

Description

The present invention relates to a process for the conversion of a hydrocarbonaceous feedstock.

US 4,514,285 discloses as illustration of a method for ballistic separation of conversion catalyst from hydrocarbonaceous products, conditions for conversion of a gas oil feed in a downflow reactor over an unspecified high activity, high alumina zeolite type cracking catalyst but makes no reference to degree of conversion or nature of products thereby obtained.

US 4,171,257 describes a process for upgrading a hydrocarbonaceous feedstock by contacting the feedstock with a ZSM-5 crystalline aluminosilicate catalyst at a pressure below 14 bar, a temperature of 260 to 427 °C and a space velocity of 0.1 to 15 l/h. The feedstock, exemplified as gas oil having a boiling point range of 230 to 437 °C, must contain less than 5 ppmw of nitrogen-containing compounds, calculated as nitrogen. The upgraded product includes olefinic hydrocarbons, such as propene and butenes.

The production of olefins is desirable as their reactivity renders them suitable for conversion to further products, in contrast to the low value lower paraffins. However, the above described process has the drawback that the initial feedstock must have been severely denitrified in order to avoid rapid catalyst deactivation.

It is also known from EP-B-131986 and US 3,758,403 to employ mixtures of aluminosilicate catalysts comprising a large pore diameter crystalline aluminium silicate and a narrow pore silicate such as ZSM-5 in the production of gasoline. C₃ and C₄ olefin byproduct obtained can be alkylated to increase the overall gasoline yield. The space velocities and other conditions employed in the examples given indicate the use of fixed bed reactors with comparatively high catalyst contact times.

It has surprisingly been found that a comparatively high yield of olefins can be obtained, under less stringent conditions as regards nitrogen content, using certain zeolitic catalysts, at high temperature with a short contact time of the feedstock with the catalyst. Furthermore, it has been surprisingly found that the conversion is suitable for comparatively heavy straight-run hydrocarbon feedstocks and a product rich in lower olefins can be obtained therefrom.

Accordingly, the present invention provides a process for the conversion of a straight-run hydrocarbonaceous feedstock containing hydrocarbons having such a boiling range that an amount thereof boils at a temperature of at least 330 °C, which process comprises contacting the feedstock with a moving bed of a zeolitic catalyst comprising a zeolite with a pore diameter of 0.3 to 0.7 nm, preferably 0.5 to 0.7 nm, at a temperature of greater than 480 °C during less than 10 seconds.

The feedstock is contacted with the zeolitic catalyst for less than 10 seconds. Suitably, the minimum contact time is 0.1 second. Very good results are obtainable with a process in which the feedstock is contacted with the zeolitic catalyst during 0.2 to 6 seconds.

The temperature during the reaction is relatively high. It is this combination of high temperature and short contact time which allows a high conversion to olefins. A preferred temperature range is 500 to 900 °C, more preferably 550 to 850 °C.

The zeolitic catalyst may comprise one or more zeolites with a pore diameter of from 0.3 to 0.7 nm. The catalyst suitably further comprises a refractory oxide that serves as binder material. Suitable refractory oxides include alumina, silica, silica-alumina, magnesia, titania, zirconia and mixtures thereof. Alumina is especially preferred. The weight ratio of refractory oxide and zeolite suitably ranges from 10:90 to 90:10, preferably from 50:50 to 85:15. The catalyst may comprise up to about 40% by weight of further zeolites with a pore diameter above 0.7 nm. Suitable examples of such zeolites include the faujasite-type zeolites, zeolite beta, zeolite omega and in particular zeolite X and Y. The zeolitic catalyst preferably comprises as zeolite substantially only zeolites with a pore diameter of from 0.3 to 0.7 nm.

The term zeolite in this specification is not to be regarded as comprising only crystalline aluminium silicates. The term also includes crystalline silica (silicalite), silicoaluminophosphates (SAPO), chromosilicates, gallium silicates, iron silicates, aluminium phosphates (ALPO), titanium aluminosilicates (TASO), boron silicates, titanium aluminophosphates (TAPO) and iron aluminosilicates.

Examples of zeolites that may be used in the process of the invention and that have a pore diameter of 0.3 to 0.7 nm, include SAPO-4 and SAPO-11, which are described in US-A-4,440,871, ALPO-11, described in US-A-4,310,440, TAPO-11, described in US-A-4,500,651, TASO-45, described in EP-A-229,295, boron silicates, described in e.g. US-A-4,254,297, aluminium silicates like erionite, ferrierite, theta and the ZSM-type zeolites such as ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-23, and ZSM-38. Preferably the zeolite is selected from the group consisting of crystalline metal silicates having a ZSM-5 structure, ferrierite, erionite and mixtures thereof. Suitable examples of crystalline metal silicates with ZSM-5 structure are aluminium, gallium, iron, scandium, rhodium and/or scandium silicates as described in e.g. GB-B-2,110,559.

During the preparation of the zeolites usually a significant amount of alkali metal oxide is present in the prepared zeolite. Preferably the amount of alkali metal is removed by methods known in the art, such as ion exchange, optionally followed by calcination, to yield the zeolite in its hydrogen form. Preferably the zeolite used in the present process is substantially in its hydrogen form.

5 The pressure in the present process can be varied within wide ranges. It is, however, preferred that the pressure is such that at the prevailing temperature the feedstock is substantially in its gaseous phase or brought thereinto by contact with the catalyst. Then it is easier to achieve the short contact times envisaged. Hence, the pressure is preferably relatively low. This can be advantageous since no expensive compressors and high-pressure vessels and other equipment are necessary. A suitable pressure range is
10 from 1 to 10 bar. Subatmospheric pressures are possible, but not preferred. It can be economically advantageous to operate at atmospheric pressure. Other gaseous materials may be present during the conversion such as steam and/or nitrogen.

The present process is carried out in a moving bed. The bed of catalyst may move upwards or downwards. When the bed moves upwards a process somewhat similar to a fluidized catalytic cracking
15 process is obtained.

During the process some coke forms on the catalyst. Therefore, it is advantageous to regenerate the catalyst. Preferably the catalyst is regenerated by subjecting it, after having been contacted with the feedstock, to a treatment with an oxidizing gas, such as air. A continuous regeneration, similar to the regeneration carried out in a fluidized catalytic cracking process, is especially preferred.

20 If the coke formation does not occur at too high a rate, it would be possible to arrange for a process in which the residence time of the catalyst particles in a reaction zone is longer than the residence time of the feedstock in the reaction zone. Of course the contact time between feedstock and catalyst should be less than 10 seconds. The contact time generally corresponds with the residence time of the feedstock. Suitably the residence time of the catalyst is from 1 to 20 times the residence time of the feedstock.

25 The catalyst/feedstock weight ratio may vary widely, for example up to 150 kg of catalyst per kg of feedstock or even more. Preferably, the catalyst/feedstock weight ratio is from 20 to 100:1.

The feedstock which is to be converted in the present process comprises hydrocarbons which have a boiling point of at least 330 °C. By means of this feature relatively light petroleum fractions, such as naphtha and kerosine, have been excluded. Preferably the feedstock has such a boiling range that at least
30 50% by weight thereof boils at a temperature of 330 °C. Suitable feedstocks include vacuum distillates, long residues, deasphalted residual oils, paraffinic feedstocks and atmospheric distillates which fulfil the requirement as to boiling range, such as gas oils. Preferably, the feedstock is a gas oil or vacuum gas oil. When these feedstocks are subjected to the present process a gas oil with a very low pour point and an olefin-rich gaseous fraction are obtained.

35 One of the advantages of the present invention over the process according to US 4,171,257 resides in the fact that a feedstock with a nitrogen content greater than 5 ppmw may be used with substantially no effect on the catalyst activity. Suitable feedstocks may have a nitrogen content of more than 10 ppmw, calculated as nitrogen. The feedstock may even have a nitrogen content of 1000 ppmw or more, calculated as nitrogen.

40 The invention will now be further described with reference to the following example.

EXAMPLE

The feedstock in this example was a gas oil having the following properties:

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IBP, °C	213
20 %wt	331
50 %wt	379
90 %wt	421
FBP	448
pour point, °C	19.5
flash point, °C	147
carbon, %wt	86.6
hydrogen, %wt	13.1
sulphur, %wt	0.3
nitrogen, ppmw	330

The gas oil was treated in a down flow reactor in which co-currently a flow of feedstock and catalyst particles, having an average particle size of 74 micrometers, was passed downwards. The catalyst used comprised ZSM-5, in hydrogen form, in an alumina matrix (weight ratio ZSM-5/alumina was 1:3). All experiments were carried out at atmospheric pressure. Further process conditions and the results of the experiments are indicated in the table below.

TABLE 1**Process conditions:**

Reactor temperature, °C	576
Catalyst/oil ratio, g/g	124
Contact time, s	1.8

Product, %w on feed

C ₁	1.9
C ₂	1.4
C ₂ =	11.3
C ₃	3.8
C ₃ =	25.4
C ₄	3.3
C ₄ =	12.2
C ₅ -221 °C	15.3
221-370 °C	12.59
370+ °C	1.1
Coke	11.1

From the above results it will be seen that a high proportion of the gaseous products was olefinically unsaturated.

Claims

1. A process for the conversion of a straight-run hydrocarbonaceous feedstock with a nitrogen content of greater than 5 ppmw containing hydrocarbons having such a boiling range that an amount thereof boils at a temperature of at least 330 °C, which process comprises contacting the feedstock with a moving bed of a zeolitic catalyst comprising a zeolite with a pore diameter of 0.3 to 0.7 nm at a temperature of greater than 480 °C during less than 10 seconds.
2. A process according to claim 1 wherein the feedstock is contacted with the zeolitic catalyst during 0.2 to 6 seconds.
3. A process according to claim 1 or 2 wherein the temperature is 550 to 850 °C.
4. A process according to any one of the preceding claims wherein the zeolite has a pore diameter of 0.5 to 0.7 nm.
5. A process according to any one of the preceding claims wherein the zeolite is selected from crystalline metal silicates having a ZSM-5 structure, ferrierite, erionite and mixtures thereof.
6. A process according to any one of the preceding claims in which the zeolite is substantially in its hydrogen form.



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6. A process according to any one of the preceding claims in which the zeolite is substantially in its hydrogen form.



7. A process according to any one of the preceding claims wherein the pressure is from 1 to 10 bar.
8. A process according to any one of the preceding claims in which the catalyst/feedstock weight ratio is from 20 to 100:1.
- 5 9. A process according to any one of the preceding claims wherein the feedstock is a gas oil.

Patentansprüche

- 10 1. Ein Verfahren zur Umwandlung eines durch Destillation gewonnenen kohlenwasserstoffhaltigen Ausgangsmaterials mit einem Stickstoffgehalt von mehr als 5 Tpm (Gew), welcher Kohlenwasserstoffe mit einem solchen Siedebereich aufweist, daß eine Anteilsmenge davon bei einer Temperatur von wenigstens 330 °C siedet, welches Verfahren das in-Berührung-bringen des Ausgangsmaterials mit einem Fließbett aus einem Zeolith-Katalysator, umfassend einen Zeolith mit einem Porendurchmesser von 0,3 bis 0,7 nm, bei einer Temperatur von mehr als 480 °C während weniger als 10 Sekunden, umfaßt.
- 15 2. Ein Verfahren nach Anspruch 1, in dem das Ausgangsmaterial mit dem Zeolith-Katalysator während 0,2 bis 6 Sekunden in Berührung gebracht wird.
- 20 3. Ein Verfahren nach Anspruch 1 oder 2, in dem die Temperatur 550 bis 850 °C beträgt.
4. Ein Verfahren nach irgendeinem der vorhergehenden Ansprüche, in dem der Zeolith einen Porendurchmesser von 0,5 bis 0,7 nm hat.
- 25 5. Ein Verfahren nach irgendeinem der vorhergehenden Ansprüche, in dem der Zeolith aus kristallinen Metallsilikaten mit einer ZSM-5-Struktur, Ferrierit, Erionit und deren Gemischen ausgewählt ist.
6. Ein Verfahren nach irgendeinem der vorhergehenden Ansprüche, in dem der Zeolith im wesentlichen in seiner Wasserstoff-Form vorhanden ist.
- 30 7. Ein Verfahren nach irgendeinem der vorhergehenden Ansprüche, in dem der Druck von 1 bis 10 bar reicht.
8. Ein Verfahren nach irgendeinem der vorhergehenden Ansprüche, in dem das Gewichtsverhältnis Katalysator/Ausgangsmaterial von 20 bis 100:1 reicht.
- 35 9. Ein Verfahren nach irgendeinem der vorhergehenden Ansprüche, in dem die Zusp eisung ein Gasöl ist.

Revendications

- 40 1. Un procédé pour la conversion d'une charge brute hydrocarbonée de première distillation présentant une teneur en azote supérieure à 5ppm en poids, renfermant des hydrocarbures présentant une gamme d'ébullition telle qu'une quantité de celle-ci boue à une température d'au moins 330 °C, ce procédé comportant la mise en contact de la charge brute avec un lit mobile d'un catalyseur zéolitique
- 45 comportant une zéolite présentant un diamètre des pores de 0,3 à 0,7 nm, à une température supérieure à 480 °C pendant moins de 10 secondes.
2. Un procédé selon la revendication 1, dans lequel la charge brute est mise en contact avec le catalyseur zéolitique pendant de 0,2 à 6 secondes.
- 50 3. Un procédé selon la revendication 1 ou 2, dans lequel la température est de. de 550 à 850 °C
4. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la zéolite présente un diamètre des pores de 0,5 à 0,7 nm.
- 55 5. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la zéolite est choisie parmi les silicates cristallins de métaux ayant une structure ZSM-5, de la ferrierite, de l'érianite et des mélanges de ceux-ci.



6. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la zéolite est pratiquement sous sa forme hydrogène.
7. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la pression est de 1 à 10 bars.
8. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le rapport pondéral du catalyseur/charge brute est de 20 à 100:1.
9. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la charge brute est un gazole.

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