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(54) Titre : PROCEDE DE VALORISATION DE CHARGES HYDROCARBUREES ET APPAREIL CORRESPONDANT

(54) Title: PROCESS FOR UPGRADING A HYDROCARBONACEOUS FEEDSTOCK AND APPARATUS FOR USE  
THEREIN

(57) **Abrégé/Abstract:**

Process for upgrading a hydrocarbonaceous feedstock Which process comprises separating the feedstock in the presence of hydrogen at elevated temperature and a partial hydrogen pressure greater than 50 bar into a high boiling fraction and a low boiling fraction and subjecting at least part of the low boiling fraction substantially boiling in the gasoline range to a hydrotreating step under substantially the same conditions as prevailing in the separation step, and recovering from the hydrotreating step a product substantially boiling in the gasoline range and being of improved quality. The invention further relates to an apparatus for carrying out the present process comprising a vessel having inlet means for the hydrocarbonaceous feedstock and hydrogen, outlet means for the high boiling fraction in the bottom section of the vessel, outlet means for the low boiling fraction in the upper section of the vessel, and a catalyst bed for carrying out the hydrotreating step arranged in the upper section of the vessel.



A B S T R A C TPROCESS FOR UPGRADING A HYDROCARBONACEOUS  
FEEDSTOCK AND APPARATUS FOR USE THEREIN

Process for upgrading a hydrocarbonaceous feedstock which process comprises separating the feedstock in the presence of hydrogen at elevated temperature and a partial hydrogen pressure greater than 50 bar into a high boiling fraction and a low boiling fraction and subjecting at least part of the low boiling fraction substantially boiling in the gasoline range to a hydrotreating step under substantially the same conditions as prevailing in the separation step, and recovering from the hydrotreating step a product substantially boiling in the gasoline range and being of improved quality.

The invention further relates to an apparatus for carrying out the present process comprising a vessel having inlet means for the hydrocarbonaceous feedstock and hydrogen, outlet means for the high boiling fraction in the bottom section of the vessel, outlet means for the low boiling fraction in the upper section of the vessel, and a catalyst bed for carrying out the hydrotreating step arranged in the upper section of the vessel.

PROCESS FOR UPGRADING A HYDROCARBONACEOUS  
FEEDSTOCK AND APPARATUS FOR USE THEREIN

The present invention relates to a process for upgrading a hydrocarbonaceous feedstock and an apparatus to be used in such a process. In particular, the present invention relates to a process for upgrading a hydrocarbonaceous feedstock which has been derived from a hydrocracking process.

In view of today's increasing tendency in refineries to convert heavy feedstocks into light products having enhanced quality, various (hydro)processing product streams require further processing before they can satisfactorily meet the present day stringent requirements for high octane, low sulphur and low aromatics content.

Quality improvement of some of these hydrocarbonaceous products 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.

A process producing various hydrocarbonaceous products which may require further upgrading is hydrocracking.

Hydrocracking is a well-established process in which heavy hydrocarbons are contacted in the presence of hydrogen with a hydrocracking catalyst. The temperature and the pressure are relatively high, so that the heavy hydrocarbons are cracked to products with a lower boiling point. Although the process can be carried out in one stage, it has been shown to be advantageous to carry out the process in a plurality of stages. In a first stage the feedstock is subjected to denitrogenation, desulphurization and



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hydrocracking, and in a second stage most of the hydrocracking reactions occur.

Conventionally, a low boiling fraction substantially boiling in the gasoline range is obtained from the total hydrocracking product by fractionation following one or more separation steps. Subsequently, the low boiling fraction substantially boiling in the gasoline range and containing an unacceptable amount of sulphur-containing compounds is subjected to a separate hydrotreating step to remove these contaminants from this fraction before the fraction is subjected to a reforming step. The conditions under which the hydrotreating step is carried out differ considerably from those applied in the separation/fractionation steps.

Surprisingly, it has now been found that such a material can very attractively be upgraded if both the separation step and the hydrotreating step are carried out in the presence of hydrogen under substantially the same conditions.

Accordingly, the present invention relates to a process for upgrading a hydrocarbonaceous feedstock which process comprises separating the feedstock in the presence of hydrogen at elevated temperature and a partial hydrogen pressure greater than 50 bar into a high boiling fraction and a low boiling fraction and subjecting at least part of the low boiling fraction substantially boiling in the gasoline range to a hydrotreating step under substantially the same conditions as prevailing in the separation step, and recovering from the hydrotreating step a product substantially boiling in the gasoline range and being of improved quality.

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According to one aspect of the present invention there is provided a process for upgrading a hydrocarbonaceous feedstock which process comprises separating the feedstock in the presence of hydrogen at  
5 elevated temperature and a partial hydrogen pressure greater than 50 bar into a high boiling fraction and a low boiling fraction and subjecting at least part of the low boiling fraction substantially boiling in the gasoline range to a catalytic hydrotreating step under substantially the same  
10 conditions as prevailing in the separation step, and recovering from the hydrotreating step a product substantially boiling in the gasoline range and being of improved quality, wherein at least part of the high boiling fraction recovered is subsequently contacted with hydrogen  
15 under conditions causing substantial hydrogenation using a catalyst comprising one or more Group VIII noble metal(s) on a support.

In this way hydrocarbonaceous products of a high quality are obtained, whilst the separation and  
20 hydrotreating step are advantageously connected in such a way that an optimum heat integration can be obtained and the application of expensive reactor equipment can be reduced.



Suitably, the hydrocarbonaceous feedstock to be upgraded has been derived from a hydroconversion process, preferably from a hydrocracking process.

The separation step is suitably carried out at a temperature between 200 and 400 °C and a partial hydrogen pressure up to 250 bar. Preferably, the separation step is carried out at a temperature between 250 and 350 °C and a partial hydrogen pressure between 100 and 200 bar. Suitably, in the process according to the present invention space velocities can be applied between 1 and 20 kg/l/h, preferably between 2 and 10 kg/l/h.

Preferably, the process according to the present invention is carried out in such a way that the separating step and the hydrotreating step are integrated. Suitably, these steps are carried out in the same apparatus.

Although it is preferred that the hydrotreating step is directed to the removal of sulphur- and nitrogen-containing compounds by way of catalytic hydrotreatment, it should be noted that the hydrotreating step can also suitably be directed to, for instance, the removal of aromatics by means of catalytic hydrogenation.

In the event that the hydrotreating step is directed to the catalytic removal of sulphur- and nitrogen-containing compounds suitably 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 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, W or Mo. The catalysts which can suitably be applied to remove sulphur- and nitrogen-containing compounds comprise commercially available catalysts and can be prepared by methods known in the art.

In the event that the hydrotreating step is directed to the removal of aromatics suitably use is made of a catalyst bringing about substantial hydrogenation of the low boiling fraction

substantially boiling in the gasoline fraction. Suitable catalysts comprise those described hereinbefore.

In an attractive embodiment of the present invention the high boiling fraction is contacted in counter-current flow operation with additional hydrogen or a hydrogen-containing gas, preferably pure hydrogen, during the separation step. In this way a very attractive sharp separation can be established between the low boiling fraction substantially boiling in the gasoline range and the high boiling fraction. Moreover, also sulphur- and nitrogen-containing compounds such as  $H_2S$  and  $NH_3$  can advantageously be stripped from the high boiling fraction resulting in a high boiling fraction being of enhanced quality. In operation the hydrogen-containing gas can suitably be supplied to the separation vessel by means of inlet means arranged in the bottom section of the vessel. In order to facilitate the separation even further the bottom section of the separation vessel can be provided with contacting means, for instance contacting trays.

In a very attractive embodiment of the present invention the high boiling fraction is firstly contacted in counter-current flow operation with additional hydrogen or a hydrogen-containing gas during the separation step. Subsequently, at least part of the high boiling fraction recovered is contacted with hydrogen under conditions causing substantial hydrogenation using a catalyst comprising one or more Group VIII noble metal(s) on a support.

Suitable supports include alumina, silica-alumina and zeolitic materials such as zeolite Y. Preferably, the catalyst comprises a support which comprises a Y-type zeolite. More preferably, the support comprises a modified Y-type zeolite having a unit cell size between 24.20 and 24.40 Å, in particular between 24.22 and 24.35 Å, and a  $SiO_2/Al_2O_3$  molar ratio of between 10 and 150, in particular between 15 and 50 and preferably between 20 and 45. Suitably, use is made of a catalyst support obtained by dealuminating a Y-type zeolite. The Group VIII noble metals to be used in this specific embodiment of the present invention comprise ruthenium, rhodium, palladium, osmium, iridium and platinum. Very good results are



obtained with platinum and with combinations of platinum and palladium. The use of catalysts containing both platinum and palladium is preferred. The noble metals are suitably applied in amounts between 0.05 and 3 %w on support material. Preferably amounts are used in the range of 0.2 and 2 %w on support material. When two noble metals are applied the amount of the two metals normally ranges between 0.5 and 3 %w on support material. When platinum and palladium are used as the noble metals normally a platinum/palladium molar ratio of 0.25-0.75 is applied. The catalysts optionally contain a binder material such as alumina and silica, preferably alumina. The noble metal(s) catalysts to be applied in this way can be prepared by methods known in the art.

In this way substantially unsaturated moieties such as olefinic compounds and in particular aromatic compounds present in the high boiling fraction are converted into the corresponding saturated compounds resulting in a high boiling fraction of enhanced quality.

When the hydrocarbonaceous feedstock to be upgraded is derived from a hydrocracking process the high boiling fraction comprises a kerosene, a gas oil and a residual fraction. Suitably, at least part of the residual fraction is recycled to the hydrocracking stage. It is preferred to recycle the complete residual fraction to the hydrocracking stage. This has the advantage that the complete hydrocracker feedstock is converted to products with a lower boiling point.

When kerosenes are hydrogenated in this way the smoke points are improved considerably and when gas oils are processed in this way the cetane numbers are increased substantially. Moreover, the amount of polynuclear aromatic compounds present in the high boiling fraction can advantageously be reduced and thus fouling of the equipment applied can be prevented. Moreover, in this way also build-up of polynuclear aromatics in the recycle stream to the hydrocracking stage is attractively prevented. Further, it should be noted that such a mode of operation enables the application of an advantageously mild pressure in the hydrocracking stage.



The hydrogenation of the high boiling fraction is normally carried out at a temperature between 150 and 400 °C, preferably between 200 and 350 °C. The partial hydrogen pressure to be applied ranges suitably between 20 and 250 bar, preferably between 25 and 200 bar, and most preferably between 30 and 150 bar. Space velocities between 0.05 and 5 kg/l/h can be applied, preferably between 0.4 and 1.5 kg/l/h. Hydrogen/feedstock ratios (Nl/kg) between 200 and 2000 can suitably be applied, preferably between 400 and 1500. As hydrogen source use can be made of pure hydrogen or of hydrogen-containing mixtures for instance the gases produced in catalytic reforming processes.

The present invention further relates to an apparatus for carrying out the process according to the present invention which apparatus comprises a vessel having inlet means for the hydrocarbonaceous feedstock and hydrogen, outlet means for the high boiling fraction in the bottom section of the vessel, outlet means for the low boiling fraction in the upper section of the vessel, and a catalyst bed for carrying out the hydrotreating step arranged in the upper section of the vessel.

Preferably, the apparatus to be applied in the present process comprises inlet means arranged in the bottom section of the separator vessel for introducing hydrogen or hydrogen-containing gas which is to be contacted with the high boiling fraction during the separating step. Suitably, the bottom section of the apparatus is further provided with contacting means, for instance contacting trays, to improve the separating step even more.

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

#### Example

A hydrocarbonaceous feedstock derived from a hydrocracking process, of which the  $C_5^+$  fraction has the properties given in Table 1, is separated in the presence of hydrogen into a high boiling fraction and a low boiling fraction at a temperature of 300 °C and a pressure of 190 bar. During the separation a stream of hydrogen is contacted with the high boiling fraction in

counter-current flow operation to optimize the separation into the respective fractions. The low boiling fraction substantially boiling in the gasoline range so obtained is subsequently subjected to an integrated hydrotreating step in the presence of a catalyst A under substantially the same conditions as prevailing in the separation step. Catalyst A comprises a commercially available hydrotreating catalyst containing nickel (3% by weight), molybdenum (13% by weight) and phosphorus (3.2% by weight) on alumina. The hydrotreated low boiling fraction is subsequently separated into a recycle gas fraction and a fraction substantially boiling in the gasoline range at a temperature of 70 °C and a pressure of 190 bar. The fraction substantially boiling in the gasoline range is then further separated into a gaseous fraction and a liquid fraction substantially boiling in the gasoline range at a temperature of 70 °C and a pressure of 12 bar. The liquid fraction so obtained is subsequently passed to a main fractionator.

The high boiling fraction recovered is subsequently subjected to a hydrogenation step in the presence of hydrogen and a catalyst B at a temperature of 300 °C and a pressure of 190 bar. Catalyst B comprises a zeolite Y having a unit cell size of 24.24 Å and a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 40 and containing 0.3% by weight of platinum and 0.5% by weight of palladium, based on zeolite. The hydrogenated high boiling fraction is then separated into a gaseous fraction and a liquid fraction at a temperature of 300 °C and a pressure of 12 bar. The liquid fraction is subsequently passed to the main fractionator.

The product properties of the fractions obtained from the main fractionator are shown in Table 2.

Table 1

d 15/4	:	0.79
C, %w	:	86.13
H, %w	:	13.86
S, ppm	:	130
N, ppm	:	4
I.B.P. (°C)	:	35
10% w rec.	:	98
20% " "	:	140
30% " "	:	178
40% " "	:	215
50% " "	:	266
60% " "	:	326
70% " "	:	379
80% " "	:	419
90% " "	:	468
F.B.P.	:	596
<u>arom., (mmol/100 g)</u>		
mono	:	40.5
di	:	1.15
tri	:	0.43



Table 2

## PRODUCT PROPERTIES

C<sub>5</sub>-82 °C

RON : 78  
S, ppm : < 1

82-155 °C

P/N/A : 47/47/16  
S, ppm : < 1

155-381 °C

cetane index : 61

381 °C<sup>+</sup>

coronene, %w : 0.01  
mono arom., %w: 2  
C<sub>7</sub><sup>+</sup> arom., %w : < 0.1

It will be clear from the above that the present invention constitutes an attractive process for upgrading a hydrocracker effluent stream.

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CLAIMS:

1.           A process for upgrading a hydrocarbonaceous feedstock which process comprises separating the feedstock in the presence of hydrogen at elevated temperature and a  
5 partial hydrogen pressure greater than 50 bar into a high boiling fraction and a low boiling fraction and subjecting at least part of the low boiling fraction substantially boiling in the gasoline range to a catalytic hydrotreating step under substantially the same conditions as prevailing  
10 in the separation step, and recovering from the hydrotreating step a product substantially boiling in the gasoline range and being of improved quality, wherein at least part of the high boiling fraction recovered is subsequently contacted with hydrogen under conditions  
15 causing substantial hydrogenation using a catalyst comprising one or more Group VIII noble metal(s) on a support.
2.           The process according to claim 1, wherein use is made of a hydrocarbonaceous feedstock which has been derived  
20 from a hydroconversion process.
3.           The process according to claim 2, wherein the hydroconversion process is a hydrocracking process.
4.           The process according to any one of claims 1 to 3, wherein the separation is carried out at a temperature  
25 between 200 and 400°C and a partial hydrogen pressure up to 250 bar.
5.           The process according to claim 4, wherein the separation is carried out at a temperature between 250 and 350°C and a partial hydrogen pressure between 100 and 200  
30 bar.

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6. The process according to any one of claims 1 to 5, wherein in the hydrotreating step, an alumina-containing catalyst is applied.

7. The process according to claim 6, wherein in the  
5 hydrotreating step a metal-containing catalyst is applied, wherein the metal-containing catalyst comprises at least one metal of the Group VIb and Group VIII metals.

8. The process according to claim 7, wherein the at least one metal is selected from Ni, Mo, W and Co.

10 9. The process according to any one of claims 1 to 8, wherein the separation step and the hydrotreating step are integrated.

10. The process according to any one of claims 1 to 9, wherein during the separation the high boiling fraction is  
15 contacted in counter-current flow operation with additional hydrogen or a hydrogen-containing gas.

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