(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 719 811 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
08.11.2006 Bulletin 2006/45

(51) Int Cl.:
C10G 1/00 *(2006.01)*

(21) Application number: **05076040.4**

(22) Date of filing: **04.05.2005**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR LV MK YU

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(54) **Process for producing liquid hydrocarbons from biomass**

(57) Process for the conversion of biomass into liquid hydrocarbons, comprising the steps of: (a) preparing an aqueous slurry comprising biomass and solid particles comprising a layered material and/or a heat-treated form thereof, the layered material being selected from the group consisting of smectites, anionic clays, layered hydroxy salts, and cationic layered materials, (b) thermally treating said slurry at a temperature in the range of 250 to 400°C, and (c) optionally separating the thermally treated slurry into (i) an aqueous phase, (ii) an organic phase containing the liquid hydrocarbons, and (iii) a solid phase.

This process allows the conversion of biomass into liquid hydrocarbons under mild pressures.

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Description

[0001] The present invention relates to a process for converting biomass into liquid hydrocarbons.

[0002] Considering the declining oil and gas reserves in the world and the desire to reduce the pollution caused by the use of fossil fuels, there exists an increasing desire for an efficient process for the production of hydrocarbons, in particular liquid hydrocarbon fuels, from biomass.

The term "biomass" refers to organic matter available on a renewable basis and includes forest and mill residues, agricultural crops, wood, and aquatic plants. It also includes biowaste, a term referring to any biomass that is not grown or harvested. Examples of biowaste are byproducts from industries, agriculture, and municipal facilities, such as industrial waste, organic waste, agricultural waste, and forestry waste.

Biomass generally comprises up to about 60 wt% of oxygen atoms, and may also contain sulfur, nitrogen, and phosphorus-containing compounds.

[0003] US 3,298,928 discloses the pyrolysis of lignocellulose, especially wood, by entraining sawdust or other small lignocellulose particles in a gaseous stream and moving the particles concurrently with the stream through a reaction zone at 600-1500°F (315-815°C) for a time not exceeding 30 seconds. The resulting pyrolysed product comprises char, non-condensable gases, and condensable gases. The gases are then cooled and separated from the char, resulting in a fluid phase containing a non-aqueous and an aqueous phase, the latter comprising the desired products: levoglucosan and carbohydrate-derived acids such as humic acids, saccharic acids, and saccharinic acids.

This process requires high gas velocities. Furthermore, the oxygen content of the resulting product is substantial.

[0004] EP 0 204 354 discloses a process for producing hydrocarbon-containing liquids from biomass by introducing biomass in the presence of water at a pressure higher than the partial vapour pressure of water at the prevailing temperature into a reaction zone at a temperature of at least 300°C and a pressure of 90-300 bar, keeping the biomass in the reaction zone for at least 30 seconds, separating the solids from the fluid leaving the reaction zone while maintaining the fluid in a single phase, and subsequently separating the liquid from the remaining fluid.

In this process, water acts as a hydrogen donor for reducing the oxygen content of the resulting product. A disadvantage of this prior art process, however, is that high pressures are required.

[0005] US 2004/0034262 A1 discloses a process for continuously producing a hydrocarbon product from biomass wherein an aqueous biomass-containing feed is treated at a pressure of 100-250 bar, heated at a temperature not exceeding 280°C for up to 60 minutes, preferably 1-5 minutes, and subsequently heated for a period up to 60 minutes, preferably 5-30 minutes, at a temperature in the range 280-350°C. Also in this process, high pressures are required.

[0006] It would be desirable to provide a slurry process for the conversion of biomass into liquid hydrocarbons that uses milder pressures than the prior art processes above. The present invention provides such a process.

[0007] The present invention relates to a process for the conversion of biomass into liquid hydrocarbons, comprising the steps of:

a) preparing an aqueous slurry comprising biomass and solid particles comprising a layered material and/or a heat-treated form thereof, the layered material being selected from the group consisting of smectites, anionic clays, layered hydroxy salts, and cationic layered materials,
b) thermally treating said slurry at a temperature in the range of 250 to 400°C, and
c) optionally separating the thermally treated slurry into (i) an aqueous phase, (ii) an organic phase containing the liquid hydrocarbons, and (iii) a solid phase.

[0008] The particles containing the (thermally treated) layered material serve as catalysts for the conversion of biomass. In addition, they can adsorb oxygen, sulfur, and nitrogen-containing hydrocarbons or convert them into lighter species, e.g. H_2S, CO_2, etc. and/or coke. Said lighter species and/or coke can be separated from the more valuable hydrocarbons. As a result, upon further processing of the resulting hydrocarbons in downstream processes - (R)FCC and/or (R)HPC - the catalysts used in these downstream processes will be less affected by these detrimental hetero atom-containing species. Consequently, the conversion of these downstream processes will improve.

Step a)

[0009] In the first step of the process, an aqueous slurry is prepared comprising water, biomass, and solid particles containing (thermally treated) layered material.

[0010] The weight ratio of water to biomass particles preferably ranges from 0.5 to 50, more preferably from 0.5 to 20, even more preferably from 2 to 15, and most preferably from 2.5 to 10.

[0011] The sluny may be mechanically treated, e.g. high-shear mixed and/or treated with ultrasound waves, in order improve the contact between the biomass and the (thermally treated) layered material-containing solid particles.

[0012] Examples of biomass include industrial waste, municipal waste, household biowaste, sugar beet pulp, bagasse,

grass, chopped straw, cotton linters, corn stalks, corn cobs, tree bark, chopped wood, sawdust, shredded pulp, peat, and brown coal.

[0013] The biomass preferably is present in the form of particles with a size of less than 50 mm, more preferably less than 5 mm, more preferably still less than 1 mm, even more preferably less than 0.1 mm.

Before the biomass is added to the slurry, it may be milled, pulverised and/or pretreated with an alkaline compound (e.g. sodium (bi)carbonate or calcium carbonate) at a pH of about 8-11 at a temperature of about 50-150°C.

[0014] The layered material is selected from the group consisting of smectites, anionic clays, layered hydroxy salts and/or cationic layered materials. Thermally treated layered materials are layered materials selected from the above group which have been thermally treated at a temperature in the range of about 300-900°C.

[0015] The particles containing the (thermally treated) layered material may additionally comprise other materials. Examples of such other materials are conventional catalyst components such as silica, alumina, aluminosilicates, zirconia, titania, boria, kaolin, acid leached kaolin, dealuminated kaolin, bentonite, (modified or doped) aluminium phosphates, zeolites (e.g. zeolite X, Y, REY, USY, RE-USY, or ZSM-5, zeolite beta, silicalites), phosphates (e.g. meta or pyro phosphates), sorbents, fillers, and combinations thereof.

Preferably, the particles also contain metals like W, Mo, Ni, Co, Fe, V, and/or Ce. Such metals may introduce a hydrotreating function into the particles (especially W, Mo, Ni, Co, and Fe) or enhance the removal of sulfur- and/or nitrogen-containing species (Zn, Ce, V).

The particles may be a spent (resid) FCC catalyst containing the (thermally treated) layered material. This would be very advantageous, as it involves the reuse of waste material. The spent catalyst may be ground of pulverised into smaller particles, thereby increasing their dispersability.

[0016] The solid particles containing the (thermally treated) layered material preferably have a high accessibility, thereby being less vulnerable to blockage during the process.

The accessibility can be measured by the method according to WO 02/99392, by adding 1 g of the solid particles to a stirred vessel containing 50 g of a 15 g/l Kuwait vacuum gas oil (KVGO) in toluene solution, circulating the solution between the vessel and a spectrophotometer, and measuring the KVGO-concentration continuously. The accessibility of the catalysts to KVGO is quantified by the Akzo Accessibility Index (AAI). The relative concentration of KVGO in the solution was plotted against the square root of time. The AAI is defined as the initial slope of this graph: $AAI = -d(C_t/C_0)/d(t^{1/2}) * 100\%$. In this equation, t is the time (in minutes) and C_0 and C_t denote the concentrations of high-molecular weight compound in the solvent at the start of the experiment and at time t, respectively.

The AAI of the particles to be used in the process of the present invention preferably is higher than 10, more preferably higher than 20.

[0017] The size of the solid particles preferably is less than 100 μm, more preferably less than 10 μm, and most preferably less than 0.1 μm.

Smectite

[0018] Smectites are the 2:1 clay minerals that carry a lattice charge and characteristically expand when solvated with water and alcohols. The layers are negatively charged. Between the layers, cations are hosted.

Examples of smectites are montmorillonite and saponite, which are Mg-, Al-, and Si-containing smectites.

Naturally occuring or synthetically prepared smectites can be used. A method for preparing Mg-, Al-, and Si-containing smectites is disclosed in WO 01/12319.

[0019] Thermal treatment, e.g. calcination at temperatures in the range 300-900°C, leads to the formation of activated smectite clays.

Anionic clay

[0020] Anionic clays are layered structures corresponding to the general formula

$$[M_m^{2+} M_n^{3+} (OH)_{2m+2n.}](X_{n/z}^{z-}). bH_2O$$

wherein M^{2+} is a divalent metal, M^{3+} is a trivalent metal, m and n have a value such that m/n=1 to 10, preferably 1 to 6, and b has a value in the range of from 0 to 10, generally a value of 2 to 6, and often a value of about 4. X is an anion with valance z, such as CO_3^{2-}, OH^-, or any other anion normally present in the interlayers of anionic clays. It is more preferred that m/n should have a value of 2 to 4, more particularly a value close to 3.

In the prior art, anionic clays are also referred to as layered double hydroxides and hydrotalcite-like materials.

Anionic clays have a crystal structure consisting of positively charged layers built up of specific combinations of metal hydroxides between which there are anions and water molecules. Hydrotalcite is an example of a naturally occurring anionic clay in which Al is the trivalent metal, Mg is the divalent metal, and carbonate is the predominant anion present.

Meixnerite is an anionic clay in which Al is the trivalent metal, Mg is the divalent metal, and hydroxyl is the predominant anion present.

In hydrotalcite-like anionic clays the brucite-like main layers are built up of octahedra alternating with interlayers in which water molecules and anions, more particularly carbonate ions, are distributed. The interlayers may contain anions such as NO_3^-, OH, Cl^-, Br^-, I^-, SO_4^{2-}, SiO_3^{2-}, CrO_4^{2-}, BO_3^{2-}, MnO_4^-, $HGaO_3^{2-}$, HVO_4^{2-}, ClO_4^-, BO_3^{2-}, pillaring anions such as $V_{10}O_{28}^{6-}$ and $MO_7O_{24}^{6-}$, monocarboxylates such as acetate, dicarboxylates such as oxalate, alkyl suffonates such as lauryl sulfonate.

[0021] Upon thermal treatment at a temperature above about 200°C, anionic clays are transformed into so-called solid solutions, i.e. mixed oxides that are re-hydratable to anionic clays. At higher temperatures, above about 800°C, spinel-type structures are formed. These are not re-hydratable to anionic clays.

The thermally treated anionic clay that can be present in the solid particles to be used in the process of the present invention can be a solid solution or a spinel-type material.

[0022] For the purpose of the present invention various types of (thermally treated) anionic clays are suitable. Examples of suitable trivalent metals (M^{3+}) present in the (thermally treated) anionic clay include Al^{3+}, Ga^{3+}, In^{3+}, Bi^{3+}, Fe^{3+}, Cr^{3+}, Co^{3+}, Sc^{3+}, La^{3+}, Ce^{3+}, and combinations thereof. Suitable divalent metals (M^{2+}) include Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Mo^{2+}, Ni^{2+}, Fe^{2+}, Sr^{2+}, Cu^{2+}, and combinations thereof. Especially preferred anionic clays are Mg-Al and Ca-Al anionic clays.

[0023] Suitable anionic clays can be prepared by any known process. Examples are the co-precipitation of soluble divalent and trivalent metal salts and slurry reactions between water-insoluble divalent and trivalent metal compounds, e.g. oxides, hydroxides, carbonates, and hydroxycarbonates. The latter method provides a cheap route to anionic clays.

Layered hydroxy salts

[0024] Metal hydroxy salts (LHS) are distinguished from anionic clays in that they are built up of divalent metals only, whereas layered double hydroxides are built up of both a divalent and a trivalent metal.

An example of a LHS is a hydroxy salt of a divalent metal according to the following idealised formula: $[(Me^{2+}, M^{2+})_2(OH)_3]^+(X^{n-})_{1/n}]$, wherein Me^{2+} and M^{2+} may be the same or different divalent metal ions and X^{n-} is an anion other than OH^-. Another example of LHS has the general formula $[(Me^{2+},M^{2+})_5(OH)_8]^{2+}(X^{n-})_{2/n}]$, wherein Me^{2+} and M^{2+} may be the same or different divalent metal ions and X is an anion other than OH^-.

If the LHS contains two different metals, the ratio of the relative amounts of the two metals may be close to 1. Alternatively, this ratio may be much higher, meaning that one of the metals predominates over the other. It is important to appreciate that these formulae are ideal and that in practice the overall structure will be maintained, although chemical analysis may indicate compositions not satisfying the ideal formula.

Examples of suitable layered hydroxy salts with one type of metal are Zn-LHS (e.g. $Zn_5(OH)_8(X)_2$, $Zn_4(OH)_6X$, $Zn_5(OH)_6(X)_2 \cdot 2H_2O$, $Zn_3(OH)_4(X)_2$), Co-LHS (e.g. $Co_2(OH)_3X$, Ni-LHS (e.g. $Ni_2(OH)_3X$), Mg-LHS (e.g. $Mg_2(OH)_3X$), Fe-LHS, Mn-LHS, and La-LHS ($La(OH)_2NO_3$). Examples of suitable layered hydroxy salts comprising two or more different types of metals are Zn-Cu LHS, Zn-Ni LHS, Zn-Co LHS, Fe-Co LHS, Zn-Mn LHS, Zn-Fe LHS, Ni-Cu LHS, Cu-Co LHS, Cu-Mg LHS, Cu-Mn LHS, Fe-Co LHS, Ni-Co LHS, Zn-Fe-Co LHS, Mg-Fe-Co LHS, and Ni-Cu-Co LHS. Especially preferred layered hydroxy salts are Zn-Mn LHS and Zn-Fe LHS.

[0025] Examples of suitable interlayer anions X^{n-} are NO_3^-, OH, Cl^-, Br^-, I^-, SO_4^{2-}, SiO_3^{2-}, CrO_4^{2-}, BO_3^{2-}, MnO_4^-, $HGaO_3^{2-}$, HVO_4^{2-}, ClO_4^-, BO_3^{2-}, pillaring anions such as $V_{10}O_{28}^{6-}$ and $Mo_7O_{24}^{6-}$, monocarboxylates such as acetate, dicarboxylates such as oxalate, alkyl sulfonates such as lauryl sulfonate.

LHS exhanged with (bi)carbonates or organic anions provides the advantage that upon calcination, the anion will decompose, thereby increasing the porosity and surface area of the LHS.

[0026] Suitable methods for the preparation of layered hydroxy salts involve the reaction of a metal oxide with a dissolved metal salt (see Inorg. Chem. 32 (1993) 1209-1215) and (co-)precipitation from metal salt solutions (see J. Solid State Chem. 148 (1999) 26-40 and J. Mater. Chem. 1 (1991) 531-537). After preparation of the LHS, the interlayer anions may be exchanged, if so desired, by a regular ionexchange procedure.

[0027] Upon thermal treatment of a LHS at a temperature above 300°C, metal oxides or mixed metal oxides are formed.

Cationic layered materials

[0028] Cationic Layered Materials (CLMs) are crystalline NH_4-Me(II)-TM-O phases with a characteristic X-ray diffraction pattern. In this structure, Me(II) represents a divalent metal and TM stands for a transition metal. The structure of a CLM consists of negatively charged layers of divalent metal octrahedra and transition metal tetrahedra with charge-compensating cations sandwiched between these layers.

Suitable divalent metals are Zn, Mn, Co, Ni, Cu, Fe, Ca, and Ba, with Zn, Co, Mn, Cu, Ni, and Fe being preferred.

Suitable transition metals are Mo, W, V, Cr, Ti, and Zr, with Mo and W being preferred.

[0029] CLMs can be prepared by several methods. One method involves the reaction of an ammonium transition metal salt (e.g. ammonium heptamolybdate) and a divalent metal salt in aqueous ammonia solution. Upon evaporation of the ammonia a precipitate is formed, which is then aged to form a CLM (M.P. Astier et al., Ann. Chim. Fr. Vol. 12, 1987, pp. 337-343).

A second method involves the precipitation of a divalent metal salt and aluminium nitrate, followed by aging to form an anionic clay, calcination to form a mixed oxide, and contacting and reacting the mixed oxide with an ammonium transition metal salt (e.g. ammonium heptamolybdate) to form a CLM. (Chem. Mater. Vol. 8, 1996, 836-843; ACS Symp. Ser. Vol. 622, 1996, 237-249; Stud. Surf, Sci. Catal. Vol. 118, 1998, 359-367).

[0030] A third method is that according to WO 04/000731, which involves the steps of (a) preparing a slurry comprising a water-insoluble aluminium source and a divalent metal source, (b) drying the slurry of step a) and calcining the dried material to form a first calcined material, (c) optionally rehydrating the product of step b) to obtain an anionic clay, followed by calcining the anionic clay to form a second calcined material, (d) contacting a slurry of either the first or the second calcined material with an ammonium transition metal salt, and (e) aging the resulting slurry.

[0031] Upon thermal treatment of a CLM at a temperature above 300°C, solid solutions are formed; above 800°C spinel-type structures are formed.

Step b)

[0032] The second step of the process involves thermal treatment of the slurry at temperatures in the range of 250-400°C, preferably 280-350°C.

The pressure preferably is in the range 1 to 200 bar, more preferably 2 to 30 bar, and most preferably autogeneous.

The pH of the slurry during this thermal treatment preferably is below 7, more preferably in the range 2-5.

[0033] The thermal treatment is generally performed for 1 minute to 24 hours, preferably for 1 minute to 12 hours, more preferably 1 minute to 6 hours, more preferably still for 1-60 minutes, even more preferably for 1-30 minutes, and most preferably for 3-10 minutes.

[0034] If desired, hydrogen may be added during this process step. The hydrogen partial pressure preferably ranges from 0 to 10 bar, more preferably from 0 to 5 bar, more preferably still from 0 to 3 bar, and even more preferably from 0 to 1 bar. Most preferably, however, the process of the invention is carried out in the absence of hydrogen.

[0035] Biomass is generally complex in nature and contains a wide spectrum of compounds. Therefore, some parts of the biomass will require a shorter treating time to produce desirable compounds than others. Thermal treatment for too long a period may result in undesired charring. It may therefore be desirable to perform the thermal treatment in several reaction zones, with intermediate removal of desired reaction products between the zones.

Step c)

[0036] The thermally treated slurry can then be separated into (i) an aqueous phase, (ii) an organic phase, and (iii) a solid phase. The organic phase contains the liquid hydrocarbons, i.e. the desired products of this process.

Any conventional separation technique may be used for separating the solids, the aqueous phase, and the organic phase from each other. Suitable forms of separation are settling, filtration, solvent extraction, and centrifugation.

[0037] The solid particles containing the (thermally treated) layered material can be regenerated by calcination and combustion at 550-700°C - optionally followed by hydrothermal treatment, e.g. steam-calcination - and re-used in step a).

[0038] Unconverted or partially converted constituents of the biomass usually are watersoluble to some extent and will be predominantly present in the aqueous phase. These constituents may be re-cycled by introduction into the slurry of step a).

[0039] If desired, the resulting liquid hydrocarbons may be separated into a lower boiling and a higher boiling fraction. Suitable forms of separation are distillation, flash-distillation, solvent extraction, centrifugation, nano-filtration, and ultra-filtration.

The lower boiling fraction contains liquid products which can suitably be treated in conventional FCC (fluid catalytic cracking) and HPC (hydroprocessing) units. This fraction generally contains gases like H_2S and hydrocarbons with boiling points up to 500°C.

The compounds in the higher boiling fraction generally have boiling points in the range from 450 to 1,050°C. This fraction can be further treated in RFCC (resid FCC) and/or RHPC (resid HPC) processes.

[0040] Any formed coke may be used as fuel, for electrode manufacture, production of electricity or synthesis gas.

Claims

1. Process for the conversion of biomass into liquid hydrocarbons, comprising the steps of:

a) preparing an aqueous slurry comprising biomass and solid particles comprising a layered material and/or a heat-treated form thereof, the layered material being selected from the group consisting of smectites, anionic clays, layered hydroxy salts, and cationic layered materials,
b) thermally treating said slurry at a temperature in the range of 250 to 400°C, and
c) optionally separating the thermally treated slurry into (i) an aqueous phase, (ii) an organic phase containing the liquid hydrocarbons, and (iii) a solid phase.

2. Process according to claim 1 wherein the layered material is Mg-Al or Ca-Al anionic clay.

3. Process according to either of the preceding claims wherein the liquid hydrocarbons are subsequently treated in a fluid catalytic cracking unit or a hydroprocessing unit.

4. Process according to any one of the preceding claims wherein the organic phase is separated into a higher boiling fraction and a lower boiling fraction.

5. Process according to claim 4 wherein the higher boiling fraction is subsequently treated by resid fluid catalytic cracking or resid hydroprocessing.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 07 6040

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	30 September 2005	Zuurdeeg, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 05 07 6040

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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