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(54) Title: CATALYTIC CRACKING OF HYDROCARBONS

(57) Abstract: Natural fats can conveniently be converted to gasoline by hydrogenating and cracking at 250?450°C with a catalyst based on a zeolite and a mesoporous inorganic oxide. Selectivity and yield are good, coke formation minimal and catalyst regeneration easy.

Catalytic cracking of hydrocarbons

The invention relates to a process for the preparation of C_2-C_8 hydrocarbons by cracking catalytically one or more hydrocarbons which have been obtained from natural fat or a derivative thereof.

Cracking is a refining process involving decomposition and recombination of organic compounds, especially hydrocarbons, affected by heat, pressure and optionally a catalyst, to form molecules suitable for different petrochemicals such as motor fuels. If the cracking is carried out by heat alone, it is called thermal cracking. If a catalyst is used, it is called catalytic cracking.

Catalytic cracking is carried out by either the fixed, moving or fluid bed technique. In the fixed bed technique, the feed is contacted with a fixed layer of catalyst. In the moving bed technique, the feed is contacted with a stirred layer of loose catalyst. In the fluidized technique, the feed is contacted with small particles of catalyst which are suspended in upwards flowing gas to be handled like a liquid and circulated through pipes and valves between reaction and regeneration vessels.

The main purpose of catalytic cracking is to convert heavy distillate into compounds of lower molecular weight in the boiling range of gasoline and middle distillate. An increase in gasoline yield and a raise of the octane number is the primary object. In catalytic cracking, the temperature typically ranges from 480 to 510°C while the catalyst is regenerated at about 600 to 700°C. Conventional operating pressures range from 150 to 200 kPa.

According to US 4 992 605, fatty acids and their triglycerides can be hydrogenated with conventional desulphurization catalysts to give diesel fuel having good ignition properties. By hydrogenation is in this publication meant the reation of hydrogen with any organic compound. The fatty acid may be a tall oil fatty acid and the triglyceride may be obtained from plant oils such as rapeseed, sunflower and palm oil.

FI 100248 discloses the hydrogenation of fatty acids or their triglycerides, based on plant oils such as rapeseed oil, tall oil, sunflower oil palm oil or soybean oil, into n-paraffins, followed by isomerisation of the n-paraffins into paraffins having good cold properties.

The above documents relate to the preparation of diesel fuel from fatty acids. Effective processes have not been presented for converting natural fat or a derivative thereof into hydrocarbons in the boiling range of gasoline having a high octane number. An objective of the invention is therefore to provide a process for the preparation of C_2-C_8 hydrocarbons from natural fat or derivatives thereof. A further object of the invention is to obtain process for the effective conversion into C_2-C_8 hydrocarbons with as little coke as possible produced. Still another object of the invention is to find a catalyst which in addition to above good process properties is also easy to regenerate for further use.

As was initially stated, the invention relates to a process for the preparation of C_2-C_8 hydrocarbons by cracking catalytically one or more hydrocarbons which have been obtained from natural fat or a derivative thereof. The above-mentioned goals of the invention have now been achieved by carrying out the cracking at a temperature between 250 and 450°C using a catalyst based on a zeolite and a mesoporous inorganic oxide.

As was already mentioned, the temperature of most known catalytic cracking processes typically ranges from 480 to 510°C, while the catalyst is regenerated at about 700°C. When using a catalyst comprising a zeolite and a mesoporous inorganic oxide for cracking hydrocarbons from natural fats, a much lower temperature may be used; only 250 to 450°C. Such low temperatures give more C_2-C_8 hydrocarbon product and less decomposed hydrocarbon in the form of coke. The regeneration temperature is also very low; just from 0 to 50°C higher than the cracking temperature. See below.

The starting material, i.e. the precursor of the hydrocarbon to be catalytically cracked, is natural fat or a derivative thereof. By fat is meant one or more solid or liquid glyceryl esters of one or more higher fatty acids. Thus, fat is genus for, among others butter, tallow, blubber, lard, oil, etc. Generally, the natural fat used in the invention is selected from the glycerides (mono, di and tri) of C_{10}-C_{26} fatty acids.

The starting material is typically an animal or plant fat selected from: the lauric-myristic acid group (C_{12}-C_{14}) including milk fats, as well as coconut oil, palmseed oil, babassu oil, muscat butter oil, laurel seed oil; from the palmitic acid group (C_{16}) including earth animal fats, as well as palm oil and stillingia tallow; the stearic acid group (C_{18}) including fats of earth animals, as well as cocoa butter, shea butter and Borneo tallow; the oleic and linoleic acid group (unsatd. C_{18}) including whale

and fish oils as well as tall oil (fatty acid fraction), olive oil, peanut oil, sesame oil, maize oil, sunflower oil, poppyseed oil, cottonseed oil and soy oil; the linolenic acid group (unsatd. C_{18}) including whale and fish oils as well as linseed oil, perilla oil and hemp oil; the erucic acid group (unsatd. C_{22}) including whale and fish oils as well as rapeseed oil and mustard seed oil; the eleostearic acid group (conjug. unsatd. C_{18}) including whale and fish oils as well as chinese wood oil; and fats with substituated fatty acids (ricinoleic acid, C_{18}) such as castor oil.

The derivative of the natural fat is typically the fatty acid component of the above listed fats, or a corresponding fatty alcohol.

The raw material of the claimed process, i.e. the object of the catalytic cracking, is generally one or more hydrocarbons which have been obtained by removing oxygen from the natural fat or derivative thereof.

Preferably, the oxygen has been removed from the natural fat or derivative thereof by hydrolyzation and decarboxylation, or, most preferably, by hydrogenation. Depending on the choice of feedstock, such hydrogenation is typically carried out at a temperature of 330-450°C, a pressure of 3−15 MPa and an LHSV of 0.5−5.0 hr^{-1} in the present of a hydrogenation catalyst. Catalysts suitable for the hydrogenation are commercial hydroprocessing catalysts including cobalt-molybdenum catalysts, nickel-molybdenum catalysts, or other transition metal based catalysts used for hydroprocessing [e.g. American Cyanamide HDS-20 or Shell S-424]. Preferably, the catalyst is the $NiMo/Al_2O_3$ or $CoMo/Al_2O_3$ catalysts mentioned in FI 1090248, see page 3, lines 30 and 31, of the document.

In some cases, the hydrogenation has been carried still further to remove unwanted double bonds from the hydrocarbon chain, or combined with isomerisation of the formed hydrocarbon.

After preparing the raw-material, it is subjected to catalytic cracking. The most important features of the claimed cracking have been disclosed above. Generally, the cracking is carried out by feeding said one or more hydrocarbons from natural fat or a derivative thereof in liquid form through a reactor containing said catalyst based on a zeolite and a mesoporous inorganic oxide.

Generally, the reactor contains the catalyst as a fixed-bed, moving-bed or fluidized bed. However, it is preferable, that the reactor contains the catalyst as a fixed bed, trough which the hydrocarbon feed is led. In one embodiment, said one or several hydrocarbons are fed to the top of the reactor and the product is recovered from

the bottom of the reactor. The catalytic cracking is preferably carried out at a temperature between 250 and 399°C, most preferably between 320 and 380°C. The pressure is preferably 0.01–5.0 MPa, most preferably 0.2−2.0 MPa.

In the claimed process, a catalyst is used which is based on a zeolite and a mesoporous inorganic oxide. This definition includes e.g. catalysts which have been prepared by mixing and optionally reacting a zeolite with a mesoporpus inorganic oxide, carrying out a zeolite synthesis in the presence of a mesoporous inorganic oxide, carrying out a mesoporous inorganic oxide synthesis in the presence of a zeolite, or carrying out a zeolite synthesis and an mesoporous inorganic oxide synthesis simultaneously in the same vessel. The zeolite may be added to the reaction mixture of the mesoporous inorganic oxide synthesis at any stage, and *vice versa*. The definition also includes mixtures of such catalysts.

Preferably the catalyst based on a zeolite and a mesoporous inorganic oxide has been prepared by synthesizing the mesoporous inorganic oxide in the presence of the zeolite. In that case, the zeolite may be added at any stage of synthesizing the mesoporous inorganic oxide.

The catalyst based on a zeolite and a mesoporous inorganic oxide preferably contains 4−80%, preferably 20–70%, of added dry zeolite, based on the total dry weight of the zeolite and the mesoporous inorganic oxide. The specific surface area of the catalyst is generally from 300 to 1400 m^2/g, preferably from 400 to 1200 m^2/g.

The catalyst based on a zeolite and a mesoporous inorganic oxide is mechanically, thermally and hydrothermally stable and can easily be handled and regenerated in a cracking process. The catalyst based on a zeolite and a mesoporous inorganic oxide is typically a mesoporous molecular sieve material matrix containing zeolite structures.

The characteristic features of the catalyst used for the claimed cracking is measurable by X-ray powder diffraction, scanning electron microscopy, transmission electron microscopy, specific surface area measurement by N_2 absorption (BET), ^{27}Al-NMR, and acidity measurements using ammonia-TPD and pyridine-FTIR. The catalyst typically has acid sites on its surface.

The catalyst based on a zeolite and a mesoporous inorganic oxide is generally based on one or more inorganic oxides such as silicon oxide SiO_2 and aluminium oxide Al_2O_3. The silicon atoms may be replaced by metal atoms. These include,

but are not limited to, metals selected from the group consisting of aluminium, titanium, vanadium, zirconium, gallium, boron, manganese, zinc, copper, gold, lanthanum, chromium molybdenum, nickel, cobalt, iron, tungsten, palladium, platinum and combinations thereof. The replacement is carried out by contacting the zeolite or a precursor thereof and/or the mesoporous inorganic oxide or a precursor thereof with a source of the metal.

Preferably, the modifying metal is aluminium, whereby the aluminium source may be selected from aluminium sulphate ($Al_2(SO_4)_3 \cdot 18H_2O$, hydrated aluminium hydroxides, aluminates, aluminium isopropoxide and alumina. The preferred aluminium content is between 0.01 and 10% by weight, most preferably between 0.5 and 5.0% by weight, based on the weight of the catalyst based on a zeolite and a mesoporous inorganic oxide. The aluminium makes the catalyst acidic and more suitable for catalytic cracking.

When preparing the catalyst based on a zeolite and a mesoporous inorganic oxide, the zeolite is preferably selected from the group consisting of medium pore (10-member ring) zeolites such as MFI-framework zeolite (ZSM-5), MTT-framework zeolite (ZSM-23), TON-framework zeolite (ZSM-22, theta-1), AEL-framework zeolite (SAPO-11), MWW-framework zeolite (MCM-22, PSH-3, ITQ-1), FER-framework zeolite (ZSM-35), MEL-framework zeolite (ZSM-11), and larger pore (12-member ring) zeolites such as BEA-framework zeolite (zeolite β), FAU-framework zeolite (zeolite X, zeolite Y, ZSM-20, SAPO-37) and MOR-framework zeolite (mordenite), MTW-framework zeolite (ZSM-12), AFI-framework molecular sieve (SAPO-5), an several other zeolites like clinoptilolite, ZSM-34, ZSM-48, SSZ-32, MCM-49, MCM-56, ITQ-2, ITQ-4, ITQ-21 and Breck-6, as well as precursors or mixtures thereof.

When the fat-based hydrocarbon raw materials are cracked according to the present invention, it is especially advantageous to use zeolites selected from the group consisting of medium pore (10−member ring) zeolites such as MFI- framework zeolite, MTT- framework zeolite, TON- framework zeolite, AEF- framework zeolite, MWW- framework zeolite, FER- framework zeolite, larger pore (12-member ring) zeolites such as BEA- framework zeolite, FAU- framework zeolite and MOR- framework zeolite, and precursors and mixtures thereof. Examples of said zeolite groups are ZSM-5, ZSM-23, ZSM-22, SAPO-11, MCM-22, ferrierite, beta, Y- and X-zeolites and mordenite. Most advantageous are the MFI-framework zeolite, MTT-framework zeolite, TON-framework zeolite, MWW-framework zeolite and precursors and mixtures thereof. The average pore diameter of the zeolite is

from 0.2 to 2.0 nm, preferably from 0.3 to 0.7 nm. When zeolite is added to the synthesis of the mesoporous inorganic oxide, the particle size of the zeolite is typically from 0.001 µm to 3.0 µm.

The other component of the catalyst used in the invention is the mesoporous inorganic oxide. It typically includes aluminium oxide Al_2O_3, silicon oxide SiO_2, or combinations thereof. In the mesoporous inorganic oxide, the volume of the mesopores preferably constitutes at least 80%, preferably at least 90%, as measured by N_2 porosimetry, of the combined volume of mesopores and micropores. According to an important embodiment of the invention, the mesoporous material of the catalyst comprising a zeolite and a mesoporous inorganic oxide is selected from the group consisting of aluminosilicates of type M41S (including hexagonal MCM-41, cubic MCM-48 and plate-like MCM-50), MSA-1, MSA-2, MSA-3, MAS-8, and mixtures thereof. The average pore diameter of the mesoporous material is by definition from 2 to 50 nm, preferably from 2 to 30 nm and most preferably from 2 to 20 nm. Typically, the pore volume of the mesoporous material from 0.2 cm^3/g to 2.4 cm^3/g.

The catalyst comprising a zeolite and a mesoporous inorganic oxide can be prepared e.g. by mixing together and, optionally, reacting the zeolite and the mesoporous inorganic oxide, preparing the zeolite in the presence of a mesoporous inorganic oxide, preparing the mesoporous inorganic oxide in the presence of the zeolite, or preparing both the zeolite and the inorganic oxide simultaneously in the same vessel. Preferably, the catalyst has been prepared by synthesizing hydrothermally the mesoporous inorganic oxide in the presence of the zeolite. This takes place by heating together the zeolite, a precursor of the mesoporous inorganic oxide, water and a mesopore forming compound. In that case, the zeolite may be added at any stage of preparing the mesoporous inorganic oxide (For example, US 20060128555 adds the zeolite before the mesoporous inorganic oxide precursor and the mesopore forming compound (templating agent), whereas WO 2006/070073 adds the zeolite after adding the mesoporous inorganic oxide precursor and a first mesopore forming compound, but before adding a second mesopore forming compound).

The mesoporous inorganic oxide precursor undergoing the hydrothermal synthesis has preferably been selected from the group consisting of silica precursors like tetraethoxy silane (= tetraethyl orthosilicate, TEOS), tetramethylammonium silicate, tetraethyl ammonium silicate, sodium silicate, water glass, colloidal silica and fumed silica, and alumina precursors like aluminium sulphate, hydrated

aluminium hydroxides, aluminates, aluminium isopropoxide, alumina, and their mixtures. The mesopore forming compound is typically a compound which mixes and forms hydrogen bonds with the inorganic oxide or its precursor. It is preferably selected from the group consisting of tetrapropyl ammonium hydroxide, tetrapropyl ammonium bromide, tetradecyl trimethyl ammonium bromide, glycerol, a glycol, a trialkyl amine, sulfolane, tetraethylene pentamine and diethylene glycol di-benzoate. Typically, the zeolite, the inorganic oxide precursor, the water and the mesopore forming compound are heated to a temperature of about 100 to about 200°C in order to form a composite containing mesopores. After the heating, the mesopore forming compound is removed from the composite by calcining and/or extraction.

Before use as cracking catalyst, the catalyst based upon the zeolite and the mesoporous inorganic oxide may be mixed with a binder or other additive in order to enlarge its activity zone and/or enable its forming into an optimal shape (e.g. extrudates, pellets, rings, etc). Such useful binders or additives are e.g. silica, silica gel and/or alumina. The catalyst may also be peptized, e.g. by using acetic acid and Boehmite.

In the claimed process, C_2-C_8-hydrocarbons are prepared by cracking catalytically one or more hydrocarbons which have been obtained from natural fat or a derivative thereof. The catalytic cracking is carried out at a temperature between 250 and 450°C using a catalyst as described above which is based on a zeolite and a mesoporous inorganic oxide. Preferably, the cracking is carried out in cycles, whereby, most advantageously, the cracking cycles last for 6 to 18 hours. Under such conditions, low coke product is produced.

Between the cracking cycles, the catalyst based on a zeolite and a mesoporous inorganic oxide is regenerated. This preferably takes place by flushing the catalyst with hot gas, preferably every 10 to 50 hours, most preferably every 15 to 30 hours. The regeneration temperature is typically 0 to 50°C higher, preferably 10 to 30°C higher, than the cracking temperature. The regeneration typically takes place by flushing with a gas selected from hydrogen, nitrogen, steam, helium, argon, a lower alkane (C_1-C_5), and mixtures thereof. Regeneration may also be carried out occasionally by burning deposited coke, preferably after several regenerations with hot gas. Then, the burning of the deposited coke is carried out by introducing air or oxygen to a bed of the catalyst. The coke burning usually takes place at a temperature of 450 to 550°C.

In the following, some examples are disclosed, the sole purpose of which are to illuminate the invention.

1 EXAMPLES 1, 2, 7 AND 9

1.1 Reactor and sampling

Test equipment consists of feed vessel and pump (Neste technology), mass flow controllers (Brooks) for nitrogen and air, gas/liquid mixer, pre-heater for product mixture, reactor and furnace, pressure controller (Kämmer), gas/liquid separator and sample collector. Nitrogen was used as internal standard for mass balance calculation and simultaneously as carrier for gaseous product. The gas/liquid mixture was fed to a heated pre-heater whose temperature was set to 300°C.

Gas and liquid products were analysed on-line with Agilent 5890 and 6890 GC and furthermore fraction analyses from liquid product off-line were carried out with another Agilent 6890 GC. The temperature of the feed and liquid product lines were 50°C and the temperature of the gas line was 100°C.

In-situ regeneration option was also available wherein air was introduced into the reactor at a temperature of 500°C. The state of regeneration was measured with an on-line CO/CO_2-analyser type Siemens Ultramat 22P.

1.2 Analysis

On-line sampling and analysis were automated with a timer to take and collect 9–10 gas and liquid samples during a day. The pressure of the gaseous sample line was adjusted into constant pressure and the concentration of hydrocarbons (C_1 - C_7) and permanent gases (H_2, O_2, N_2, CO and CO_2) were analysed simultaneously. Permanent gases were separated with HayeSepQ and molecular sieve connected in series and hydrocarbons with a capillary column. Gas sample quantification was achieved with external calibration. A separation column was used for liquid on-line samples, which was of the type DB-1. The identified compounds ranged from methane up to boiling point 221°C. Fraction analyses on off-line samples were carried out with a DB-1 column.

1.3 Experiment protocol

1.0 g of catalyst/inert mixture (70% / 30%) was loaded in the middle of the reactor between layers of quarts wool and inert material. A measuring and temperature

controlling thermo element was placed in the middle of the catalyst bed. Before every experiment catalyst was dried under nitrogen flow overnight at 350°C.

The test run was started by adjusting the set point of pressure with a controller and increasing the pressure with nitrogen flow. Simultaneously a feed line was pre-filled through a 3-way valve and the reactor temperature was set to the test value. After the reaction conditions were reached, the test was started by directing the feed flow into the reactor using a 3-way valve. Sampling timer and analysing sequences were started at the same time. During and at the end of the experiment the amounts of liquid product collected to the vials were weighted.

The experiment was finished by stopping the feed flow and flushing the reactor with nitrogen flow until all liquid came out. After that the heating of the pre-heater and the reactor furnace were turned off and reactor was cooled under nitrogen flow.

1.4 Regeneration protocol

In-situ regeneration was carried out introducing air into the reactor at 500°C under ambient pressure. The regeneration was continued over night for at least 12 hours and the state of regeneration was measured with an on-line CO/CO_2-analyser. After regeneration, the gas flow was changed to nitrogen and the reactor was cooled into ambient temperature.

2 EXAMPLES 3 TO 6 AND 8

2.1 Reactor and sampling

Reaction tests were carried out in a Sotelem LCT-570 tubular reactor which had been modified for this work. The reactor tube as well as all the piping was made of stainless steel. The reactor was operated in downward flow mode.

Argon was fed through a mass flow controller and used as an internal standard, and as a carrier gas for the reactant and products. The reactant was pumped with a HPLC-pump to the reactor through a stainless steel line which was kept hot with heating tapes. Also, the body of the pump was heated with a circulating water jacket. The feed vessel was placed on a scale to monitor the exact feed rate. After the reactor, nitrogen was added to the product stream using a mass flow controller in order to increase the flow rate, and thus to decrease the propensity for the thermal reactions prior to the analysis of the product stream. The product diluted

with nitrogen was lead from the reactor through a heated line to a Tescom-back-pressure valve. Thereafter, the product stream was cooled in a small "pipe and shell-type" heat exchanger with circulating water from a thermostated bath. A small gas-liquid-separator was used to separate the gaseous products from heavy condensable liquids. Gases were analyzed on-line and liquid samples were collected in vials.

2.2 Analysis

The gaseous product stream collected from the gas-liquid separator was analysed on-line by GCs. The product was introduced through a heated stainless steel line to the analysis system. The analysis system consisted of two HP-5890 gas chromatographs, one for the analysis of heavy hydrocarbons (>C_7) and permanent gases, and the other for the analysis of light hydrocarbons (C_1-C_7) and when necessary also oxygenates. The gas chromatographs were equipped with three FID:s, one TCD, five pneumatic valves and six wide-bore capillary or packed columns. The columns used were Porapak Q 80/100, Molecular sieve 13X 45/60, HP-1 (hydrocarbons > C_7), PAW 80/100 and 10 µm Al_2O_3/KCl (light hydrocarbons up to C_7). If necessary, yet another column was used (the polar compounds separated by the TCEP). This additional column may become necessary for the analysis of aromatic compounds or oxygenates.

In the analyses, nitrogen was used as the carrier gas making it possible to analyze also hydrogen. The FID responses were corrected using response factors published by Dietz[1] whereas TCD responses were measured by using known gas mixtures. Methane, which could be detected by all the four detectors, was used for the calibration of the sensitivities of the detectors. Data storage and handling were performed using a HP-Chemstation and a Custom Report Generator software. The data from the resulting four report files (one for each detector) were collected by a command macro on the final report template, where the calculation of yield and the generation of figures took place.

2.3 Run protocol

Typically 2 g of catalyst was loaded in the reactor tube on top of glass wool, and 1.3 g of SiC was added on top of the catalyst bed to heat the feed. The fixed bed reactor was fixed into its position, and the reactor was pressure tested with argon

[1] W.A. Dietz, J. Gas Chromatography, 1967, 68-71

(40 bar, 0.5h). After acceptable performance (no visible reduction in pressure), a constant Ar flow of 2 l/h was commenced, and the temperature of the reactor was elevated to the reaction temperature at a rate of overnight.

When the temperature had been stabilised to the desired setpoint, the liquid feed was first pumped via a 3-way valve to an outlet test line to certify that the feed line is filled with the feed. Thereafter, the following actions were taken:

- check that all line heating elements are on, and water bath for gas-liquid separator is at 20°C and cycle is on
- adjust gas feeds: Ar 2 l/h and nitrogen carrier gas 4 l/h
- fill feed bottle, set scale to zero, and commence the liquid feed
- adjust pressure to 40 bar by a Tescom pressure regulator valve
- start data logging and start timer
- load run methods on GCs and switch flows from bypass to GCs.

During the run the following actions were taken:

- on line gas samples drawn to analysis every 30 minutes
- liquid samples drawn and weighed every 15 or 30 min depending on the feed rate
- feed scale readings recorded every 15 or 30 min depending on the sampling interval.

Typically, the duration of the run is 5 hours. In the end, the liquid flow is stopped, the oven is allowed to cool overnight, and the gas flows are left running. In the following morning, the liquid trap is emptied and the amount of liquid product is weighed. The gas flows are stopped, the pressure is released and the catalyst is collected and stored for later analyses. Alternatively, the catalyst is regenerated *in situ* and used in further experiments.

After each run, the gas-liquid separator is cleaned, and it always contains minor amounts of liquid product. In addition, the Tescom pressure regulator was cleaned after each catalyst sample (in runs 0506-0639). It should be noted that after the reaction-regeneration sequence, the pressure regulator typically contained a significant amount of liquid product. This amount could not be accurately weighed, but the amount was estimated by captivating the liquid on a pre-weighed paper, and by weighing the "wet" paper. In a typical run of 5 hours with a feed rate of 4,3–6,0 g/h it can accounts as much as approx. 5–10% meaning that a mass balance of approx. 90% is excellent. On the other hand, if the feed rate is lower, such as

2.3 g/h, the mass balance is not likely to remain at approx. 80% max, and if the feed rate is high, such as 18 g/h, the effect of this accumulation is less significant.

The maintenance tasks also include flushing the reactor lines with argon after the reaction-regeneration cycles upon change of the catalysts. In addition, the on-line GC lines and valves were cleaned with elongated flow of inert gas after each catalyst sample, that is, after reaction-regeneration cycles.

2.4 Regeneration protocol

The *in situ* regeneration of the catalysts was carried out as follows:

1) The catalyst is cooled to room temperature under argon-flow.

2) Argon flow was changed to air flow of 5 l/h.

3) Temperature was increased at a rate of 1°C/min to 500°C or 550°C.

4) The catalyst was kept at the set point temperature for two hours.

5) The gas flow at the outlet of the reactor was monitored by IR for determination of hydrocarbons, CO, CO_2 and water during stages 3) and 4).

6) The catalyst was cooled to reaction temperature (or room temperature). The air flow was changed to argon (2l/h), and the catalyst was kept under argon atmosphere for later use. This equilibration time was at least 1 h.

The method for preparation of catalyst materials performed in inventive way is described in details in WO patent application 2006/070073. The main properties of the catalysts used in examples are summarized in Table 1.

EXAMPLES

Example 1.

The preparation of the catalyst comprising a zeolite and a mesoporous inorganic oxide used by the invention is described in example 20a of WO patent application 2006/070073. Before the test reactions, the catalyst is pressed to plates, crushed and sieved to desired particle size.

Example 2.

The preparation of the catalyst comprising a zeolite and a mesoporous inorganic oxide used by the invention is described in example 20b of WO patent application 2006/070073. Before the test reaction, the catalyst material is pressed to plates, crushed and sieved to desired particle size.

Example 3.

Before pressing, crushing and sieving as described in example 2, the catalyst material thereof was mixed with silica gel (Ludox-AS40). The catalyst to silica gel weight ratio is 1:1. The formed gel mixture is baked on a plate and dried at 115°C overnight. The material is calcined at 500°C for 2 hours. Then, the catalyst is crushed and sieved to desired particle size.

Example 4.

The catalyst comprising a zeolite and a mesoporous inorganic oxide, before pressing, crushing and sieving, as described in example 2, is peptized by using 2.5 wt-% acetic acid and boehmite (Catapal B). The amount catalyst was 10 g and amount of boehmite was 4 g that were carefully mixed. Then, the acetic acid was drop wise added to the mixture to get a formable paste. The paste is baked on the plate and dried at 120°C overnight. The catalyst material is calcined at 500°C for 2 hours. Then, the catalyst is crushed and sieved to desired particle size.

Example 5.

The method of preparation of catalyst material 6 used in the present invention is described in example 8 in WO patent application 2006/070073. The catalyst material is mixed with silica gel (Ludox-AS40). The weight ratio of catalyst to silica gel (Ludox-AS40) is 1:1. The formed gel mixture is baked on a plate and dried at 115°C overnight. The material is calcined at 500°C for 2 hours. Then, the catalyst is crushed and sieved to desired particle size.

Example 6.

The method of preparation of inventive catalyst material is described in example 6 in WO patent application 2006/070073. The mesoporous catalyst material is mixed with silica gel (Ludox-AS40). The ratio of mesoporous material to silica gel (Ludox-AS40) weight to weight is 1:1. The formed gel mixture is baked on the plate and

dried at 115°C overnight. The material is calcined at 500°C for 2 hours. Then, the catalyst is crushed and sieved to desired particle size.

Example 7.

The synthesis of a catalyst useful in the invention was in this example carried out using following steps. Firstly, solutions A, B and C are prepared. Solution A was prepared by mixing fumed silica with distilled water with continuous stirring (r.m.p. 196) for 20 minutes. Solution B was prepared by adding tetramethylammonium silicate to sodium silicate with continuous stirring (r.m.p 180) and the mixture was stirred for 20 minutes. Solution C was prepared by dissolving tetradecyl trimethyl ammonium bromide in distilled water with vigorous stirring (r.m.p. 336) for 20 minutes. Solution B was added to Solution A slowly (in 15 min) with vigorous stirring (r. m. p. 320) after the addition of all of solution B the mixture was stirred for further 20 min. Solution C was added to mixture (A + B) slowly (20 min) with vigorous stirring (r. m. p. 336) after addition of solution C the mixture was further stirred for 20 minutes. This is the gel into which TON zeolite nucleis are added.

Then, zeolite nucleis with code TON were prepared. Reagents used in the synthesis of TON structure zeolite nucleis were Ludox AS 40, aluminium sulphate, potassium hydroxide, 1, 6 - diamino hexane and distilled water. Three different solutions A, B and C were made for TON zeolite nuclei preparation. Solution A was prepared by adding Ludox AS40 silica to distilled water. Solution B was prepared by dissolving aluminium sulphate and potassium hydroxide in Solution B was added to Solution A and the obtained gel mixture stirred for 20 minutes. Solution C was prepared by dissolving 1,6-diaminohexane in distilled water and stirring for 20 minutes. Solution C was added to the gel mixture (A+B) and stirred for 15 minutes. The synthesis was carried out at 160 °C for 48 h. After the completion of the synthesis the product was filtered, washed with distilled water, dried and calcined and TON zeolite nuclei were obtained.

After that, the TON zeolite nuclei precursor prepared above was added to the gel solutions (A +B +C) under vigorous stirring (r.m.p. 340) for 20 min. The homogenisation of the dispersed TON was carried out by further stirring (r.m.p. 340) of the gel for 35 minutes. After that gel was allowed to ripen for three hours with stirring (r.m.p 180) at ambient temperature. The gel was introduced in Teflon cups which were then inserted in an autoclave. The synthesis was carried out for 96 h at 100°C.

After completion of the synthesis, the reactor was cooled for 30 min and mesoporous molecular sieve material embedded with TON structure was mixed with distilled water, filtered and washed thoroughly with distilled water for 3 h. As synthesized Na-MM-TON was dried at 110°C and calcined at 550°C using step calcinations procedure for 10 h in a muffle oven.

The mesoporous catalyst material is then transformed to the proton form by ammonium ion exchange and calcination procedures to replace the sodium ions of materials with protons

Before the test reaction, the catalyst material is pressed to plates, crushed and sieved to desired particle size.

Example 8.

Comparative catalyst

Commercial Y-zeolite (TOSOH Corporation HSZ395HUA) was mixed with silica gel (Ludox-AS40). The weight ratio of Y-zeolite to silica gel is 1:1. The formed gel mixture is baked on a plate and dried at 115°C overnight. The material is calcined at 500°C for 2 hours. Then, the catalyst is crushed and sieved to desired particle size.

Example 9.

Comparative catalyst

Mesoporous silica alumina tablets were purchased from Nikki Chemicals. This catalyst is crushed and sieved to the desired particle size, and tested in paraffin cracking.

The properties of the catalyst as well as the cracking conditions and results when using the catalysts are listed in Tables 1 and 2.

Table 1. The properties of catalysts used in the cracking tests.

	Material properties						Catalyst properties		
	Si/Al of material (mol/mol)	Na (mg/kg)	BET (m^2/g)	Meso-porous area (m^2/g)	NH_3-TPD (µmol NH_3/g	Max T NH_3-TPD (°C)	Support content	BET (m^2/g)	NH_3-TPD (µmol NH_3/g
Ex 1	11	50	780	640	290	480	None	780	290
Ex 2	19	40	810	770	180	455	None	810	180
Ex 3	14	12	900	870	210	260	30% silica	600	170
Ex 4	14	121	900	870	210	460	30% alumina	730	380
Ex 5	18	12	715	600	180	390	30% silica	500	143
Ex 6	102	2	775	920	110	425	30% silica	500	80
Ex 7	21	31	800	765	310	500	None	800	310
Ex 8	215	35	685	110	80	360	30% silica	500	12
Ex 9	5	300	400	400	405	350	None	400	405

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 8	Ex. 9
FEED	HDO treated animal fat ATRIA säiliö 17603	HDO treated animal fat ATRIA säiliö 17603	Vetykä sitelty palmu öljy	Vetykä sitelty palmu öljy	n-C16	n-C16	HDO treated animal fat ATRIA säiliö 17603	n-C16	n-C16	HDO treated animal fat ATRIA säiliö 17603
Reaction conditions										
Temperature	350	350	350	350	350	350	350	350	500	350
Pressure, bar(a)	4.0	4	10	10	10	10	4	40	10	4
Feed flow, g/h	3.0	3.0	6.8	6.0	5.6	11.0	3.0	2.4	5.6	3.0
Inert flow, g/h	2.5	2.5	3.6	3.6	3.6	7.1	2.5	3.6	3.6	2.5
Catalyst amount, g	0.7	0.5	2.0	2.0	2.0	4.0	0.7	2.0	2.0	0.7
Conversion, mass balance and yields of fractions										
Coke, %	0.1	0.1	1.0	1.0	1.0	1.0	0.1	1.0	1.0	0.1
Mass balance, %	99.9	99.8	98.4	96.3	98.3	99.4	100.0	99.6	75	100.0
Conversion < 221	**96.3**	**93.3**	**88.2**	**86.8**	**90.6**	**84.1**	**73.1**	**1.5**	**61.5**	**7.8**
DryGas, wt-%	0.3	0.7	0.1	0.1	0.2	0.2	0.5	0.1	4.6	0.0
LPG, wt-%	41.9	49.6	25.9	23.8	22.8	21.8	30.1	0.5	11.4	1.9
Gasoline, wt-%	54.1	43.0	62.2	62.8	67.6	62.1	42.6	1.0	45.6	5.8
221-343	3.4	6.6	2.8	4.5	3.1	3.1	26.6	0.1	6.5	91.9
343 - 410	0.2	0.0	8.5	8.4	5.7	12.3	0.1	98.3	30.7	0.2
> 410	0.1	0.1	0.5	0.4	0.5	0.5	0.2	0.1	1.3	0.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Distribution of compounds in fractions										
DRY GAS										
C1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0
C2	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.1	2.9	0.0
C2=	0.3	0.6	0.1	0.1	0.2	0.2	0.4	0.0	0.7	0.0
Total	**0.3**	**0.70**	**0.11**	**0.11**	**0.22**	**0.18**	**0.49**	**0.12**	**4.56**	**0.02**

Table 2. The parameters and result of examples 1–9.

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 8	Ex. 9
Yield of LPG and selectivity of LPG compounds										
LPG-paraf	8.4	13.6	6.6	6.3	12.3	9.9	11.3	0.2	6.5	0.4
LPG-olef	33.4	36.0	19.3	17.6	10.4	11.8	18.7	0.3	4.9	1.6
Total	**41.9**	**49.6**	**25.9**	**23.8**	**22.8**	**21.8**	**30.1**	**0.5**	**11.4**	**1.9**
C3, wt-%	2.6	5.2	2.0	1.9	4.9	4.2	5.5	0.1	4.1	0.2
C3=	4.4	4.1	1.8	1.6	1.2	1.7	4.7	0.1	2.2	0.3
C4	5.8	8.4	4.6	4.4	7.4	5.8	5.9	0.1	2.5	0.2
iC4	16.7	23.0	11.0	10.1	5.3	3.5	3.7	0.0	0.2	0.7
C4 olefins										
iC4=	5.8	4.0	3.2	2.9	1.8	2.8	4.9	0.0	0.2	0.3
1C4=	1.4	1.0	1.9	1.5	1.3	1.9	0.0	0.1	1.6	0.0
Cis-2C4=	2.1	1.6	1.1	1.0	0.6	0.9	1.7	0.0	0.6	0.1
Trans-2C4=	3.0	2.3	0.4	0.5	0.2	0.2	3.7	0.0	0.1	0.2
Butadiene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	**41.9**	**49.6**	**25.9**	**23.8**	**22.8**	**20.9**	**30.1**	**0.5**	**11.4**	**1.9**
Gasoline (C5-221°C) yield and PONA-distribution										
i-Pentane	4.1	10.4	3.1	2.8			2.6		0.1	0.6
n-Pentane	2.6	3.4	3.2	2.5			4.8		1.1	0.1
Other C5	12.8	7.2	20.4	15.8			10.5		1.4	0.7
C6-hydrocarbons	12.8	11.1	14.4	12.3			11.1		4.7	1.2
C7-hydrocarbons	10.1	7.2	8.2	9.0			6.5		6.5	1.2
Paraffines	3.0	0.8	3.0	4.7	28.0	20.4	1.3		12.7	0.7
Olefins	3.8	0.8	4.9	6.7	26.6	25.2	2.5		7.4	0.7
Naftenes	1.3	0.4	1.6	2.8	3.4	6.7	1.1		2.3	0.2
Aromatics	3.6	1.6	3.4	6.3	9.6	9.7	2.2		9.5	0.4
Total	**54.1**	**43.0**	**62.2**	**62.8**	**67.6**	**62.1**	**42.6**		**45.6**	**5.8**
Gasoline (C5-221°C) yield and PiONA-distribution										
i-Pentane	4.1	10.4	3.1	2.8			2.6		0.1	0.6
n-Pentane	2.6	3.4	3.2	2.5			4.8		1.1	0.1
Other C5	12.8	7.2	20.4	15.8			10.5		1.4	0.7
C6-hydrocarbons	12.8	11.1	14.4	12.3			11.1		4.7	1.2
C7-hydrocarbons	10.1	7.2	8.2	9.0			6.5		6.5	1.2
n-paraffines	1.6	0.4	1.6	2.5	12.4	11.3	0.8		11.5	0.5
i-paraffines	1.4	0.4	1.4	2.1	15.6	9.2	0.5		1.2	0.2
n-Olefins	2.7	0.6	3.4	5.5	12.4	12.6	1.8		6.4	0.6
i-Olefins	0.1	0.0	0.5	0.0	11.8	10.8	0.1		0.0	0.0
Dienes	1.1	0.2	1.0	1.2	2.3	1.8	0.6		0.9	0.0
parafinic naftenes	1.0	0.4	1.3	2.2	1.9	4.2	0.8		2.0	0.1
olefinic naftenes	0.3	0.0	0.3	0.6	1.6	2.6	0.2		0.3	0.2
Aromatics	3.6	1.6	3.4	6.3	9.6	9.7	2.2		9.5	0.4
Total	**54.1**	**43.0**	**62.2**	**62.8**	**67.6**	**62.1**	**42.6**		**45.6**	**5.8**

Table 2, cont.

Claims

1. Process for the preparation of C_2-C_8-hydrocarbons by cracking catalytically one or more hydrocarbons which have been obtained from natural fat or a derivative thereof, **characterized** in that the catalytic cracking is carried out at a temperature between 250 and 450°C using a catalyst based on a zeolite and a mesoporous inorganic oxide.

2. Process according to claim 1, **characterized** in that the natural fat is selected from the glycerides (mono, di and tri) of C_{10}-C_{26} fatty acids.

3. Process according to claim 2, **characterized** in that the natural fat is an animal or plant fat or oil selected from the lauric-myristic acid group (C_{12}-C_{14}) including milk fats as well as coconut oil, palmseed oil, babassu oil, muscat butter oil, laurel seed oil, from the palmitic acid group (C_{16}) including earth animal fats, as well as palm oil and stillingia tallow, the stearic acid group (C_{18}) including fats of earth animals, as well as cocoa butter, shea butter and Borneo tallow, the oleic and linoleic acid group (unsatd. C_{18}) including whale and fish oils as well as tall oil (fatty acid fraction), olive oil, peanut oil, sesame oil, maize oil, sunflower oil, poppy-seed oil, cottonseed oil and soy oil, the linolenic acid group (unsatd. C_{18}) including whale and fish oils as well as linseed oil, perilla oil and hemp oil, the erucic acid group (unsatd. C_{22}) including whale and fish oils as well as rapeseed oil and mustard seed oil, the eleostearic acid group (conjug. unsatd. C_{18}) including whale and fish oils as well as chinese wood oil, fats with substituated fatty acids (ricinoleic acid, C_{18}) such as castor oil.

4. Process according to claim 1, 2 or 3, **characterized** in that the derivative of the natural fat is its corresponding fatty acid component or fatty alcohol.

5. Process according to any one of claims 1–4, **characterized** in that the one or more hydrocarbons have been obtained by removing oxygen from the natural fat, natural oil, or derivative thereof.

6. Process according to claim 5, **characterized** in that the oxygen has been removed by hydrolyzing and decarboxylating, or, preferably, by hydrogenating the natural fat or derivative thereof.

7. Process according to any one of the preceding claims, **characterized** in that the cracking is carried out by feeding said one or more hydrocarbons which have been obtained from a natural fat or a derivative thereof in liquid form through a

reactor containing said catalyst based on a zeolite and a mesoporous inorganic oxide.

8. Process according to claim 7, **characterized** in that the reactor contains the catalyst based on a zeolite and a mesoporous inorganic oxide as a fixed bed.

9. Process according to any one of the preceding claims, **characterized** in that in said catalytic cracking, said one or several C_{10}-C_{22} hydrocarbons are fed to the top of the reactor and the product is recovered from the bottom of the reactor.

10. Process according to any one of the preceding claims, **characterized** in that the catalytic cracking is carried out at a temperature of between 250 and 399°C, preferably between 320 and 380°C.

11. Process according to any one of the preceding claims, **characterized** in that the catalytic cracking is carried out at a pressure of between 0.01–5.0 MPa, preferably between 0.2 and 2.0 MPa.

12. Process according to any one of the preceding claims, **characterized** in that the catalyst based on a zeolite and a mesoporous inorganic oxide is modified with aluminium.

13. Process according to claim 12, **characterized** in that the aluminium content of the catalyst based on a zeolite and a mesoporous inorganic oxide is between 0.5 and 5.0% by weight.

14. Process according to any one of the preceding claims, **characterized** in that the average pore diameter of the zeolite is from 0.2 to 2.0 nm, preferably from 0.3 to 0.7 nm.

15. Process according to any one of the preceding claims, **characterized** in that the zeolite of the catalyst based on a zeolite and a mesoporous inorganic oxide is selected from the group consisting of medium pore zeolites such as MFI-framework zeolite, MTT-framework zeolite, TON-framework zeolite, AEF-framework zeolite, MWW-framework zeolite, FER-framework zeolite and larger pore zeolites such as BEA-framework zeolite, FAU-framework zeolite and MOR-framework zeolite, as well as precursors and mixtures thereof.

16. Process according to claim 15, **characterized** in that the zeolite is selected from the group consisting of MFI-framework zeolite, MTT-framework zeolite, TON-

framework zeolite and MWW-framework zeolite and precursors and mixtures thereof.

17. Process according to any one of the preceding claims, **characterized** in that the mesoporous material of the catalyst based on a zeolite and a mesoporous inorganic oxide comprises Al_2O_3, SiO_2, or a combination of Al_2O_3 and SiO_2.

18. Process according to any one of the preceding claims, **characterized** in that the mesoporous material of the catalyst based on a zeolite and a mesoporous inorganic oxide is selected from the group consisting of aluminosilicates of type M41S (including hexagonal MCM-41, cubic MCM 48 and plate-like MCM-50), MSA-1, MSA-2, MSA-3, MAS-8, and mixtures thereof.

19. Process according to any one of the preceding claims, **characterized** in that the average pore diameter of the mesoporous material is from 2 to 30 nm, most preferably from 2 to 20 nm.

20. Process according to any one of the preceding claims, **characterized** in that the catalyst based on a zeolite and a mesoporous inorganic oxide has been prepared by heating together the zeolite, a precursor of the mesoporous inorganic oxide, water and a mesopore forming compound.

21. Process according to claim 20, **characterized** in that the precursor of the mesoporous inorganic oxide has been selected from the group consisting of silica precursors like tetraethoxy silane (= tetraethyl orthosilicate, TEOS), tetramethyl ammonium silicate, tetraethyl ammonium silicate, sodium silicate, water glass, colloidal silica and fumed silica, and alumina precursors like aluminium sulphate, hydrated aluminium hydroxides, aluminates, aluminium isopropoxide, alumina, and their mixtures.

22. Process according to claim 20 or 21, **characterized** in that the mesopore forming compound has been selected from the group consisting of tetrapropyl ammonium hydroxide, tetrapropyl ammonium bromide, tetradecyl trimethyl ammonium bromide, glycerol, a glycol, a trialkyl amine, sulfolane, tetraethylene pentamine and diethylene glycol dibenzoate.

23. Process according to any one of the preceding claims, **characterized** in that the cracking is carried out in cycles, preferably at between 295 and 395°C and from 6 to 18 hours.

24. Process according to claim 23, **characterized** in that between the cracking periods, the catalyst based on a zeolite and a mesoporous inorganic oxide is regenerated.

25. Process according to claim 24, **characterized** in that the catalyst based on a zeolite and a mesoporous inorganic oxide is regenerated by flushing with hot gas, preferably every 10 to 50 hours, most preferably every 15 to 30 hours.

26. Process according to claim 24 or 25, **characterized** in that the catalyst based on a zeolite and a mesoporous inorganic oxide is regenerated with hot gas at a temperature which is 0 to 50°C, preferably 10 to 30°C higher than the cracking temperature.

27. Process according to claim 24, 25 or 26, **characterized** in that catalyst based on a zeolite and a mesoporous inorganic oxide is regenerated by burning deposited coke, preferably after several hot gas regenerations.

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2009/050324

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G3/00 C10G11/05 C10G11/10 C10G11/18 B01J29/00
B01J35/10 B01J38/04 C10L1/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G B01J C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/027955 A2 (BRAZEN BIOFUELS INC [US]; BRADIN DAVID [US]) 8 March 2007 (2007-03-08) page 2, line 21 - page 3, line 2 page 4, line 6 - line 12 page 6, line 28 - line 30 page 7, line 8 - line 28 page 11, line 6 - page 13, line 2 page 27, line 14 - page 28, line 13 page 29, line 9 - page 31, line 5 ----- -/--	1-27

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
11 September 2009	18/09/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Fax: (+31–70) 340–3016	Bernet, Olivier

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2009/050324

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 2008/020048 A2 (BIOECON INTERNAT HOLDING N V [NL]; O'CONNOR PAUL [NL]; STAMIRES DENNI) 21 February 2008 (2008-02-21) figure 1	1-27
A	CHEW T L; BHATIA S: "Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery" BIORESOURCE TECHNOLOGY, ELSEVIER, GB, vol. 99, no. 17, 23 April 2008 (2008-04-23), pages 7911-7922, XP023182685 ISSN: 0960-8524 [retrieved on 2008-04-23] paragraph [3.1.4]	1-27
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A	EP 1 681 337 A1 (NESTE OIL OYJ [FI]) 19 July 2006 (2006-07-19) the whole document	1-27

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/FI2009/050324

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