Products		
Sulphur in C_5^+ (ppmw)	100	
RON-0 of C_5^+	101	
C_5^+ yield (%wt)	84.8	
aromatics in C_5^+ (%wt)	71.0	

The claims defining the invention are as follows:

1. A process for upgrading a sulphur-containing feedstock comprising a hydrocarbon mixture substantially boiling in the gasoline range which process comprises subjecting the feedstock to a reforming step and subsequently to a hydrotreating step, and recovering therefrom a product substantially boiling in the gasoline range and having increased aromaticity and decreased sulphur content, wherein in the reforming step a catalyst is applied which comprises a metal(M)-containing crystalline silicate having an X-ray diffraction pattern containing the four strongest lines at interplanar spacings (d), expressed in Å, of 11.1 ± 0.2, 10.0 ± 0.2, 3.84 ± 0.07 and 3.72 ± 0.06, wherein M represents at least one of Al, Fe, Ga, W, Mo or Zn, and wherein the metal(M)-containing crystalline silicate comprises either a crystalline aluminosilicate having a SiO_2/Al_2O_3 molar ratio of at least 20 or an iron-containing crystalline (alumino)silicate having a SiO_2/Fe_2O_3 molar ratio of 25 to 1000, and in case alumina is present a SiO_2/Al_2O_3 molar ratio of 20 to 2000.

2. A process according to claim 1, wherein said hydrocarbon mixture has been derived from a cracking process.

3. A process according to claim 1, wherein said hydrocarbon mixture has been derived from a catalytic cracking process.

4. A process according to any one of claims 1 to 3, wherein the hydrocarbon mixture is a fraction substantially boiling in the range of 70 to 220°C.

5. A process according to claim 4 wherein said fraction boils in the range of 70 to 180°C.

6. A process according to any one of claims 1 to 5, wherein the feedstock consists essentially of the hydrocarbon mixture substantially boiling in the gasoline range.

7. A process according to any one of claims 1 to 6, wherein the feedstock comprises more than 50ppmw of sulphur.

8. A process according to any one of claims 1 to 7, wherein a sulphur-containing feedstock which comprises a hydrocarbon mixture substantially boiling in the range of 140 to 220°C is coprocessed with the product from the reforming step in the hydrotreating step.

9. A process according to any one of claims 1 to 8, wherein additional hydrogen is coprocessed with the product from the reforming step in the hydrotreating step.

10. A process according to any one of claims 1 to 9, wherein a hydrocarbon mixture substantially comprising C_{2-4} olefins and/or C_7 paraffins is coprocessed with the feedstock in the reforming step.

11. A process according to any one of claims 1 to 10, wherein in the reforming step a catalyst is applied which increases the aromatics content of the feedstock.

12. A process according to claim 11, wherein a catalyst is applied which effects aromatization of at least 50% of olefins and/or naphthenes initially present in the feedstock.

13. A process according to any one of claims 1 to 12, wherein in the reforming step a catalyst is applied which comprises from 0.01 to 10% by weight of at least one Ga, W, Mo or Zn.

14. A process according to any one of claims 1 to 12, wherein in the reforming step a catalyst is applied which comprises a metal-containing crystalline silicate having a Si/M molar ratio of 25 to 250, and wherein M is at least one of the metals Ga, Mo, W or Zn.

15. A process according to any one of claims 1 to 14, wherein the metal comprises Ga.

16. A process according to any one of claims 1 to 15, wherein in the hydrotreating step an alumina-containing catalyst is applied.

17. A process according to claim 16, wherein in the hydrotreating step a metal-containing catalyst is applied, whereby the metal is at least one of the Group VIB and/or Group VIII metals.

18. A process according to claim 17, wherein the metal is at least one of Ni, Mo or Co.

19. A process according to any one of claims 1 to 18, wherein the reforming step is carried out at a temperature of 350 to 600°C, a pressure of from 1 to 40 bar and a space velocity of from 0.5 to 10g/g/h, and wherein the hydrotreating step is carried out at a temperature of 230 to 370°C, a hydrogen partial pressure of 2 to 30 bar and a space velocity of from 0.5 to 15g/g/h.

20. A process for upgrading a sulphur-containing feedstock comprising a hydrocarbon mixture substantially boiling in the gasoline range substantially as hereinbefore described with reference to any one of the Examples.

21. Aromatic hydrocarbon-containing mixtures whenever prepared according to a process as described in any one of claims 1 to 20.

Dated 24 February, 1993
Shell Internationale Research Maatschappij B.V.

Patent Attorneys for the Applicant/Nominated Person
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