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(54) Process for preparing a diesel fuel fraction by oligomerisation

Verfahren zur Herstellung einer Dieselfraktion durch Oligomerisierung

Procédé pour préparer une coupe diesel par oligomerisation

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Description

The present invention concerns a process in accordance with the preamble of claim 1 for refining oil.

According to a process of the present kind, a charge containing in particular light olefins is oligomerized in the presence of a zeolite catalyst in order to prepare a diesel fuel product.

The catalyst ZSM-5 is widely used in the oil industry. It is employed, for instance, as an additive or promoter for cracking catalysts (FCC), in the preparation of synthetic gasoline (MTG), for converting propane and butane to aromatic compounds (Cyclar) and for selective hydrocracking of n-paraffines (M-forming and Dewaxing). It is further known that zeolites and particularly the ZSM-5 catalyze alkylation of aromatic hydrocarbons and oligomerization of olefins. By the last-mentioned process it is possible to prepare mixtures containing abundant C₁₁₊ hydrocarbons from light olefins, said mixtures yielding products of the diesel fuel type upon hydrogenation.

The benefits of the ZSM-5 zeolite as a catalyst in oil refining primarily stem from its form selectivity and its lower rate of coke formation in comparison to other zeolites.

The lattice structure of zeolites is formed by silicon and aluminium cations tetrahedrally joined together by oxygen bridges. Since the charge of silicon in a zeolite is +4 whereas the aluminium is three-coordinate, a third cation is needed for balancing the lower positive charge of aluminium in comparison to silicon. The balancing cation may, for instance, be a sodium, potassium or hydrogen ion. Conventionally the ZSM-5 comprises a sodium cation as a balancing ion at the ion exchange site. Since the ZSM-5 zeolite in this form is not catalytically active, the sodium ion has to be at least partially exchanged for a hydrogen ion, whereby acidic sites are formed on the zeolite, which catalyze some of the typical oil refining reactions.

Of the many patents which deal with the preparation of conventional ZSM-5 zeolites reference may be made to, in particular, the U.S. Patent Specification No. 3,702,886.

It is known in the art that, in addition to the alkaline metal cations mentioned above, other basic cations, such as Ca, Cs, Sr and Ba, may be incorporated into the zeolites by ion exchange. By means of the ion exchange it is possible to improve the catalytic properties of the zeolite. Thus, it has been discovered that the calcium ion improves the stability of the zeolite catalyst in connection with conversion of methanol to gasoline. U. S. Patent Specification No. 4,675,460 teaches the use of a Ca-modified ZSM-5 zeolite catalyst in a process wherein light olefins first are oligomerized in the presence of a ZSM catalyst modified with Ca (or by another basic cation) for preparing products of the gasoline class, which then are oligomerized by means of a Friedel Crafts-type catalyst to provide gas oils.

The present invention is based on the surprising observation that by using a Ca modified ZSM-5 zeolite as a oligomerization catalyst for light olefins, a product mixture is obtained whose cetane number after hydrogenation is higher than that of a product mixture prepared in the presence of an unmodified ZSM-5 zeolite.

According to the invention, there is provided a process for preparing a diesel fuel fraction comprising the steps of

- preoligomerizing a charge containing light C₂ - C₆ olefins in the presence of a Ca modified ZSM-5 zeolite catalyst containing a minimum of 0.01 %wt. of Ca, in order to produce a product stream which contains 10 to 95 %wt C₅₊ olefins,
- oligomerizing the preoligomerized charge in the presence of a Ca modified ZSM-5 zeolite catalyst containing a minimum of 0.01 %wt of Ca, in order to prepare a product composition which at least partially consists of C₈₊ hydrocarbons, and
- hydrogenating the product composition thus obtained to prepare a diesel fuel fraction with a high cetane number that boils in the range from 200 to 320°C.

Considerable benefits are obtained by means of the invention. Thus, by using a Ca modified ZSM-5 zeolite it is possible substantially to raise the cetane number of the hydrogenated diesel product obtained from oligomerization of light olefins. As the working examples below will show, the engine cetane number of a hydrogenated diesel product prepared by using an unmodified catalyst is in the range from 45 to 47, whereas the use of a Ca modified catalyst raises the cetane number to above 50. This makes it possible substantially to decrease or even entirely to eliminate the need for the additives conventionally used for increasing the cetane number.

In particular, it should be noticed that the improvement of the diesel fuel quality cannot be attributed to an increase of the average molecular size. The experiments below were carried out in such a way that the average carbon number of the product obtained by a Ca modified zeolite catalyst was lower or at the most as high as that of the reference product obtained by an unmodified catalyst.

In the following, the invention will be examined by means of a detailed description and some working examples.

A. Catalyst preparation

The base zeolite of the Ca modified catalyst used in the present invention may be prepared as described in, for instance, the U.S. Patent Specification No. 3,702,886. It is required that, for the oligomerization of hydrocarbons, the size of the pores of the base zeolite are optimal as regards the form selectivity of the zeolite.

Upon distillation the hydrocarbons obtained will yield high quality diesel fuels or isoparaffinic solvents, for instance. The ratio of Si to Al of the base zeolite and at the same time also of the Ca modified zeolite is preferably less than 400, in particular it is in the range from about 30 to 200.

The Ca ion exchange is carried out by using a zeolite, which is in H⁺ form. It is not decisive whether the zeolite has been converted into the H⁺ form already during the synthesis or by ion exchange after the synthesis. There might be small amounts, preferably less than 1000 ppm, of Na present in the zeolite.

The Ca ion exchange may be performed in liquid or in solid phase. Typically it is carried out by using aqueous calcium salts. The technology used is widely known. The salts may be selected from the group comprising chlorides, nitrates, sulfates and acetates. According to a preferred embodiment of the present invention the Ca ion is exchanged to the zeolite from a calcium acetate solution. The amount of calcium in the solution in relation to the zeolite depends to a large extent on the zeolite used and is typically in the range from 1 to 10 000 $\mu\text{mol Ca}^{2+}/\text{g zeolite}$, preferably 5 to 2000 $\mu\text{mol Ca}^{2+}/\text{g zeolite}$. The molarity of the calcium acetate solution is generally in the range from 0.005 to 1 M, preferably 0.05 to 0.5 M.

The ion exchange is carried out under stirring at a temperature in the range from 25 to 100 °C, preferably at 40 to 90 °C. The duration of the ion exchange is 0.1 to 4 h, preferably 0.5 to 2 h. The ion exchange zeolite is washed with hot water. The sample is dried at 100 to 120 °C over night. Calcination is carried out at 500 °C for 3 h. Calcination may be performed in air, vacuum or in an inert gas atmosphere.

After drying and calcination the amount of ion exchanged or impregnated calcium is 0.01 to 1.0 % wt, preferably 0.05 to 0.5 % wt. Too high amounts of calcium may impair the activity of the catalysts. However, if the concentration of calcium is within the ranges indicated above, calcium does not lessen the zeolite activity. On the contrary, in some cases calcium may even improve said activity.

When the zeolite has been ion exchanged by Ca and then calcined, it may be used as the active part of the catalyst. Because the catalyst generally is required to have certain physical, thermal and mechanical properties, the zeolite is mixed with a carrier which is inert as far as the reaction is concerned. The carrier may also, on some occasions, have catalytical properties. Typically the carrier is selected from the group comprising clays, silicates, aluminas and other metal oxides. These may be naturally occurring or synthetic. The carrier may also comprise a mixture of several metal oxides. Different organic and inorganic adjuvants and binders, such as methyl cellulose, may be employed for the preparation of the catalyst. The particle size of the catalyst depends on the type and diameter of the reactor. Thus, in the case of micro reactors, catalysts with particle sizes in the range from 0.149 to 0.350 mm were used in

the examples. Test runs were also carried out in larger reactors, the catalyst particle sizes being in the ranges from 0.35 to 1.0 mm or from 1.0 to 2.0 mm. The catalyst amounts charged into the micro reactors typically varied between 2 and 20 g and those used in the larger reactors between 50 and 200 g.

B. Oligomerization

In the present invention a Ca modified ZSM-5 zeolite is used as a catalyst for oligomerization of light C₂ - C₆ olefines, preferably of n-butene, to provide C₅ - C₂₂ hydrocarbons. The products of the reaction are typically comprised of mixtures of branched olefines. There are no aromatic hydrocarbons present in the products or, possibly, their concentration is less than 0.2 % wt. By distillation gasoline, kerosine and diesel fractions can be separated from the oligomerization product. For the purposes of the present invention, the term "diesel fraction" designates a fraction boiling in the range from 200 ° to 320 °C. It should be pointed out that several different solvent fractions containing branched paraffines may further be separated from the oligomerization product by distillation.

Oligomerization was carried out at a temperature in the range from 160 ° to 350 °C, preferably in the range from 200 ° to 310 °C and at a pressure in the range from 1 to 150 bar, preferably from 10 to 80 bar. It has been found out that an increase of the pressure promotes the reaction. However, since high pressures place severe requirements on the reactor design, it is not preferred to use pressures in excess of 150 bar. The conversion rate can be raised by increasing the temperature. Too high temperature may lead to too much cracking and aromatization reactions instead of oligomerization. The flow rates depend on the oligomerization reactor. Typically the weight hourly space velocity (WHSV) is in the range from 0.5 to 10, preferably from about 1 to 5 in a conventional tubular reactor. The flow rates and the temperature may also be changed during the reaction to provide an even degree of conversion.

Ca modification of the ZSM-5 catalyst will increase the cetane number of the hydrogenated diesel fraction in comparison to a corresponding product prepared by using unmodified catalyst by at least 2 units, generally from about 45 to about 50. The cetane number mentioned in the examples below have been determined as engine cetane numbers.

In connection with the present invention it has been discovered that products of diesel fuel type with a high cetane number may be prepared at high yields by using Ca modified zeolite catalyst in a process wherein a charge mainly comprising light olefins is contacted at least twice with said zeolite. By way of an example, the process according to the invention is carried out by first preoligomerizing olefine feed in the presence of a Ca modified zeolite in order to increase the proportion of the C₈₊ fraction, the actual oligomerization being carried

out subsequently. Alternatively the oligomerization product may be fed a second time through the same catalyst bed to increase the yield of the diesel product. In this respect, the invention differs from the prior art represented by the U.S. Patent Specification No. 4,675,460 which requires that the product obtained from a first oligomerization step be alkylated in the presence of a Friedel-Crafts-catalyst to obtain products of diesel fuel type.

According to one preferred embodiment, the process according to the invention is carried out in a plurality of successive reactors, which all contain the same kind of Ca modified zeolite catalyst.

By means of process embodiments comprising circulation of the products or employment of several successive oligomerization reactors, the first oligomerization step of the C₄ fraction will produce a product stream which contains 10 to 90 % wt, preferably 40 to 80 % wt C₅ + olefins. In this case, the product stream will contain at least some, generally about 5 to 50 % wt C₈₊-components and also C₁₁₊ fractions will be present (in amounts ranging from about 5 to 25 %). Thus, the last-mentioned components will be formed already during the first oligomerization stage, and their relative amounts will increase when the mixture is contacted again with the catalyst.

The product mixture of oligomerization is hydrogenated in a manner known *per se*, for instance, by hydrogen in the presence of a nickel catalyst to form a diesel fuel product.

It should also be noticed that even if the test result presented below have been obtained in laboratory reactors charged with almost 100 % olefins, the process will work also on industrial scale with charges whose olefin content lies in the range from 20 to 100 %, usually from about 30 to 95 %.

The paraffines, if any, contained in the feed stream do not to any large extent impair the oligomerization reaction.

The product prepared by the invention may be used as such as a diesel fuel or it may be mixed with conventional straight-run distillation fractions.

Next, the invention will be examined in more detail by means of working examples.

Example 1

Preparation of a Ca modified zeolite catalyst

A ZSM-5 zeolite was prepared according to the method described in the U.S. Patent Specification No. 3,702,886. Na-ZSM-5 was ion exchanged three times with a NH₄NO₃ (3 M) solution while stirring. 15 g of the ammonium nitrate solution were used for each g of the zeolite. The duration of one ion exchange step was 1.5 h. The temperature of the ion exchange solution was 80 °C. After the ion exchanges the zeolite was washed with 100 ml hot water/1 g zeolite. The ion exchanged zeolite

was dried at 110 °C over night, and subsequently calcined at a temperature of 540 °C for 3 hours.

After the above-described ion exchanges with ammonium nitrate the zeolite was subjected to Ca ion exchange. An ion exchange solution was prepared by mixing 100 ml of a calcium acetate solution (1 M) with 900 ml of water. 50 g of zeolite were mixed with the solution. During the ion exchange the solution was continuously stirred. The temperature of the solution was 80 °C and the time of the ion exchange 1 hour. After the ion exchange the zeolite was washed with 100 g hot water for each gram of zeolite. Subsequently the zeolite was dried at 110 °C. Calcination was carried out at 500 °C for 3 hours. After the ion exchange the calcium content of the zeolite was 0.24 % wt.

The zeolite was admixed with 35 % wt of SiO₂ carrier (Silica gel, Ludox AS-40). After the addition of the carrier the catalyst was dried and calcined at 540 °C for 3 h. The catalyst was screened to a particle size of 1.0 to 2.0 mm.

Example 2

Preparation of a Ca modified zeolite catalyst

The preparation of the zeolite and the ion exchange with the NH₄NO₃ solution were carried out as described in example 1. The Ca ion exchange solution was prepared by mixing 25 ml of a calcium acetate solution (1 M) with 975 ml of water. 50 g of zeolite were admixed with the solution. The ion exchange was carried out as described in example 1. The Ca concentration of the zeolite was after the ion exchange 0.092 % wt. The carrier was added in the same way as in example 1.

Example 3 (comparative)

The use of an unmodified zeolite catalyst for oligomerization; the properties of the diesel fuel fraction

200 g of catalyst was charged into a tubular steel reactor whose diameter was 30 mm. The catalyst particle size was in the range from 1.0 to 2.0. First 1-butene was fed through the catalyst bed. Then, in order to increase the yield of diesel fractions, the product obtained was fed a second time through the same catalyst. The composition of the liquid feed was C₄ = 42.2 %, C₈ = 42.4 %, C₁₁₊ = 11.3 %, C₅+C₆+C₇+C₉+C₁₀ = 4.1 %

Test conditions	
Reactor temperature (°C)	240 - 280
Pressure (bar)	50
WHSV (h ⁻¹)	1
Catalyst	unmodified ZSM-5

The product was collected in a cooled vessel. The product was distilled with the following cut points:

Distillation fraction:	
IBP - 30 °C	total gases
30 - 180 °C	gasoline
180 - 200 °C	kerosine
200 - 285 °C	diesel
285 - FBP	bottoms

The yield of the diesel fraction was 23.1 %. The diesel fraction was hydrogenated before analyzing its product properties. The engine cetane number of the diesel fraction (IBP 200 °C, FBP 285 °C) was **45**. The average carbon number was 13.25. The remaining data of the product analysis were as follows:

Product analysis	
Density (15 °C, kg/m ³)	778.2
Bromine number	0.3
Viscosity (mm ² /s, 20 °C)	2.08
Cloud point (°C)	<-50
Pour point (°C)	<-50
Filterability (°C)	<-50

Example 4 (comparative)

Properties of a diesel fraction distilled with different cut points

The product obtained from the tubular reactor of example 3 was distilled with different cut points.

The product was collected in a cooled vessel. The product was distilled with the following cut points.

Distillation fractions:	
IBP - 30 °C	total gases
30 - 180 °C	gasoline
180 - 200 °C	kerosine
200 - 315 °C	diesel
315 - FBP	bottoms

The yield of the diesel fraction was 23.1 %. The diesel fraction was hydrogenated before analysing is for its product properties. The engine cetane number of the diesel fraction (IBP 200 °C, FBP 315 °C) was **46**. The average carbon number was 13.45. The other data of the product analysis:

Product analysis	
Density (15 °C, kg/m ³)	798.8
Bromine number	0.4
Viscosity (mm ² /s, 20 °C)	2.60

(continued)

Product analysis	
Cloud point (°C)	<-50
Pour point (°C)	<-50
Filterability (°C)	<-50

Example 5

The use of a Ca modified zeolite in oligomerization; the properties of the diesel fuel fraction

200 g of the catalyst were charged into a tubular steel reactor whose diameter was 30 mm. The catalyst particle sizes were in the range from 1.0 to 2.0 mm. First, 1-butene was fed through the catalyst bed. Thereafter, in order to increase the diesel yield, the product obtained was fed once more through the same catalyst bed. The composition of the liquid feed was C₄ = 43.9 %, C₈ = 40.6 %, C₁₁₊ = 11.2 %, C₅+C₆+C₇+C₉+C₁₀ = 4.3 %

Test conditions:	
Reactor temperature (°C)	240 - 270
Pressure (bar)	50
WHSV (h ⁻¹)	1
Catalyst	Ca modified ZSM-5

The product was collected in a cooled vessel. The product was distilled according to the following cut points.

Distillation fractions	
IBP - 30 °C	total gases
30 - 180 °C	gasoline
180 - 200 °C	kerosine
200 - 318 °C	diesel
318 - FBP	bottoms

The yield of the diesel fraction was 23.4 %. The diesel fraction was hydrogenated before analysing it for its product properties. The engine cetane number (IBP 200 °C, FBP 318 °C) was **50**. The average carbon number was 13.10. The other data of the product analysis were:

Product analysis	
Density (15 °C, kg/m ³)	783.6
Bromine number	1.8
Viscosity (mm ² /s, 20 °C)	2.74
Cloud point (°C)	<-50
Pour point (°C)	<-50
Filterability (°C)	<-50

Example 6 (comparative)**The use of an unmodified zeolite catalyst in oligomerization; the properties of the diesel fuel fraction**

50 g of the catalyst were charged into a tubular steel reactor whose diameter was 30 mm. The catalyst particle sizes were in the range from 0.5 to 1.0 mm. First, 1-butene was fed through the catalyst bed. In order to increase the diesel yield, the product obtained was fed still another time through the same catalyst. The composition of the liquid feed was $C_4 = 55.0\%$, $C_8 = 33.2\%$, $C_{11+} = 9.3\%$, $C_5+C_6+C_7+C_9+C_{10} = 2.5\%$

Test conditions:	
Reactor temperature (°C)	210 - 235
Pressure (bar)	50
WHSV (h ⁻¹)	10-3
Catalyst	unmodified ZSM-5

The product was collected in a cooled vessel. The product was distilled with the following cut points:

Distillation	
IBP - 30 °C	total gases
30 - 180 °C	gasoline
180 - 200 °C	kerosine
200 - 317 °C	diesel
317 - FBP	bottoms

The yield of the diesel fraction was 37 %. The diesel fraction was hydrogenated before analyzing it for its product properties. The engine cetane number of the diesel fraction (IBP 200 °C, FBP 318 °C) was **46**. The average carbon number was 13.23. The other data of the product analysis were the following:

Product analysis	
Density (15 °C, kg/m ³)	784.4
Bromine number	0.4
Viscosity (mm ² /s, 20 °C)	2.68
Cloud point (°C)	<-50
Pour point (°C)	<-50
Filterability (°C)	<-50

Example 7 (comparative)**The properties of a diesel fraction distilled with different cut points**

The product obtained from the tubular reactor of example 6 was distilled with different cut points.

The product was distilled with the following cut

points.

Distillation fractions	
IBP - 30 °C	total gases
30 - 180 °C	gasoline
180 - 205 °C	kerosine
205 - 318 °C	diesel
318 - FBP	bottoms

The yield of the diesel fraction was 31.7 %. The diesel fraction was hydrogenated before analyzing it for its product properties. The engine cetane number of the diesel fraction (IBP 205 °C, FBP 318 °C) was **47**. The average carbon number was 13.61. The other data of the product analysis were the following:

Product analysis	
Density (15 °C, kg/m ³)	788.9
Bromine number	1.4
Viscosity (mm ² /s, 20 °C)	2.75
Cloud point (°C)	<-50
Pour point (°C)	<-50
Filterability (°C)	<-50

Example 8**The use of a modified zeolite catalyst in oligomerization; the properties of the diesel fuel fraction**

50 g of catalyst were fed into a tubular steel reactor, the diameter of the tubes being 30 mm. The catalyst particle size was 0.35 to 1.0 mm. First, 1-butene was fed through the catalyst bed. In order to increase the yield of diesel oil, the product obtained was fed still another time through the same catalyst. The composition of the liquid feed was $C_4 = 56.1\%$, $C_8 = 34.3\%$, $C_{11+} = 6.8\%$, $C_5+C_6+C_7+C_9+C_{10} = 2.8\%$.

Experimental conditions:	
Reactor temperature (°C)	260 - 305
Pressure (bar)	50
WHSV (h ⁻¹)	8-2
Catalyst	Ca modified ZSM-5

The product was collected in a cooled vessel. The product was distilled with the following

Distillation fractions:	
IBP - 30 °C	light gas
30 - 180 °C	gasoline
180 - 200 °C	kerosine
200 - 317 °C	diesel

(continued)

Distillation fractions:	
317 - FBP	bottoms

The yield of the diesel fraction was 41 %. It was hydrogenated before analyzing its product properties. The engine cetane number of the diesel fraction (IBP 200 °C, FBP 317 °C) was 50. The average carbon number was 13.32. The other results obtained by product analysis were:

Product analysis	
Density (15 °C, kg/m ³)	774.4
Bromine number	1.2
Viscosity (mm ² /s, 20 °C)	2.64
Cloud point (°C)	<-50
Pour point (°C)	<-50
Filterability (°C)	<-50

Claims

1. A process for preparing a diesel fuel fraction comprising the steps of
 - preoligomerizing a charge containing light C₂ - C₆ olefins in the presence of a Ca modified ZSM-5 zeolite catalyst containing a minimum of 0.01 %wt. of Ca, in order to produce a product stream which contains 10 to 95 %wt C₅₊ olefins,
 - oligomerizing the preoligomerized charge in the presence of a Ca modified ZSM-5 zeolite catalyst containing a minimum of 0.01 %wt of Ca, in order to prepare a product composition which at least partially consists of C₈₊ hydrocarbons, and
 - hydrogenating the product composition thus obtained to prepare a diesel fuel fraction with a high cetane number that boils in the range from 200 to 320°C.
2. A process as claimed in claim 1, in which a diesel fuel fraction is prepared having a cetane number higher than 47, preferably higher than 49.
3. A process as claimed in claim 1 or claim 2, in which a Ca modified ZSM-5 zeolite is used having a ratio of Si to Al less than 400, preferably in the range from 30 to 200.
4. A process as claimed in any one of claims 1 to 3, in which a Ca modified ZSM-5 zeolite is used containing from 0.01 to 1.0% wt, preferably 0.05 to 0.5 % wt, of ion exchanged calcium.
5. A process as claimed in any one of the preceding claims, in which the oligomerization is carried out at a temperature in the range from 160 to 350°C, preferably at 200 to 310°C, and at a pressure in the range from 1 to 150 bar, preferably at 10 to 80 bar.
6. A process as claimed in any one of the preceding claims, in which the charge for the preoligomerizing step contains 20 to 100 % wt, preferably 30 to 95 % wt, olefins.
7. A process as claimed in any one of the preceding claims, wherein the preoligomerized charge of the oligomerizing step comprises a hydrocarbon fraction with 40 to 80 % wt C₅₊ olefins.
8. A process as claimed in claim 7, in which the preoligomerized charge contains at least some, preferably 5 to 50 % wt. C₈₊ olefins.
9. A process as claimed in claim 1, in which the catalysts used in the preoligomerizing and the oligomerizing steps are the same as each other.
10. A process as claimed in any one of the preceding claims, in which the charge for the oligomerizing step is obtained by combining a part of the product composition of the oligomerizing step with fresh feed containing light olefins.
11. A process as claimed in claim 1, in which the oligomerization is carried out in a reactor to which a part of the product composition of the oligomerization is recirculated and combined with fresh feed of light olefins.
12. A process as claimed in claim 1, in which the oligomerization is carried out in at least two successive reactors, the following reactor also being fed with the reaction composition of the previous reactor and each reactor using a Ca modified ZSM zeolite as catalyst.

Patentansprüche

1. Verfahren zur Herstellung einer Dieseltreibstoff-Fraktion, umfassend die Stufen:

Voroligomerisierung von einer Beschickung mit leichten C₂- bis C₆- Olefinen in Gegenwart von einem mit Calcium modifizierten ZSM-5-Zeolith-Katalysator mit einem Minimalgehalt an Calcium von 0,01 Gew.-% zur Bildung eines Produktstroms, der 10 bis 95 Gew.-% an C₅₊-Olefinen enthält,

Oligomerisierung der voroligomerisierten Be-

schickung in Gegenwart von einem mit Calcium modifizierten ZSM-5-Zeolith-Katalysator mit einem Minimalgehalt an Calcium von 0,01 Gew.-% zur Bildung einer Produktmischung, die mindestens teilweise aus C_{8+} - Kohlenwasserstoffen besteht, und

Hydrierung der so erhaltenen Produktmischung zur Bildung einer Dieseltreibstoff-Fraktion, die eine hohe Cetanzahl aufweist und im Bereich von 200 bis 320 ° C siedet.

2. Verfahren gemäß Anspruch 1, bei dem eine Dieseltreibstoff-Fraktion hergestellt wird, die eine Cetanzahl höher als 47, vorzugsweise höher als 49 aufweist. 15
3. Verfahren gemäß Anspruch 1 oder 2, wobei ein calciummodifizierter ZSM-5-Zeolith verwendet wird, in dem ein Verhältnis von Si : Al von weniger als 400, vorzugsweise im Bereich von 30 bis 200 vorliegt. 20
4. Verfahren gemäß einem jeden der Ansprüche 1 bis 3, wobei ein calciummodifizierter ZSM-5-Zeolith verwendet wird, der vermittelt Ionenaustausch Calcium in einer Menge von 0,01 bis 1,0 Gew.-%, vorzugsweise 0,05 bis 0,5 Gew.-%, enthält. 25
5. Verfahren gemäß einem jeden der vorangehenden Ansprüche, wobei die Oligomerisierung bei einer Temperatur im Bereich von 160 bis 350 °C, vorzugsweise bei 200 bis 310 °C, und bei einem Druck im Bereich von 1 bis 150 bar, vorzugsweise bei 10 bis 80 bar, durchgeführt wird. 35
6. Verfahren gemäß einem jeden der vorangehenden Ansprüche, wobei die Beschickung für die Voroligomerisierungsstufe 20 bis 100 Gew.-%, vorzugsweise 30 bis 95 Gew.-% an Olefinen enthält. 40
7. Verfahren gemäß einem jeden der vorangehenden Ansprüche, wobei die voroligomerisierte Beschickung für die Oligomerisierungsstufe eine Kohlenwasserstoff-Fraktion mit 40 bis 80 Gew.-% an C_{5+} - Olefinen umfaßt. 45
8. Verfahren gemäß Anspruch 7, wobei die voroligomerisierte Beschickung mindestens einige, vorzugsweise 5 bis 50 Gew.-% an C_{8+} - Olefinen enthält. 55
9. Verfahren gemäß Anspruch 1, wobei die Katalysatoren, die in der Voroligomerisie-

rungsstufe und in der Oligomerisierungsstufe verwendet werden, dieselben sind.

10. Verfahren gemäß einem jeden der vorangehenden Ansprüche, wobei die Beschickung für die Oligomerisierungsstufe durch Kombinieren von einem Teil der Produktmischung aus der Oligomerisierungsstufe mit einer leichte Olefine enthaltenden frischen Einspeisung erhalten wird.
11. Verfahren gemäß Anspruch 1, wobei die Oligomerisierung in einem Reaktor durchgeführt wird, in dem ein Teil von der Produktmischung aus der Oligomerisierung rezirkuliert und mit frisch eingespeisten leichten Olefinen kombiniert wird.
12. Verfahren gemäß Anspruch 1, wobei die Oligomerisierung in mindestens zwei aufeinanderfolgenden Reaktoren durchgeführt, der nachfolgende Reaktor mit der Reaktionsmischung aus dem vorangehenden Reaktor gespeist und in jedem Reaktor ein mit Calcium modifizierter ZSM-Zeolith als Katalysator verwendet wird.

Revendications

1. Procédé pour la préparation d'une fraction de carburant diesel, comprenant les étapes de :
 - préoligomérisation d'une charge contenant des oléfines légères en C_{2-6} en présence d'un catalyseur à base de zéolite ZSM-5 modifiée par du Ca contenant un minimum de 0,01% en poids de Ca, pour produire un courant de produits qui contient 10 à 95% en poids d'oléfinen en C_{5+} ,
 - oligomérisation de la charge préoligomérisée en présence d'un catalyseur à base de zéolite ZSM-5 modifiée par du Ca contenant un minimum de 0,01% en poids de Ca, pour préparer une composition de produits qui consiste au moins partiellement en hydrocarbures en C_{8+} , et
 - hydrogénation de la composition de produits ainsi obtenue pour préparer une fraction de carburant diesel qui bout dans la gamme de 200 à 320°C.
2. Procédé suivant la revendication 1, dans lequel il est préparé une fraction de carburant diesel ayant un indice de cétane supérieur à 47, de préférence supérieur à 49.
3. Procédé suivant les revendications 1 ou 2, dans lequel il est utilisé une zéolite ZSM-5 modifiée par du

calcium ayant un rapport de Si à Al inférieur à 400, de préférence compris dans la gamme de 30 à 200.

4. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel il est utilisé une zéolite ZSM-5 modifiée par du calcium contenant de 0,01 à 1,0% en poids, de préférence de 0,05 à 0,5% en poids de calcium introduit par échange d'ion. 5
5. Procédé suivant l'une quelconque des revendications précédentes, dans lequel l'oligomérisation est conduite à une température comprise dans la gamme de 160 à 350°C, de préférence dans la gamme de 200 à 310°C et à une pression comprise dans la gamme de 1 à 150 bar, de préférence de 10 à 80 bar. 10
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6. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la charge pour l'étape de préoligomérisation contient 20 à 100% en poids, de préférence 30 à 95% en poids d'oléfines. 20
7. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la charge préoligomérisée de l'étape d'oligomérisation comprend une fraction hydrocarbonée ayant 40 à 80% en poids d'oléfines en C₅₊. 25
8. Procédé suivant la revendication 7, dans lequel la charge préoligomérisée contient au moins un peu d'oléfines en C₅₊, de préférence de 5 à 50% en poids de celles-ci. 30
9. Procédé suivant la revendication 1, dans lequel les catalyseurs utilisés dans l'étape de préoligomérisation et dans l'étape d'oligomérisation sont les mêmes. 35
10. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la charge pour l'étape d'oligomérisation est obtenue par combinaison d'une partie de la composition de produits de l'étape d'oligomérisation avec une charge d'alimentation fraîche contenant des oléfines légères. 40
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11. Procédé suivant la revendication 1, dans lequel l'oligomérisation est conduite dans un réacteur dans lequel une partie de la composition de produits de l'oligomérisation est remise en circulation et combinée avec une charge d'alimentation fraîche d'oléfines légères. 50
12. Procédé suivant la revendication 1, dans lequel l'oligomérisation est conduite dans au moins deux réacteurs successifs, le réacteur suivant étant aussi alimenté avec la composition réactionnelle du réacteur précédent et chaque réacteur utilisant une zéolite ZSM modifiée par du Ca comme catalyseur. 55