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(54) Title: STABLE SUSPENSIONS OF BIOMASS COMPRISING INORGANIC PARTICULATES

(57) Abstract: Liquid suspensions are disclosed comprising a suspending medium, small particles of biomass, and small particles of an inorganic material. The inorganic material stabilizes the suspension, so that it may be transported by pipeline or tank car without developing a sediment. The suspension may be used in manufacturing a bio-fuel.

STABLE SUSPENSIONS OF BIOMASS COMPRISING INORGANIC PARTICULATES

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] An important aspect of the economics of the use of biomass as a source of fuel or of specialty chemicals is the cost involved in transporting the biomass from the location where it is produced to the location where conversion to a fuel or to specialty chemicals takes place. It is desirable to provide a process for converting biomass at or near the place of production into a pumpable liquid so it may be transported in tank cars or a pipe-line.

[0002] The present invention provides a liquid composition of biomass suspended in a liquid suspension medium, further comprising small particles of an inorganic material.

[0003] Of particular importance is that these suspensions are stable, meaning that the solid and liquid phases do not separate within the time needed to store and transport the suspensions (for example via pipe-line, rail, or road transport) to a location where they can be further processed.

[0004] It is known from the paper industry to make suspensions of cellulose fibers and inorganic materials. These suspensions do not need to be stable. To the contrary, the cellulose fibers are precipitated from the suspension and need to make inter-fiber hydrogen bonds (also referred to as paper-making bonds).

[0005] It is known from GB 2 310 865 to mix a slurry of biomass material with catalytic particles and to subject the resulting slurry to pyrolytic conditions. The slurry is processed immediately following its preparation, so there is no need for the slurry to be stable.

[0006] The composition of the present invention may be transported, for example by pipeline, or in a tank car or tank truck. The composition may also be stored in tanks. The composition is particularly suitable for use in processes whereby the biomass material is converted to liquid or gaseous fuels and/or to the valuable specialty chemicals.

[0007] In a specific embodiment the inorganic particulates also possess a catalytic functionality, meaning that the subsequent conversion of the biomass may be performed under milder conditions (lower temperature and/or lower pressure and/or shorter time) than was heretofore the case, resulting in improved products and superior process economics.

[0008] In a specific embodiment, the biomass comprises polymeric material. More specifically, the polymeric material comprises cellulose or lignocellulose. In a preferred embodiment the polymeric material comprises both cellulose and lignocellulose.

2. Description of the Related Art

[0009] Biomass is produced in large volumes in agriculture and forestry. Many of these materials are intended for use as food products for human consumption, in animal feed, or other forms of valuable materials. For example, forestry products are used as construction materials in the form of lumber, plywood, paper and paper products and paper byproducts and the like.

[0010] Incidental to the production of agricultural and forestry products, the world produces vast quantities of agricultural and forestry waste. Examples include wood chips, saw dust, straw, corn husks, bagasse, and the like. Attempts have been made to convert these waste materials to useful products. In general, these waste materials are converted to products of low intrinsic value, such as compost.

[0011] Attempts to convert these materials to products of a higher value have met with limited success. For example, conversion of agricultural waste to ethanol by fermentation is a time-consuming and expensive process. Moreover, even the most sophisticated fermentation enzymes are only able to convert at most about 50 percent of the available material. The remaining 50 percent is immune to attack by fermentation enzymes and is sometimes referred to as "recalcitrant cellulose" for this reason.

[0012] An alternative to the above approach involves converting the biomass at the location where it is produced (plantation etc) into a liquid (via pyrolysis or hydrothermal upgrading) or a gas stream (gasification) and to process these streams further in an oil or bio refinery, making optimal use of the economy of scale.

[0013] Unfortunately, transporting gas is a difficult and costly task, while most of the bio-liquids produced from biomass via thermal means are instable, in the sense that they deteriorate over time in terms of viscosity and/or chemical composition.

[0014] It is therefore an object of the present invention to provide a new liquid composition that can be made from agricultural or forestry products, or waste materials from agriculture and forestry, and that is sufficiently stable for transportation to a centralized processing

location. It is a further object of the present invention to provide a biomass composition that is more easily converted to liquid or gaseous fuel or to specialty chemicals than the biomass materials from which it is derived.

BRIEF SUMMARY OF THE INVENTION

[0015] The present invention relates to a liquid composition comprising a liquid suspension medium having suspended therein small particles of a biomass material and small particles of an inorganic material, said composition being stable.

[0016] These liquid compositions are stable in the sense that the solid and liquid phases do not separate within the time necessary to store and transport them (via pipe-line or road transport) to a location where they can be further processed.

[0017] The inorganic material may be inert, for example a salt of an alkali metal or earth alkaline metal. In an alternate embodiment, the inorganic material may have catalytic activity. Examples include clays, silicas, silica aluminas, zeolites, anionic clays, cationic layered materials, metal hydroxyl salts and the like.

[0018] In a specific embodiment, the biomass comprises polymeric material. More specifically, the polymeric material comprises cellulose and/or lignocellulose.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0019] The present invention relates to a stable liquid composition comprising biomass particles. The liquid composition may be produced at the location where biomass is harvested or where it is produced as a byproduct of, for example an agricultural process. The liquid compositions of the present invention are sufficiently stable to allow them to be transported to a processing plant where they may be subjected to further processing.

[0020] The liquid compositions of the present invention comprises a liquid suspension medium having suspended therein small particles of a biomass material and small particles of an inorganic material. Although these compositions require the transportation of the liquid suspension medium and of the particles of an organic material, the pumpability of these compositions improves the economics of transportation in such a way that it more than

offsets the additional costs of transporting the liquid suspension medium and the inorganic material.

[0021] The liquid suspension medium preferably comprises water, an alcohol, or a carboxylic acid. For reasons of costs and availability, water-based liquid suspension mediums are preferred. Alcohol and carboxylic acid may be added to an aqueous liquid suspension medium so as to change its properties. Preferred alcohols for use herein include glycols, in particular ethylene glycol.

[0022] Before incorporation into the liquid composition, the biomass material is reduced to a particle size preferably in the range of from 3 mm to 50 micrometers, more preferably from 1 mm to 0.1 mm. Any suitable method may be used for reducing the particle size of the biomass material. The selection of the method will depend in part on the nature and hardness of the biomass material, the availability of specific forms of energy at the location where the biomass is produced or harvested, the desired particle size, and the like.

[0023] Suspensions of small particles of biomass material in a liquid to suspension medium tend to be unstable. Biomass particles may either settle to the bottom of such a suspension, or float to the surface, whereby a biomass-rich phase is created. As many biomass materials are rich in cellulose, the biomass-rich phase may solidify as a result of hydrogen bonding between the biomass particles. The mechanism of this process is not unlike that of papermaking from a suspension of cellulose fibers. Once solidified, the biomass cannot readily be brought back into suspension by agitation. In addition, biomass particles in the presence of water are subject to microbial deterioration.

[0024] It is therefore desirable to provide a way of increasing both the physical stability and the microbial stability of a liquid composition comprising biomass particles suspended in a liquid suspension medium. It has now been discovered that the presence of small particles of an inorganic material in such a liquid composition improves both the physical stability and the microbial stability of the composition.

[0025] The physical stability of the liquid composition may be determined by the following standardized stability test. A centrifuge tube is filled with the appropriate amount of suspension, as described in the manual of the equipment. The tube is closed with a stopper and the suspension is centrifuged for 10 min at 5000 rpm. Immediately after centrifuging, the tube is removed from the centrifuge and slowly turned upside down and back (5 times). Then the content of the tube is carefully emptied. The tube is visually examined for the presence of

a layer of solid material left on the bottom. If no solid material is present on the bottom of the tube the suspension is considered to be stable. Therefore, the term “stable” as used herein is made with reference to this centrifuge test.

[0026] Even if the presence of the inorganic particles may not sufficiently improve the physical stability of the suspension, the coating of inorganic material onto the biomass particles may decrease the amount of hydrogen bonding that takes place between biomass particles. As a result, a suspension that has undergone phase separation may be restored by simple agitation.

[0027] The stability of the suspension may be further improved by the addition of an anti-flocculant. Anti-flocculants are charged materials that attach to the surface of a suspended particle. As a result the zeta-potential of the particle is increased, which reduces the probability of coagulation or agglomeration with other particles in the suspension. In general, any multivalent soluble ion is suitable as an anti-flocculant. Pyrophosphate is a suitable example.

[0028] An alternate method for further improving the stability of the suspension comprises the use of a surfactant material. Surfactant materials are often considered a special form of anti-flocculants, but their mechanism of action is different. Surfactant molecules are characterized by a polar head and a non-polar tail. The polar head may be ionic or non-ionic. The polar head will attach to the surface of a suspended particle, with the non-polar tail sticking out into the solvent. As a result the particle becomes hydrophobic. Preferred are low-cost surfactants, such as soaps.

[0029] Swelling agents promote the absorption of solvent molecules into the suspended particles. As a result of the swelling, the density of the suspended particle becomes closer to the density of the solvent, thereby reducing the tendency of the particles to settle or to float to the surface. Suitable swelling agents include acids and bases. The choice of swelling agent will depend on the nature of the inorganic particles, for compatibility reasons.

[0030] In a preferred embodiment, the biomass material comprises a polymeric material, more preferably cellulose and/or lignocellulose. More preferred are biomass materials that contain both cellulose and lignocellulose.

[0031] The inorganic material preferably is in crystalline or quasi-crystalline form. The purpose of the present invention may be achieved with an inorganic material that is an inert inorganic material. The term “inert” as used herein refers to materials that do not have a

catalytic effect on a conversion reaction (such as pyrolysis or hydrothermal treatment) to which the composition may be subjected.

[0032] It is, however, desirable to use inorganic material that has catalytic properties in a subsequent conversion reaction. Examples of such materials include clays, silicas, silica aluminas, transition metal hydroxides, metal hydroxyl salts, zeolites, cationic layered materials, anionic clays, layered double hydroxides (LDHs), smectite clays, saponites, sepiolites, and mixtures thereof.

[0033] The present invention further provides a method for preparing a liquid composition of biomass suspended in a liquid suspension medium, said composition being stabilized by small particles of an inorganic material, said method comprising the steps of:

- a. contacting particles of the biomass with the liquid suspension medium having dissolved therein precursor material to the inorganic particles in;
- b. allowing the solution to coat and/or penetrate the polymeric material;
- c. modifying the conditions to cause the formation of an inorganic particulate material from the precursor material.

[0034] Step c. may involve changing the pH, changing the temperature, evaporating part of the liquid suspension medium, changing the ionic strength, etc.

[0035] Preferably, the liquid suspension medium comprises water, and may further comprise an alcohol and/or a carboxylic acid. The liquid suspension medium may further comprise a swelling agent, for example a Bronstedt acid or a Bronstedt base. Suitable acids include mineral acids, such as hydrochloric acid, sulfuric acid, and phosphoric acid. Suitable bases include the hydroxides and carbonates of the alkali and earth alkaline metals. If the liquid suspension medium comprises a carboxylic acid, the swelling agent preferably is also an acid.

[0036] The biomass material preferably comprises a polymeric material, more preferably cellulose and or lignocellulose. The inorganic material is preferably in crystalline or quasi crystalline form.

[0037] In a specifically preferred embodiment, the biomass comprises cellulose and the inorganic material is a hydrotalcite like material. The hydrotalcite like material may conveniently be formed in situ. Accordingly, the present invention provides a method for

preparing a cellulose-containing polymeric liquid suspension comprising small particles of an inorganic material, said method comprising the steps of:

- a. providing a cellulose-containing polymeric material;
- b. providing an aqueous solution of a divalent metal and a trivalent metal;
- c. soaking the cellulose polymeric material with the aqueous solution;
- d. initiating the formation of a microcrystalline inorganic material.

[0038] The preferred hydrotalcite like material is hydrotalcite itself. Accordingly, the preferred divalent metal in step b. is magnesium, and the preferred trivalent metal is aluminum. The microcrystalline inorganic material formed in step d. is preferably an anionic clay, and most preferably hydrotalcite.

[0039] In yet another embodiment the inorganic material is an inorganic oxide, such as alumina. Accordingly, the present invention provides a method for preparing a cellulose-containing polymeric liquid suspension comprising small particles of an inorganic material, said method comprising the steps of:

- a. providing a cellulose-containing polymeric material, such as biomass;
- b. providing an aqueous solution of a cation or anion of a metal capable of forming a particulate inorganic compound;
- c. soaking the cellulose polymeric material with the aqueous solution;
- d. initiating the formation of a precursor to a particulate inorganic compound;
- e. aging to convert the precursor to the particulate inorganic compound.

[0040] In this embodiment, a preferred cation for use in step b. is Al^{3+} , and a preferred anion is aluminate ($\text{Al}_2\text{O}_4^{2-}$).

[0041] The liquid composition of the present invention may be used to produce a variety of useful materials. For example, it may be used in the preparation of a bio-oil, it may be converted to a binder material, or to a construction material.

[0042] The liquid composition may be transported by pipeline or road transport or rail transport to a central processing location. Further, the liquid composition may be used as a feedstock in processes whereby the biomass material is converted to liquid or gaseous fuels and/or to valuable specialty chemicals.

[0043] Examples of such a process include one of a variety of processes present in a traditional oil refinery, such as gasification, steam reforming, thermal cracking, coking, catalytic cracking, hydro-cracking, and hydro-processing. The inorganic material may be selected such that it functions as a catalyst in any of these processes.

[0044] The liquid composition of the present invention may be used as a feedstock in a fluid catalytic cracking unit. For this purpose, the cracking catalyst in the unit should have a low cracking activity, because biomass materials are much more prone to cracking than the traditional feedstocks derived from crude oil. For this reason, it may be desirable to feed the liquid composition into a low cracking activity zone of a fluid catalytic cracking unit. Examples of such low activity zones include the stripper and the regenerator of a traditional FCC unit.

WHAT IS CLAIMED IS:

1. A stable liquid composition comprising a liquid suspension medium having suspended therein small particles of a biomass material and small particles of an inorganic material.
2. The composition of claim 1 wherein the suspension does not precipitate solid particles when centrifuged for 10 minutes at 5000 rpm.
3. The composition of claim 1 or 2 wherein the inorganic material is in crystalline or quasi-crystalline form.
4. The composition of any one of the preceding claims, wherein the biomass material comprises a polymeric material.
5. The composition of claim 4, wherein the polymeric material comprises cellulose and lignocellulose.
6. The composition of any one of the preceding claims wherein the particles of inorganic material have an average particle size in the range of from 3 nm to 50 micrometers, preferably from 1 nm to 0.1 μ m.
7. The composition of any one of the preceding claims wherein the inorganic material is an inert inorganic material.
8. The composition of any one of claims 1-6, wherein the inorganic material has catalytic properties.

9. The composition of claim 8 wherein the inorganic material is selected from the group consisting of clays, silicas, silica-aluminas, transition metal hydroxides, metal hydroxyl salts, zeolites, cationic layered materials, anionic clays, layered double hydroxides, smectite clays, saponites, sepiolites and mixtures thereof.

10. A method for preparing a liquid composition of biomass material suspended in a liquid suspension medium, said composition being stabilized by small particles of an inorganic material, said method comprising the steps of:
 - a. contacting particles of the biomass with the liquid suspension medium having dissolved therein precursor material to the inorganic particles in;
 - b. allowing the solution to coat and/or penetrate the biomass material;
 - c. modifying the conditions to cause the formation of an inorganic particulate material from the precursor material.

11. The method of claim 10 wherein the biomass comprises polymeric material

12. The method of claim 10 or 11 wherein the liquid suspension medium comprises water.

13. The method of claims 10-12 wherein the liquid suspension medium comprises an alcohol.

14. The method of claims 10-12 wherein the liquid suspension medium comprises a carboxylic acid.

15. The method of claim 10 or 14 wherein the liquid suspension medium further comprises a swelling agent.

16. The method of claim 15 wherein the swelling agent is a Bronstedt acid or a Bronstedt base.
17. The method of any one of claims 10 – 15, wherein the modification of conditions in step c) comprises a change in temperature, a change in pH, evaporation of the liquid suspension medium, or a combination thereof.
18. The method of any one of claims 10-17, wherein the polymeric material comprises cellulose and/or lignocellulose.
19. The method of any one of claims 10-18, wherein the inorganic material is in crystalline or quasi-crystalline form.
20. A method for preparing a cellulose-containing polymeric liquid suspension comprising small particles of an inorganic material said method comprising the steps of:
 - a. providing a cellulose-containing polymeric material;
 - b. providing an aqueous solution of a divalent metal and a trivalent metal;
 - c. soaking the cellulose polymeric material with the aqueous solution;
 - d. initiating the formation of a microcrystalline inorganic material.
21. The method of claim 20 wherein the divalent metal is Mg.
22. The method of claim 20 or 21 wherein the trivalent metal is Al.
23. The method of claim 20 wherein the microcrystalline inorganic material is an anionic clay.
24. The method of claim 21 wherein the anionic clay is hydrotalcite.

25. A method for preparing a cellulose-containing polymeric liquid suspension comprising small particles of an inorganic material, said method comprising the steps of:
- a. providing a cellulose-containing polymeric material, such as biomass;
 - b. providing an aqueous solution of a cation or anion of a metal capable of forming a particulate inorganic compound;
 - c. soaking the cellulose polymeric material with the aqueous solution;
 - d. initiating the formation of a precursor to a particulate inorganic compound;
 - e. aging to convert the precursor to the particulate inorganic compound.
26. The process of claim 25 wherein the cation of step b. is Al^{3+} .
27. The process of claim 25 or 26 wherein the anion is an aluminate ($\text{Al}_2\text{O}_4^{2-}$).
28. The composition of any one of the preceding claims for use in the preparation of a bio-oil.
29. The composition of any one of the preceding claims for use as a binder.
30. The composition of any one of the preceding claims for use as a construction material.
31. The composition of any one of the preceding claims whereby the suspension is transported by pipe-line or road transport to a central processing location.

32. The composition of any one of the preceding claims whereby the suspension is used as a feedstock in a process whereby the biomass material is converted to liquid or gaseous fuels and/or to the valuable specialty chemicals.
33. The composition of claim 32 whereby the process is an oil refinery process such as Gasification, Steam reforming, Thermal Cracking, a Coking, Catalytic Cracking, a Hydro-cracking, or Hydro processing.
34. The composition of claim 32 and 33, whereby the inorganic material functions as a catalyst.
35. The composition of claim 33 or 34, whereby the process is a Fluid Catalytic Cracking process with a low cracking activity catalyst.
36. The composition of claim 34 and 35, whereby the suspension is fed into a low cracking activity zone of the FCC unit, such as the stripper or regenerator