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(71) Applicant: **EXXONMOBIL RESEARCH AND ENGINEERING COMPANY** [US/US]; 1545 Route 22 East, P.O. Box 900, Ammandale, NJ 08801-0900 (US).

(72) Inventors: **BUCHANAN, John, S.**; 309 Jamestown Court, Flemington, NJ 08822 (US). **KLIEWER, Wayne, Richard**; 5 Austin Hill Road, Clinton, NJ 08809 (US). **OUMAR-MAHAMAT, Halou**; 501 Township Line Road, Belle Mead, NJ 08502 (US).

(74) Agents: **SHANLEY, Matthew, T.** et al.; Exxonmobil Research and Engineering Company, 1545 Route 22 East, P.O. Box 900, Ammandale, NJ 08801-0900 (US).

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(54) Title: CATALYTIC CRACKING PROCESS FOR BIOFEEDS

(57) Abstract: A process of catalytically cracking a feedstock based on a biocomponent contacts the feedstock with a catalytic cracking catalyst comprising a basic metal oxide on a porous oxide support at an elevated cracking temperature to eliminate oxygen from the biocomponent to form cracked hydrocarbon residues. The basic metal oxide of the cracking catalyst is preferably a metal oxide of Group 2 of the Periodic Table (IUPAC) such as calcium or magnesium on a support comprised of a non-acidic form of alumina such as gibbsite or boehmite. Preferred feedstocks are those based on triglycerides, especially vegetable oils, animal fats and algae oils.



CATALYTIC CRACKING PROCESS FOR BIOFEEDS

FIELD

[0001] This invention relates to the catalytic cracking of biofeeds and more particularly in its preferred forms to the catalytic cracking of triglyceride materials using a basic catalyst.

BACKGROUND

[0002] Petroleum derived fuels supply the majority of the world's energy and petroleum based products are used in a wide range of industrial applications; petrochemicals serve as raw materials for the chemical industry in the manufacture of numerous products. The enormous growth in consumption of crude petroleum during the middle and late twentieth century can be attributed to the ease with which petroleum can be discovered, produced, transported, processed, and utilized. The oil crisis in the 1970s, the depletion of reserves resulting from the growth in consumption, national security issues, price uncertainty, and growing environmental concern over the combustion of fossil fuels highlight major issues associated with the current levels of petroleum use. As a result, there has been renewed interest in the discovery of non-petroleum or "green" fuels, chemicals and sources of energy including wind power, solar power, hydrogen production, fuel cells, and biomass.

[0003] Government regulations are expected to drive the use of increasing amounts of bio-derived liquid fuels. A significant proportion of renewable energy research is devoted to harnessing energy from biomass. Biomass is the only renewable energy source that yields solid, gaseous and liquid fuels and has been described as the renewable energy source with the highest potential to contribute to the energy needs of modern society. Biomass also has the

significant environmental advantage of maintaining some level of carbon balance: even though biomass combustion releases carbon dioxide into the atmosphere, plants consume carbon dioxide in the process of photosynthesis thus tending to an improved carbon balance.

[0004] Ethanol is one option as a gasoline component. Ethanol can be made efficiently from sugar cane in tropical climates but much less efficiently from corn and other crops in temperate zones. Vegetable oils (mainly triglycerides) can be produced effectively in warm climates (e.g. palm oil) or temperate zones (rapeseed, soy) but triglycerides must be converted by some means for use in vehicles. Transesterification is one option for making diesel fuel suitable for use in road vehicles, commonly referred to as biodiesel. Biodiesel (100%, referred to as B100) is a renewable fuel, defined officially by the National Biodiesel Board (USA) according to ASTM D 6751 as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. It is typically produced by a reaction of a vegetable oil or animal fat with an alcohol such as methanol or ethanol in the presence of a catalyst to yield mono-alkyl esters and glycerin, which is removed as a by-product. Biodiesel can be blended with petroleum based diesel fuels for use in existing diesel engines usually with little or no modification to the engine or fuel systems and is thus distinct from the vegetable and waste oils used in diesel engines which have been suitably modified.

[0005] Another potential biomass conversion process is hydrocracking; the process is proven technology but incurs considerable cost for operation, especially in extra hydrogen consumption. Yet another technique used to convert biomass into valuable liquid derivatives is pyrolysis. Pyrolysis is a severe form of thermal cracking with subsequent rearrangement of fragments. The resulting bio-oil can then be used as fuel or for the production of chemicals. Although triglyceride based vegetable oils or animal fats have the potential to be

a suitable source of fuel or hydrocarbons under the right processing conditions, pyrolysis of triglyceride materials is not as well established as with other lignocellulosic biomass sources such as switchgrass, bagasse, etc. and it has been shown that these two types of bio-oils are entirely different in nature. Triglycerides such as those found in canola and other vegetable oils and animal fats are, however, promising feeds for catalytic cracking as they are essentially aliphatic hydrocarbons, apart from the three ester groups. The loss of the six oxygens from the ester groups as water will however leave the remaining hydrocarbon fragments deficient in hydrogen and thus prone to coking and other sorts of aromatization.

[0006] Catalytic cracking of bio-derived liquids has previously been reported. U.S. Patent No. 8,231, 777 (Silva) describes a method of converting oils of vegetable origin to products in the diesel boiling range using conventional fresh or equilibrium FCC catalysts such as zeolites, e.g. ZSM-5, faujasite or mordenite, or with silica-aluminum phosphate (SAPO) or aluminum phosphate (ALPO) in a twin reactor unit with one reactor dedicated to use with the vegetable oil feed. The catalytic cracking of rapeseed oil using commercial FCC equilibrium catalyst (Ecat) and Ecat catalysts with deposited metal (nickel and platinum) is also described by Rao et al in *ChemSusChem* 2010, 3, 807–810¹ with the conclusion that with such catalysts, a judicious choice of metal is vital for performance. The increase in aromatization is confirmed by Dupain et al in *Applied Catalysis B: Environmental*, vol. 72, Issues 1–2, 8 March 2007, 44–61² which reported a high aromatization rate of rapeseed oil fatty acids causing the formation of large amounts of aromatics of up to 30–40 wt.% in the gasoline fraction with relatively high amounts of coke when cracking with a commercial equilibrium catalyst under FCC conditions.

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[0007] Idem et al., *Fuel Processing Technology* 51 (1997) 101-125³ described the catalytic conversion of canola oil over a suite of catalysts, including ZSM-5, silica, silica-alumina, gamma-alumina, calcium oxide and magnesium oxide.

[0008] Thus, while vegetable oils are amenable to catalytic cracking, the yields and product distributions are less than desired when using conventional catalysts such as the commercial FCC catalysts used in this earlier work. For this reason, catalytic cracking of biofeeds is not known to be practiced commercially anywhere.

SUMMARY

[0009] We have now found that basic catalysts, in particular those containing metal oxides such as magnesium and calcium oxides, have the capability to lead to a desirable product distribution in catalytic cracking of feeds containing biocomponents, in particular, to a higher distillate selectivity, a notable advantage with the current increased demand for distillate product for use as road diesel and kerojet. In addition, this distillate is relatively high in non-aromatics (paraffins/naphthenes/olefins) which again is favorable for blending into road diesel and kerojet.

[0010] According to the present invention, a process of catalytically cracking a feedstock which comprises a biocomponent contacts the feedstock with a catalytic cracking catalyst comprising a basic metal oxide on a porous oxide support at an elevated cracking temperature to eliminate oxygen from the biocomponent to form cracked hydrocarbon residues. The basic metal oxide of the cracking catalyst is preferably an oxide of a metal Group 2 of the Periodic

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Table (IUPAC) such as calcium or magnesium on a support comprised of a non-acidic form of alumina such as gibbsite or boehmite. Preferred feedstocks are those based on triglycerides, especially vegetable oils, animal fats and algae oils.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIGURE 1 is an X-ray diffraction pattern from a catalyst containing hydrotalcite as described in the Examples.

[0012] FIGURE 2 is a plot of X-ray diffraction patterns from catalysts containing magnesium oxide and calcium oxide as well as from the calcined alumina support material as described in the Examples.

DETAILED DESCRIPTION OF THE EMBODIMENTS

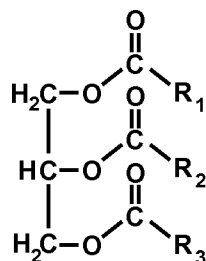
Biofeeds for Catalytic Cracking

[0013] The feed used in the present catalytic cracking process comprises a biocomponent; that is, a component which has been derived from biological sources such as a triglyceride-containing feed. By carrying out the cracking under suitable and effective conditions using a basic cracking catalyst, a feedstock containing triglycerides can be at least partially deoxygenated to produce a cracking product with a substantial portion of useful liquid products.

[0014] A feed derived from a biological source (i.e., a biocomponent feed or feedstock) can be a feedstock derived from a biological raw material component, such as vegetable fats/oils or animal fats/oils, fish oils, pyrolysis oils, and algae lipids/oils, as well as components of such materials, and in some embodiments can specifically include one or more types of lipid compounds. Lipid compounds are typically biological compounds that are insoluble in water, but soluble in nonpolar (or fat) solvents such as alcohols, ethers, chloroform, alkyl

acetates, benzene, and combinations of them. Major classes of lipids include, but are not necessarily limited to, fatty acids, glycerol-derived lipids (including fats, oils and phospholipids), sphingosine-derived lipids (including ceramides, cerebroside, gangliosides, and sphingomyelins), steroids and their derivatives, terpenes and their derivatives, fat-soluble vitamins, certain aromatic compounds, and long-chain alcohols and waxes.

[0015] Biofeeds containing triglycerides are preferred for this catalytic cracking process. Triglycerides are present in many typical sources used as feedstock for making renewable products and are promising feeds for catalytic cracking. Typical triglycerides useful for making renewable products include a three carbon glycerol backbone that has ester linkages to three longer side chains shown in the structure:



where R_1 , R_2 and R_3 are three alkyl groups, typically long chain alkyl groups of about 12 to about 30 carbon atoms, more usually from 16 to 22 carbon atoms. If the six oxygens from the ester groups leave as H_2O , the remaining hydrocarbon fragments are deficient in hydrogen, and the fragments are then prone to aromatization which, through the formation of polycyclic aromatics, may lead to coking and a decrease in liquid products. According to the present invention, however, the use of basic cracking catalysts, in particular those containing calcium or magnesium, can lead to a desirable product distribution with increased yields of non-aromatic distillate.

[0016] Triglycerides are plentiful in nature and can be found in a wide variety of natural sources, described briefly below. The main classes of such sources include vegetable oils, animal fats and oils and algae lipids and oils. Examples of vegetable oils that can be used include, but are not limited to rapeseed (canola) oil, soybean oil, coconut oil, sunflower oil, palm oil, palm kernel oil, peanut oil, linseed oil, tall oil, corn oil, castor oil, jatropha oil, jojoba oil, olive oil, flaxseed oil, camelina oil, safflower oil, babassu oil, tallow oil and rice bran oil. Useful vegetable oils also include processed vegetable oil materials such as the fatty acids and fatty acid alkyl esters derived from vegetable oils, e.g. typically, C₁-C₅ alkyl esters with the methyl, ethyl, and propyl esters preferred. Examples of animal fats that can be used include beef fat (tallow), hog fat (lard), turkey fat, fish fats/oils especially from forage fishes such as menhaden, and chicken fat. The animal fats can be obtained from any suitable source including restaurants, meat production facilities and slaughterhouses. Animal fats (also including processed animal fat materials) also include fatty acids and fatty acid alkyl esters, e.g. the C₁-C₅ alkyl esters with the methyl, ethyl, and propyl esters being again preferred.

[0017] Algae oils or lipids can typically be contained in algae in the form of membrane components, storage products, and/or metabolites. Certain algal strains, particularly microalgae such as diatoms and cyanobacteria, can contain proportionally high levels of lipids. Algal sources for the algae oils can contain varying amounts, *e.g.*, from 2 wt% to 40 wt% of lipids, based on total weight of the biomass itself.

[0018] Algal sources for algae oils can include, but are not limited to, unicellular and multicellular algae. Examples of such algae can include a rhodophyte, chlorophyte, heterokontophyte, tribophyte, glaucophyte, chlorarachniophyte, euglenoid, haptophyte, cryptomonad, dinoflagellum, phytoplankton, and the like, and combinations thereof. In one embodiment,

algae can be of the classes Chlorophyceae and/or Haptophyta. Specific species can include, but are not limited to, *Neochloris oleoabundans*, *Scenedesmus dimorphus*, *Euglena gracilis*, *Phaeodactylum tricornutum*, *Pleurochrysis carterae*, *Prymnesium parvum*, *Tetraselmis chui*, and *Chlamydomonas reinhardtii*. Additional or alternate algal sources can include one or more microalgae of the *Achnanthes*, *Amphiprora*, *Amphora*, *Ankistrodesmus*, *Asteromonas*, *Boekelovia*, *Borodinella*, *Botryococcus*, *Bracteococcus*, *Chaetoceros*, *Carteria*, *Chlamydomonas*, *Chlorococcum*, *Chlorogonium*, *Chlorella*, *Chroomonas*, *Chrysosphaera*, *Cricosphaera*, *Crypthecodinium*, *Cryptomonas*, *Cyclotella*, *Dunaliella*, *Ellipsoidon*, *Emiliana*, *Eremosphaera*, *Ernodesmius*, *Euglena*, *Franceia*, *Fragilaria*, *Gloeothamnion*, *Haematococcus*, *Halocafeteria*, *Hymenomonas*, *Isochrysis*, *Lepocinclis*, *Micractinium*, *Monoraphidium*, *Nannochloris*, *Nannochloropsis*, *Navicula*, *Neochloris*, *Nephrochloris*, *Nephroselmis*, *Nitzschia*, *Ochromonas*, *Oedogonium*, *Oocystis*, *Ostreococcus*, *Pavlova*, *Parachlorella*, *Pascheria*, *Phaeodactylum*, *Phagus*, *Platymonas*, *Pleurochrysis*, *Pleurococcus*, *Prototheca*, *Pseudochlorella*, *Pyramimonas*, *Pyrobotrys*, *Scenedesmus*, *Skeletonema*, *Spyrogyra*, *Stichococcus*, *Tetraselmis*, *Thalassiosira*, *Viridiella*, and *Volvox* species, and/or one or more cyanobacteria of the *Agmenellum*, *Anabaena*, *Anabaenopsis*, *Anacystis*, *Aphanizomenon*, *Arthrospira*, *Asterocapsa*, *Borzia*, *Calothrix*, *Chamaesiphon*, *Chlorogloeopsis*, *Chroococcidiopsis*, *Chroococcus*, *Crinalium*, *Cyanobacterium*, *Cyanobium*, *Cyanocystis*, *Cyanospira*, *Cyanothece*, *Cylindrospermopsis*, *Cylindrospermum*, *Dactylococcopsis*, *Dermocarpella*, *Fischerella*, *Fremyella*, *Geitleria*, *Geitlerinema*, *Gloeobacter*, *Gloeocapsa*, *Gloeothece*, *Halospirulina*, *Iyengariella*, *Leptolyngbya*, *Limnothrix*, *Lyngbya*, *Microcoleus*, *Microcystis*, *Myxosarcina*, *Nodularia*, *Nostoc*, *Nostochopsis*, *Oscillatoria*, *Phormidium*, *Planktothrix*, *Pleurocapsa*, *Prochlorococcus*, *Prochloron*, *Prochlorothrix*, *Pseudanabaena*, *Rivularia*, *Schizothrix*, *Scytonema*, *Spirulina*, *Stanieria*, *Starria*, *Stigonema*, *Symploca*, *Synechococcus*, *Synechocystis*, *Tolypothrix*, *Trichodesmium*, *Tychonema*, and *Xenococcus* species.

[0019] Table 1 below compares the fatty acid analysis (wt. pct. by gas chromatography) of various natural sources.

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Table 1
Fatty Acid Profiles of Natural Source Oils

Fatty acid	Double bond position ²	Rapeseed	Sunflower	<i>Nannochloropsis salina</i>	<i>Phaeodactylum tricornutum</i>	<i>Botryococcus braunii</i>
C12:0 ¹	—	—	—	5	—	0.7
C14:0	—	—	—	—	4.5	0.8
C15:0	—	—	—	0.5	—	0.5
C16:0	—	4.9	6.2	37.5	25.8	21
C16:1	9	—	0.1	23.3	37.5	2
C16:2	7, 10	—	—	—	—	6.5
C16:3	7,10,13	—	—	—	—	15.2
C17:0	—	—	—	0.4	—	0.1
C18:0	—	1.6	3.7	0.9	1.3	2.9
C18:1	9	33	25.2	11.9	—	3.2
C18:2	9,12	20.4	63.1	1.5	5.1	13.6
C18:3	9,12,15	7.9	0.2	—	2	33
C20:0	—	—	0.3	0.1	—	0.2
C20:1	11	9.3	0.2	—	—	—
C22:0	—	—	0.7	—	—	0.1
C20:4	5,8,11,14	—	—	3.3	1.6	—
C20:5	5,8,11,14,17	—	—	15.3	13.1	—
C22:0	—	—	—	0.4	—	—
C22:1	13	23	0.1	—	—	—
C24:0	—	—	0.2	—	—	0.2
C24:1	15	—	—	—	—	—

Notes:

1. Fatty acid with chain length of 12 carbon atoms and 0 double bonds. The same nomenclature applies for all other fatty acids
2. Double bond position beginning from the carboxyl group.

[0020] The preferred biocomponent feeds include any of those which comprise primarily triglycerides and free fatty acids (FFAs). The triglycerides and FFAs typically contain aliphatic hydrocarbon chains in their structure having from 8 to

36 carbons, preferably from 10 to 26 carbons, for example from 14 to 22 carbons. Types of triglycerides can be determined according to their fatty acid constituents. The fatty acid constituents can be readily determined using Gas Chromatography (GC) analysis. This analysis involves extracting the fat or oil, saponifying (hydrolyzing) the fat or oil, preparing an alkyl (*e.g.*, methyl) ester of the saponified fat or oil, and determining the type of ester using GC analysis. In one embodiment, a majority (*i.e.*, greater than 50%) of the triglyceride present in the lipid material can be comprised of C₁₀ to C₂₆ fatty acid constituents, based on total triglyceride present in the lipid material. A majority of triglycerides present in the biocomponent feed are preferably comprised of C₁₂ to C₁₈ fatty acid constituents, based on total triglyceride content. Other types of feed that are derived from biological raw material components can include fatty acid esters, such as fatty acid alkyl esters (*e.g.*, FAME and/or FAEE).

[0021] The biocomponent portion of a feedstock can also be characterized relative to the olefin content of the feed. The olefin content of a biocomponent feed can vary widely depending on the source of the feed. For example, a feed based on soybean oil may contain up to 100% of molecules that contain at least one degree of unsaturation. Palm oils typically include 25 – 50 wt% of olefinic molecules, while coconut oil may include 15% or less of olefinic molecules. Depending on the embodiment, a biocomponent portion of a feed can include at least about 20 wt% olefins, such as at least about 40 wt% olefins, or at least about 50 wt% olefins, or at least about 75 wt% olefins where the olefin is any compound that includes an olefin bond. Thus, there are two ways that the proportion of olefins in a feed can be modified. If all olefins in a molecule are saturated, the molecule is no longer an olefin. Alternatively, if a molecule is broken down into smaller components, such as by the cracking, the proportion of olefins may be reduced if one or more of the smaller components does not contain an olefin. As an example, a triglyceride with an olefin bond in only one of the three side chains would be considered an olefin. Therefore, the entire

weight of the triglyceride would count toward the olefin weight percentage in the feed. After a deoxygenative cracking that preserved olefin bonds, only the fatty acid resulting from the side chain including the olefin bond would count toward the olefin weight percentage. The other two fatty acids formed from the side chains would be separate molecules and therefore would not be considered olefins. Thus, even though no olefins were saturated, the weight percentage of olefins in the feed would still be lower.

[0022] The biocomponent portion of the feedstock (such as the triglycerides) can be a hydrotreated or non-hydrotreated portion. A non-hydrotreated feed can typically have an olefin content and an oxygen content similar to the content of the corresponding raw biocomponent material. Examples of treated biocomponent feeds include food grade vegetable oils, and biocomponent feeds that are refined, bleached, and/or deodorized.

[0023] Biocomponent based feeds will normally contain oxygen in addition to nitrogen and sulfur as other heteroatoms. A biocomponent feedstream based on a vegetable oil may include up to about 10 wt% oxygen, for example, at least about 1 wt% oxygen, for example at least about 2 wt%, at least about 3 wt%, at least about 4 wt%, at least about 5 wt%, at least about 6 wt%, or at least about 8 wt% or even more, e.g. up to about 12 wt% or up to about 14 wt%. The olefin content of the biocomponent feedstream (assuming no prior hydrotreatment), can include an olefin content of at least about 3 wt%, for example at least about 5 wt% or at least about 10 wt%, depending on the source of the biocomponent. The number of double bonds in the fatty acid portions of the biofeeds can typically vary from zero up to four: oleic acid, for example, has one double bond, linoleic acid has two, and others have three or four as shown in Table 1. Since olefinic double bonds have a faster cracking rate, the presence of olefinic bonds in the hydrocarbon fragments is favorable to the cracking process so that biocomponents such as the triglycerides derived from oleic, linoleic, linolenic,

arachidonic acids are favored for their amenability to cracking has four as are the fatty acids in fish oils which may contain up to six or more double bonds.

[0024] The feed can include at least about 10 wt% of feed based on a biocomponent source or sources, or higher amounts, for example, at least about 25 wt%, at least about 50 wt%, or at least about 75 wt%, or at least about 90 wt%, or at least about 95 wt%. Given the differing cracking characteristics of biocomponent feeds and mineral oil feeds it is normally preferred to carry out the cracking in a unit dedicated to biocomponent feed cracking, i.e. with a feed comprised entirely of biocomponent(s).

[0025] Biocomponent feedstreams can have a wide range of nitrogen and/or sulfur contents in addition to the oxygen content. For example, a biocomponent based feedstream based on a vegetable oil source can contain up to about 300 wppm nitrogen while a biomass based feedstream containing whole or ruptured algae can contain even more nitrogen, for instance, at least about 2 wt%, for example at least about 3 wt%, at least about 5 wt%, or at least about 10 wt%; algae with still higher nitrogen contents are known. The sulfur content of a biocomponent feed can also vary. In some cases, the sulfur content can be about 500 wppm or less, for example about 100 wppm or less, about 50 wppm or less, or about 10 wppm or less.

Cracking Catalyst

[0026] According to the present invention, the cracking feed including a biocomponent, preferably one which contains triglycerides, is subjected to catalytic cracking over a cracking catalyst which contains a basic metal component. The catalyst will normally have the basic metal component on a porous oxide support in order to provide a greater surface area on which the cracking reactions can occur; support materials with a high surface area,

typically at least $100 \text{ m}^2/\text{g}$ are preferred. The support may typically comprise a metal oxide such as activated alumina, titania ceria, zirconia or may be a mixed oxide such as silica-alumina. Supports that have a low degree of acidity (as typically measured by the alpha value) are preferred such as the non-acidic forms of alumina e.g. boehmite ($\gamma\text{-AlO(OH)}$), gibbsite, silica titania.

[0027] Gamma-alumina represents a good choice for catalytic applications because of a defect spinel crystal lattice that imparts to it a structure that is both open and capable of high surface area. Gamma-alumina, commonly used as a catalytic support for automotive and industrial catalysts, typically has a face-centered cubic close-packed oxygen sublattice structure having a high surface area typically of $150\text{-}300 \text{ m}^2/\text{g}$, a large number of pores with diameters of $30 - 120 \text{ \AA}$ and a pore volume of 0.5 to $> 1 \text{ cm}^3/\text{g}$, making it particularly useful as a catalytic support. Flash calcined gibbsite (rho-alumina), e.g. CP powder manufactured by Almatris AC, Inc. of Vidalia, LA, is notable for its high surface area, typically over 100 or $200 \text{ m}^2/\text{g}$, e.g. with a BET surface area of $120\text{-}150 \text{ m}^2/\text{g}$ and even higher, e.g. 250 or $350\text{-}420 \text{ m}^2/\text{g}$.

[0028] The support may suitably be formed into catalyst particles suitable for use in the FCC process by spray drying a slurry of the support material in the conventional manner, to produce catalyst particles with a particle size not more than 100μ and in most cases in the range of $20\text{-}100\mu$.

[0029] The basic component of the catalyst is provided by a basic metal compound, typically an alkaline earth metal (in oxide form) of Group 2 of the Periodic Table (IUPAC table), especially calcium and magnesium; beryllium will not normally be used in view of its toxicity while the heavier metals strontium and barium are not expected to offer any advantage over the more readily accessible calcium and magnesium. The metals of Group 1 (alkali metals) are not favored in view of the reactivity in oxide form towards water

which is generated during the cracking reaction by release of the oxygens from the biofeed component. Basic mixed metal oxides of a basic metal such as magnesium are useful, for example, hydrotalcite, $(\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4(\text{H}_2\text{O}))$ are also useful. Supported catalysts with hydrotalcite as the basic metal oxide may be particularly effective in view of the high surface area of the hydrotalcite component. The proportion of alkaline earth metal in the catalyst is normally at least 5 mol percent relative to the metal of the porous support material and preferably higher, typically at least 10 mol percent or more, e.g. 20, 25, 30, 40 or 50 mol percent (mol percent = molar ratio of total non-support metals/support metals x 100).

[0030] The basic metal component may conveniently be incorporated into the support by impregnation using an aqueous solution of a salt of the metal, preferably by the incipient wetness technique. Incorporation by ion-exchange will not normally be an option since the support material will not have sufficient acid sites capable of engaging in cation exchange with the cations of the basic metal. Suitable metal salts of the preferred basic metals will include acetates, nitrate and chlorides; magnesium sulfate is also a choice, being readily soluble in water although the corresponding calcium salt is not. Following impregnation, the support with the impregnated salt is calcined to convert the salt to oxide form; calcination temperatures of at least about 400°C are preferred with higher temperatures being also suitable, e.g. 500°C, 600°C, 700°C or 800°C, depending on available equipment.

[0031] As an alternative to the impregnation of the basic metal, it may be directly added during the catalyst formulation by mixing with a slurry of the support material and optional binders followed by spray drying of the slurry in the normal way with calcination to confer finished strength. In this way, relatively high proportions of the basic metal oxide may be incorporated, for example, up to 50 wt. pct. of the catalyst or even more. If the basic metal oxide

inherently has a high surface area such as the hydrotalcite mentioned above, a finished catalyst with a desirably high surface area may be made.

[0032] One parameter of the finished cracking catalyst that is significant is its acidity and activity for catalytic cracking as measured by the conventional alpha value. Alpha activity is a dimensionless value which reflects the relative activity of the catalyst with respect to a high activity silica-alumina cracking catalyst. The method of determining alpha, is described in the Journal of Catalysis, Vol. VI, pages 278-287, 1966. For the present purposes, it is preferred that the alpha activity of the catalyst should be not more than 5, and preferably not more than 2 or even less, preferably less than 1 or less than 0.5. Aluminas, e.g. gamma alumina, typically have alpha values less than 1, and thus are considered low-acidity materials compared to zeolite or the silica-alumina components of cracking catalysts.

Catalytic Cracking

[0033] The cracking of the biocomponent-containing feed is suitably carried out by the fluid catalytic cracking process (FCC) although moving bed cracking is also contemplated if lower catalyst:feed ratios can be accepted. Fluid catalytic cracking can be operated using conventional equipment and under the normal FCC conditions with a temperature (riser top temperature in a riser type unit) of at least about 400°C and usually higher, e.g. 500°C or 550°C although lower temperatures may be feasible with a practical minimum of 300°C, and typically in the range 300-500°C, e.g. 350-450°C. Catalyst:feed ratios (by weight) will typically be at least about 2:1 and preferably higher, e.g. 4:1, 5:1 6:1 or even higher. Pressures in the cracker will be within normal limits i.e. at moderate pressures up to about 2 barg, e.g. about 1.5-1.7 barg. Other conditions such as steam:feed ratio, riser residence time, etc. can be chosen according to the specific catalyst and feed in use, as dictated by empirical means to achieve the

desired hydrocarbon product distribution which will of course, vary with the selected cracking conditions.

[0034] The boiling range for biocomponent feedstreams can vary depending on the nature of the biocomponent source. Although biocomponent feedstreams with final boiling points up to about 540°C (1000°F) may be suitable for use, many will have lower boiling ranges. One parameter that will be significant in the selected cracking conditions in normal commercial scale operation is, however, not the boiling point of the feed but its smoke point since this is the value at which decomposition and charring of the oil begins. Depending on the residence time of the biocomponent in the feed preheating system it may be desirable to limit the preheat temperature of the feed to the value of the smoke point or a value not far removed above it if excessive thermal degradation of the feed during the preheating is to be avoided and coking of the preheat furnace kept at an acceptable level. While preheater furnace temperatures as high as about 360°C (680°F) or 420°C (about 785°F), depending on location of measurement, are common when cracking mineral oil feeds, restriction of the preheat to a value not much above the smoke point of the feed (or, the smoke point of the biofeed component with the lowest smoke point with mixed feeds) may limit preheat temperature so as not to exceed about 225°C (about 440°F) except for feeds containing refined vegetable oils. The smoke points of some typical unrefined vegetable oils can be quite low, e.g. about 110°C (about 225°F) for canola, flaxseed or sunflower oils, about 160°C (about 320°F) for corn oil, high-oleic sunflower oil, peanut, soy walnut and olive oil; while the smoke points of refined vegetable oils and animal fats can be significantly higher, their use will not normally be economically attractive and for this reason, use of the lower preheat temperatures will frequently be favored with the unrefined oils, again depending on residence time in the preheat system. If preheat temperatures are kept at a low order, it may be necessary or desirable to increase the catalyst circulation rate (catalyst:oil ratio) and/or to increase regenerator

temperature in order to reach normal cracking temperatures (e.g. 550°C). The use of the relatively lower cracking temperatures referred to above may therefore be favored if the degree of preheat has to be limited.

[0035] The use of the basic cracking catalysts with the biocomponent feeds is capable of producing an enhanced yield of distillate hydrocarbons boiling above the gasoline boiling range (i.e. above 200°C/392°F) which is of particular advantage at present times with an increased demand for distillate product for use as road diesel and kerojet fuel. Typically, the distillate proportion of the C₅+ liquid fraction will be at least 25 wt. pct. of the total C₅+ liquid hydrocarbon fraction. In addition, the distillate fraction contains a higher proportion of non-aromatics (paraffins/naphthenes/olefins) which again is favorable for blending into road diesel and kerojet. The P/N/O proportion is typically at least 40 wt. pct. or even at least 50 wt. pct., as compared to not more than 30 wt. pct when using a conventional FCC cracking catalyst.

Blended Feeds

[0036] While the present cracking process achieves its most notable effects when the basic catalyst is used to crack feeds comprising 100 percent of the biocomponent, mixed feeds of the biocomponent and a mineral oil component such as those typically derived from crude oil or shale oil that has optionally been subjected to one or more separation and/or other refining processes may be combined with the biocomponent feed. These feeds have the potential to be used even though the normal acid-mediated cracking reactions cannot be expected to occur to any significant if any extent although some thermal cracking may be expected especially at higher temperatures. For this reason, the use of 100% biocomponent feeds is favored.

[0037] One option for increasing the biocomponent content of a feed is to use recycled product from processing of biocomponent feed as a diluent. A recycled product from processing a biocomponent feed is still derived from a biocomponent source, and therefore such a recycled product can be counted as a feed portion from a biocomponent source. Thus, a feed containing 60% biocomponent feed that has not been processed and 40% of a recycled product from processing of the biocomponent feed can be considered as a feed that derived wholly from biocomponent. As an example, at least a portion of the product from processing of a biocomponent feed can be a diesel boiling range (200-350°C) product. If a recycled product flow is added to the input to a deoxygenation process, the amount of recycled product can correspond to at least about 10 wt% of the feed to the deoxygenation process, such as at least about 25 wt%, or at least about 40 wt%. Alternatively, the amount of recycled product in a feed can be about 60 wt% or less, such as about 50 wt% or less, 40 wt% or less, or about 25 wt% or less.

Additional Embodiments

[0038] Embodiment 1. A process of catalytically cracking a feedstock comprising a biocomponent which comprises contacting a feedstock comprising a biocomponent with a catalytic cracking catalyst comprising a basic metal oxide on a porous oxide support at an elevated cracking temperature to eliminate oxygen from the biocomponent to form cracked hydrocarbon residues.

[0039] Embodiment 2. A process according to embodiment 1, wherein the basic metal oxide comprises an oxide of a metal of Group 2 of the Periodic Table (IUPAC).

[0040] Embodiment 3. A process according to any prior embodiment, wherein the basic metal oxide is calcium or magnesium.

[0041] Embodiment 4. A process according to any prior embodiment, wherein the cracking catalyst has a surface area (BET) of at least 30 m²/g.

[0042] Embodiment 5. A process according to any prior embodiment, wherein the cracking catalyst has a surface area (BET) of at least 50 m²/g.

[0043] Embodiment 6. A process according to any prior embodiment, wherein the porous oxide support comprises a metal oxide.

[0044] Embodiment 7. A process according to any prior embodiment, wherein the porous oxide support comprises a low-acidity alumina.

[0045] Embodiment 8. A process according to embodiment 6, wherein the proportion of the metal of the basic metal oxide in the catalyst is at least 5 mol percent relative to the metal of the porous support material.

[0046] Embodiment 9. A process according to embodiment 6, wherein the proportion of the metal of the basic metal oxide in the catalyst is at least 10 mol percent relative to the metal of the porous support material.

[0047] Embodiment 10. A process according to embodiment 6, wherein the proportion of the metal of the basic metal oxide in the catalyst is at least 20 mol percent relative to the metal of the porous support material.

[0048] Embodiment 11. A process according to any prior embodiment, wherein the feedstock comprises a biocomponent comprising at least one triglyceride.

[0049] Embodiment 12. A process according to any prior embodiment, wherein the feedstock comprises a biocomponent comprising a vegetable oil.

[0050] Embodiment 13. A process according to any prior embodiment, wherein the feedstock comprises a biocomponent and a mineral oil.

[0051] Embodiment 14. A process according to any of embodiments 1-12, wherein the feedstock comprises a biocomponent and a processed biocomponent.

[0052] Embodiment 15. A process according to any prior embodiment, wherein the hydrocarbon residues produced from the catalytic cracking comprise not more than 60 weight percent aromatics.

[0053] Embodiment 16. A process according to any prior embodiment, wherein the hydrocarbon residues produced from the catalytic cracking comprise not more than 50 weight percent aromatics.

[0054] Embodiment 17. A process according to any prior embodiment, wherein the hydrocarbon residues produced from the catalytic cracking comprise at least 40 weight percent paraffins/naphthenes/olefins.

[0055] Embodiment 18. A process according to any of embodiments 1-14, wherein in the hydrocarbon residues produced from the catalytic cracking comprise at least 50 weight percent paraffins/naphthenes/olefins.

[0056] Embodiment 19. A process according to any prior embodiment, wherein the hydrocarbon residues produced from the catalytic cracking comprise at least 15 weight percent distillate boiling above the gasoline boiling range.

[0057] Embodiment 20. A process according to any prior embodiment, wherein the hydrocarbon residues produced from the catalytic cracking comprise at least 2 weight percent ethylene.

[0058] Embodiment 21. A process according to any prior embodiment, wherein the catalyst comprises MgO.

[0059] Embodiment 22. A process according to embodiment 21, wherein the catalyst further comprises Al_2O_3 .

EXAMPLE

Catalyst Formulation

[0060] Basic catalysts were formulated as follows. Two slurries were prepared. Both slurries contained 12 wt% aluminum chlorohydrate with 38 wt% kaolin to bind the material. Each slurry was then mixed to contain 50 wt% of either gibbsite alumina or hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4(\text{H}_2\text{O})$). Subsequent spray drying occurred at 174 kPag (25 psig) air pressure, a feed rate of 300 cc/min, and an outlet temperature of 149°C (300°F). The resulting particulate matter was then calcined at 500°C with a temperature ramp of 7°C/min with a hold at 500°C for 15 minutes and then cooled.

[0061] The calcined gibbsite alumina support was then impregnated using the incipient wetness technique with either Ca acetate or Mg acetate (as aqueous solution) followed by calcination calcined at 800°C with a temperature ramp of 4.3°C/min with a hold at 500°C for 15 minutes followed by cooling in order to convert the metal acetates to metal oxides.

[0062] The catalysts were then characterized using density measurements, alpha activity, temperature programmed ammonia adsorption, Brunauer-Emmett-Teller (BET) surface area (SA), metal loadings analysis, and x-ray diffraction (XRD) to give the characteristics shown in Table 2 below. The BET

surface area and density of an FCC equilibrium catalyst recovered from a commercial FCCU are also given for purposes of comparison.

Table 2
Catalyst Characteristics

Catalyst	Total BET SA, m ² /g	NH ₃ Adsorption, meq/g	Alpha Activity(1)	Metal Loading(2)	Density, g/ml.
Hydrotalcite	141	0.348	0.44	0.23230	0.5854
CaO/Al₂O₃	72	0.087	0.52	0.10860	0.9144
MgO/Al₂O₃	56	0.058	0.2	0.59840	1.0910
Equilibrium	126	--	--	--	0.8695

Notes:

1. Determined by the method described in the *Journal of Catalysis*, Vol. VI, pages 278-287, 1966.
2. Metal loading: molar ratio of total non-Al metals/Al

[0063] The X-ray diffraction pattern of the gibbsite/hydrotalcite catalyst is shown in Figure 1 and those for the CaO/gibbsite and MgO/gibbsite catalysts in Figure 2. On the basis of data on MgO and CaO standards from the International Center for Diffraction Data, pure CaO has a dominant peak at 37.4 degrees (2-theta), and smaller ones at 53.6 and 32.2 degrees. There are almost no peaks in the XRD pattern for the CaO/Al₂O₃ catalyst, indicating a largely amorphous material, certainly not mainly CaO. Pure MgO (mineral name: periclase) has major peaks at 43 and 62.3 degrees, and a minor peak at about 37 degrees. In the XRD pattern for the MgO/Al₂O₃ catalyst, small peaks can be seen at those positions but the major peaks (e.g. 37, 45, 65 degrees) correspond to the mineral spinel, with the formula MgAl₂O₄. Comparison with the XRD pattern for spinel implies that the dominant phase is the spinel as a result of reaction between the Mg with the alumina support in the course of the final 800°C calcination, to form the mixed metal oxide although a small amount of MgO is also present.

Catalyst Evaluation

[0064] The catalysts were evaluated by cracking low erucic acid rapeseed oil (also known as Canola oil) using a batch FCC microreactor at 552°C (1025°F) and catalyst-to-oil ratio of 6. The commercial equilibrium catalyst was run as a standard for data comparison. The results are shown in Tables 3 and 4 below. Table 3 reports the total product distribution and Table 4 the hydrocarbon analysis of the liquid phase.

Table 3
Product Distribution of Rapeseed Oil Catalytic Cracking

Catalyst	Hydrotalcite	CaO/Al ₂ O ₃	MgO/Al ₂ O ₃	Equilibrium
Hydrogen	0.06	0.10	0.06	0.07
Methane	1.59	1.52	1.35	0.99
Ethane	2.23	2.08	1.93	0.69
Ethylene	2.84	2.95	2.81	1.12
Propane	1.57	1.57	1.46	1.32
Propylene	3.93	3.35	3.20	5.80
Total C ₁ -C ₃	12.22	11.57	10.81	9.99
Butane/Butenes	5.21	4.69	4.46	8.97
Gasoline	40.16	41.48	42.14	44.53
Distillate	17.87	17.39	18.35	13.64
Bottoms	4.05	4.58	5.07	3.06
Coke	7.66	7.62	6.19	7.46
Total C ₅ + Liquids	67.29	68.14	70.02	70.2
Gasoline wt % of TLP	59.68	60.87	60.18	63.43
Distillate wt % of TLP	26.56	25.52	26.21	19.43
CO,CO ₂ ,H ₂ O	12.82	12.66	12.98	12.36

Table 4
Microhydrocarbon Analysis (MHA) Composition Liquid Phase
Cracking of Rapeseed Oil

Catalyst	Hydrotalcite	CaO/Al₂O₃	MgO/Al₂O₃	Equilibrium
Paraffins	4.1	3.9	2.7	7.6
Naphthenes/Olefins	51.4	52.6	55.4	21.9
Total P/N/O	55.4	56.5	58.1	29.5
1 Ring Aromatics	29.9	29.0	28.8	41.2
2 Ring Aromatics	10.9	10.7	10.0	21.2
3-5 Ring Aromatics	3.8	3.7	3.1	8.1
Total Aromatics	44.6	43.5	41.9	70.5

[0065] The results displayed in Tables 3 and 4 demonstrate the advantage of using basic catalysts over zeolite-containing acidic catalysts: the basic catalysts produce more distillate and the resulting FCC liquid fraction contains less aromatics, potentially requiring less hydrogen treatment to upgrade to finished fuels. In addition, surprisingly, the MgO/Al₂O₃ had notably lower coke make, lower C1-C3 yields, and lower aromatics in the liquid phase compared to the other catalysts.

CLAIMS:

1. A process of catalytically cracking a feedstock comprising a biocomponent which comprises contacting a feedstock comprising a biocomponent with a catalytic cracking catalyst comprising a basic metal oxide on a porous oxide support at an elevated cracking temperature to eliminate oxygen from the biocomponent to form cracked hydrocarbon residues.
2. A process according to claim 1, wherein the basic metal oxide comprises an oxide of a metal of Group 2 of the Periodic Table (IUPAC).
3. A process according to claim 2, wherein the basic metal oxide is calcium or magnesium.
4. A process according to any of claims 1-3, wherein the cracking catalyst has a surface area (BET) of at least 30 m²/g.
5. A process according to claim 4, wherein the cracking catalyst has a surface area (BET) of at least 50 m²/g.
6. A process according to any of claims 1-5, wherein the porous oxide support comprises a metal oxide.
7. A process according to claim 6, wherein the porous oxide support comprises a low-acidity alumina.
8. A process according to claim 6 or claim 7, wherein the proportion of the metal of the basic metal oxide in the catalyst is at least 5 mol percent relative to the metal of the porous support material.

9. A process according to claim 8, wherein the proportion of the metal of the basic metal oxide in the catalyst is at least 10 mol percent relative to the metal of the porous support material.

10. A process according to claim 9, wherein the proportion of the metal of the basic metal oxide in the catalyst is at least 20 mol percent relative to the metal of the porous support material.

11. A process according to any of claims 1-10, wherein the feedstock comprises a biocomponent comprising at least one triglyceride.

12. A process according to any of claims 1-11, wherein the feedstock comprises a biocomponent comprising a vegetable oil.

13. A process according to any of claims 1-12, wherein the feedstock comprises a biocomponent and a mineral oil.

14. A process according to any of claims 1-13, wherein the feedstock comprises a biocomponent and a processed biocomponent.

15. A process according to any of claims 1-14, wherein the hydrocarbon residues produced from the catalytic cracking comprise not more than 60 weight percent aromatics.

16. A process according to claim 15, wherein the hydrocarbon residues produced from the catalytic cracking comprise not more than 50 weight percent aromatics.

17. A process according to claim 16, wherein the hydrocarbon residues produced from the catalytic cracking comprise at least 40 weight percent paraffins/naphthenes/olefins.

18. A process according to any of claims 1-17, wherein in the hydrocarbon residues produced from the catalytic cracking comprise at least 50 weight percent paraffins/naphthenes/olefins.

19. A process according to any of claims 1-18, wherein the hydrocarbon residues produced from the catalytic cracking comprise at least 15 weight percent distillate boiling above the gasoline boiling range.

20. A process according to any of claims 1-19, wherein the hydrocarbon residues produced from the catalytic cracking comprise at least 2 weight percent ethylene.

1/2

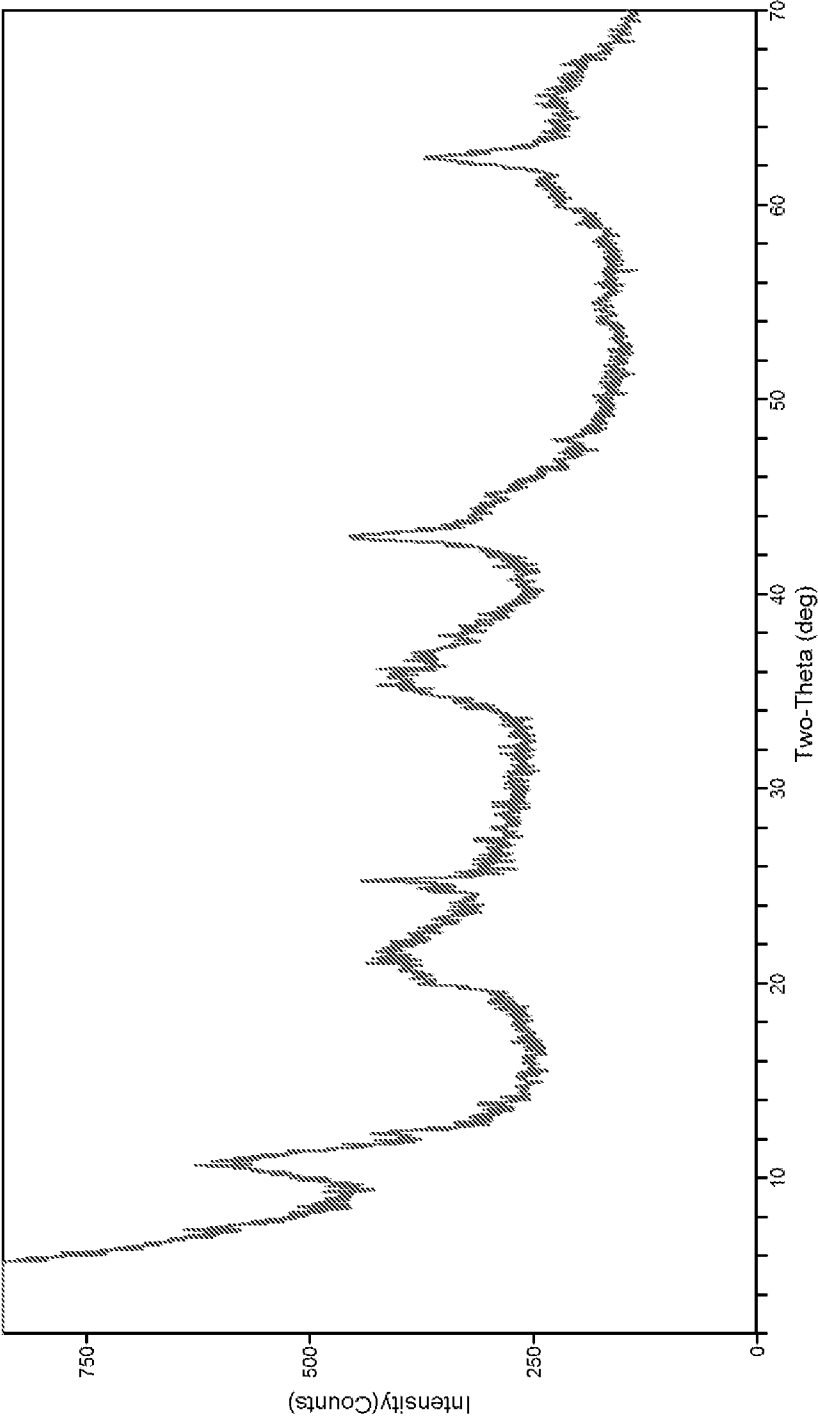


FIGURE 1

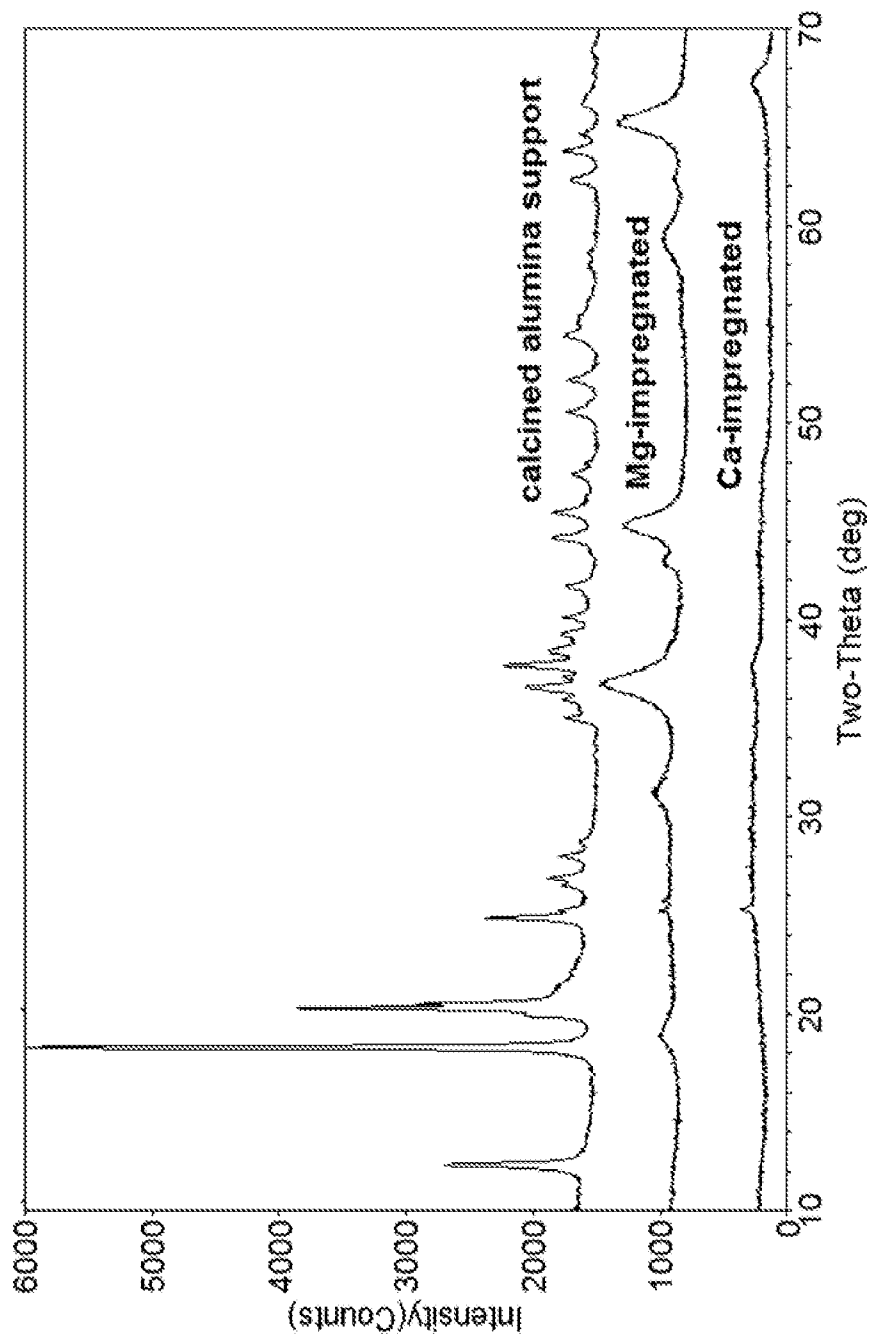


FIGURE 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/069025

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J21/10 B01J21/14 B01J21/16 B01J23/00 B01J35/10
B01J37/02 C10G11/04 C10G11/18 C10G3/00
ADD. C07C1/24 C01B33/40

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 C01B C07C

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 practicable, 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	US 2009/000984 A1 (DE GRAAF ELBERT ARJAN [NL] ET AL) 1 January 2009 (2009-01-01)	1-5
Y	abstract paragraphs [0001], [0006] - [0009], [0011] - [0012], [0017] - [0018], [0020] - [0021], [0031] - [0034], [0037], [0039] - [0041], [0050], [0071] claims 1,15 ----- -/--	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

31 January 2014

Date of mailing of the international search report

17/02/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Marchand, Karin

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/069025

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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 589 902 B1 (STAMIREN DENNIS [US] ET AL) 8 July 2003 (2003-07-08) column 1, lines 33-43 column 1, line 64 - column 2, line 5 column 2, lines 40-46, 53-67 column 3, lines 45-61 column 4, lines 15-18, 57-58 column 5, lines 20-21, 37-38 column 6, lines 19-20, 21-29, 46-57 examples 1-8, 14-18 -----	2, 3, 8
Y	US 2012/137572 A1 (BARTEK ROBERT [US] ET AL) 7 June 2012 (2012-06-07) abstract paragraphs [0005] - [0006], [0016] - [0019], [0033] - [0034], [0067] - [0068], [0095] - [0096], [0098], [0100] claims 16, 38 -----	1-5, 11-13
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INTERNATIONAL SEARCH REPORT

International application No
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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	paragraphs [0009], [0017], [0026], [0032], [0039] - [0043], [0045], [0047], [0061] claim 1 -----	1-20
Y	US 5 095 166 A (FORSCHNER THOMAS C [US] ET AL) 10 March 1992 (1992-03-10) abstract column 2, lines 29-34 column 3, lines 33-42 column 4, lines 31-33, 41-43, 49-57 column 5, lines 3-4, 17-21 column 6, lines 34-36 column 7, lines 35-41; example 1; table 1 -----	2-7, 11-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/069025

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