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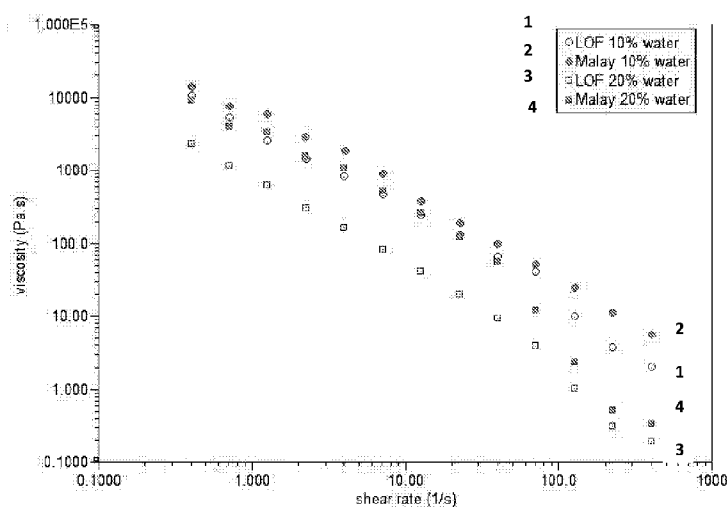


FIGURE 1

(57) Abstract: Disclosed is a liquid biofuel comprising carbonaceous material particles having a D_{50} ranging from 0.1 μm to 200 μm suspended in a liquid biodiesel composition.

Liquid biofuel compositions

Field of the invention

5 The present invention relates to the field of biofuel compositions.

Background of the invention

10 The recent emphasis on finding alternative energy sources is leading to an accelerated search for new fuels or new sources of fuel. Producing a liquid fuel from biomass, or biofuel, is an important focus of many alternative energy strategies. Ethanol production from plant biomass is one example of this. Another example of a newer fuel is biodiesel. Refined vegetable oils have been the typical starting materials for the production of biodiesel. Biodiesel can be produced from the oils of many plants. Biodiesel is an alternative, non-toxic, biodegradable and renewable diesel fuel. These characteristics of
15 biodiesel reduce the emission of carbon monoxide, hydrocarbons, and particulate matter in the exhaust gas, as compared to diesel fuel.

 Biodiesel is commonly referred to as fatty acid methyl esters (FAMES), which are usually obtained from renewable resources such as various plant oils including rapeseed oil, soybean oil, palm oil and the like, animal oils including beef tallow and the
20 like, and waste cooking oils, etc. Biodiesel production relies on a chemical reaction, called trans-esterification, that transforms esters such as triglycerides into mono-alkyl esters. Conventionally, this reaction requires a large excess of methanol, or in some cases of ethanol, and an acid or a base catalyst under heated conditions. Since biodiesel has similar physical properties to diesel oil, it can be used for compression-ignition type diesel engines
25 instead of diesel oil or in combination with diesel oil. That is, biodiesel may be defined as an alternative fuel to diesel oil, which is prepared by the chemical reaction of animal or plant fatty acid with methanol.

 Therefore, the production and use of biodiesel increases with time, as an alternate reproducible energy source due to the exhaustion of petroleum energy resources
30 and to reduce the generation of carbon dioxide attributable to the excessive use of fossil fuel.

Thus, biodiesel is a clean, safe, ready-to-use, alternative fuel which runs in any diesel engine without requirement for modification.

Futher, in view of the expected shortage of crude oil as a fuel due to the decline in natural reserves worth producing on the one hand and the need to use them as a chemical raw material on the other hand, energy-recovery processes in which aqueous coal suspensions are subjected to high-temperature combustion have recently been gaining in importance. Aqueous coal or biocoal suspensions offer the major advantage over coal in solid, albeit finely divided, form in that they may be conveyed over relatively long distances at relatively low cost in transport systems known from the transport of crude oil, for example pipelines or overland pipelines. However, the disadvantage is that the dispersion medium, water, which is inert to combustion, reduces the gross calorific value of aqueous coal or biocoal suspensions. So far as the coal content of aqueous coal or biocoal suspensions is concerned, an excessive particle content has to be avoided with transportability in mind whereas as high a particle content as possible is desired with the gross calorific value in mind.

It is known from the prior art that aqueous coal or biocoal suspensions may be provided with additives which improve fluidity during transport in pipelines, but which on the other hand allow an increase in the coal or biocoal content of suspensions and hence considerably increase the gross calorific value. Such additives also improve the combustion properties of the aqueous coal suspensions. Providing the coal or biocoal used to prepare the coal suspensions has a suitable sieve analysis, it is possible to produce readily pumpable suspensions having particle contents of from 10 to 50% by weight.

However, it is generally desired to further increase the particle content in order to increase the gross calorific value of aqueous coal or biocoal suspensions, because aqueous coal or biocoal suspensions can only be economically used for industrial combustion processes for energy recovery beyond a substantial particle content by weight coal, based on the total weight of the suspension. In addition, it is desired to further reduce the viscosity of aqueous particle suspensions to provide for convenient transport even through pipelines of comparatively narrow cross-section. It is also generally desired to obtain coal or biocoal suspensions having a high stability over time.

Summary of the invention

The present invention relates to a liquid biofuel comprising carbonaceous material particles having a D_{50} ranging from 0.1 μm to 200 μm suspended in a liquid biodiesel composition.

5 In some embodiments, the carbonaceous material particles content is of at least 10% w/w of the said biofuel, preferably of at least 20% w/w of the said biofuel, and most preferably of at least 30% w/w of the said biofuel.

In some embodiments, the carbonaceous material particles consist of a torrefied biomass, preferably torrefied wood particles.

10 In some embodiments, the said liquid biofuel further comprises further water in an amount ranging from 0.5% w/w to 25% w/w.

In some embodiments, the said liquid biofuel does not comprise any added surfactant compound.

15 Description of the figures

Figure 1 illustrates the viscosity of a liquid biofuel under the form of an oil-in-water emulsion. Abscissa : Shear rate, expressed as 1/s; Ordinate : viscosity expressed as Pa.s. Curve ○ : O/W emulsion of LOF biofuel with 10% w/w water; Curve ● : O/W emulsion of LOF biofuel with 20% w/w water; Curve □ : O/W emulsion of Malaysian biofuel with 10% w/w water; Curve ■ : O/W emulsion of Malaysian biofuel with 20% w/w water

Detailed description of the invention

The inventors have conceived specific liquid biofuel compositions comprising a substantial amount of biomass material particles, which liquid biofuel compositions are stable without the requirement for an added stabilizing additive such as a surfactant compound or a viscosity agent.

25 Surprisingly, the inventors have shown herein that stable liquid biofuel compositions comprising a significant amount of carbonaceous material particles are obtained, without requiring any added stabilizing additive such as a surfactant compound or a viscosity agent, when liquid biodiesel is used instead of fossil fuel.

30 Thus, the present invention provides stable biodiesel-based liquid biofuel compositions comprising suspended carbonaceous material particles.

This invention pertains to a liquid biofuel comprising carbonaceous material particles having a D_{50} ranging from 0.1 μm to 200 μm suspended in a liquid biodiesel composition.

When using such finely grinded carbonaceous material particles, what was
5 expected is (i) a rapid settlement of these particles in the resting liquid biofuel and (ii) an aggregation of the settled particles at the container bottom, due to the known phenomenon of particle association.

However, the inventors have unexpectedly shown that a liquid biofuel as described herein is not subject to settlement (sedimentation) of the carbonaceous material
10 particles contained therein for a significant period of time of storage.

Indeed, detectable sedimentation of the carbonaceous material particles may be observed after long time periods of storage of a liquid biofuel as described herein, i.e. several months of storage without stirring of the said liquid biofuel. However, particle sedimentation with the time of storage does not consist of a significant drawback of a
15 liquid biofuel as described herein.

Importantly, the inventors have shown that the carbonaceous material particles contained in a liquid biofuel as described herein remain dispersible with time, even after a very long time period of storage.

Consequently, according to an important feature of a liquid biofuel as
20 described herein, the carbonaceous material particles that may sediment with a long time period of storage are poorly subject to aggregation and remain dispersible when the said liquid biofuel is stirred or pumped.

Further, the inventors have shown that the rheological properties of a liquid biofuel as described herein fully complies with the requirement for workability, and
25 especially for the requirement of pumpability, of a liquid fuel composition.

Notably, the inventors have shown that a liquid biofuel as described herein behaves as a “shear thinning” liquid, i.e. having a fluid’s resistance to flow which decreases with an increasing rate of shear stress.

It can be easily understood that the shear thinning property of a liquid biofuel
30 as described herein is an important feature since it allows the liquid biofuel to be easily pumped, without requiring a high energy amount, even after a long period of time of storage.

In view of the foregoing, it has been shown according to the invention that liquid biofuels complying with the various workability and regulatory requirements may be prepared from a liquid biodiesel to which small size carbonaceous material particles are added.

5 **Biodiesel**

As intended herein, the term "biodiesel" refers to a vegetable oil- based or animal fat-based diesel fuel consisting of long-chain alkyl esters, which encompasses long-chain methyl esters, long-chain ethyl esters and long-chain propyl esters. Conventionally, biodiesel is prepared by chemically reacting lipids contained in a vegetable oil or an animal
10 fat with an alcohol (e.g. methanol, ethanol, propanol) for producing the corresponding fatty acid esters.

For the purpose of the present description, it shall be understood that a liquid biodiesel composition does not contain any fossil fuel and thus does not contain any fuel originating from non-renewable source. Thus the term biodiesel means fossil fuel-free
15 biodiesel composition.

Biodiesel materials, such as methyl esters of fatty acids derived from vegetable or animal fats, are conventionally manufactured by freeing fatty acids from glycerol (e.g., via a trans-esterification process). Exemplary methods are described in U.S. Pat. Nos. 6,399,800; 6,348,074; 6,015,444; 6,203,585; 6,174,501; 6,235,104; and 7,270,768, each of
20 which are incorporated herein by reference in their entirety. In a typical mechanism, an animal or plant fat and/or oil (composed of triglycerides -- esters that contain both fatty acids and glycerol) is reacted with an alcohol, such as ethanol or methanol. A base can be used to deprotonate the alcohol to speed the reaction, while heat and catalysts (e.g., alkaline catalysts -- typically strong bases, such as sodium or potassium hydroxide) can be
25 used to speed the reaction. Because the trans-esterification reaction is an equilibrium reaction, the reaction is often incomplete, and yields of biodiesel products can vary significantly (e.g., 40-90 percent) depending on the reactants, catalysts, temperature and pressure conditions, and the amount of time permitted to pass. Through the trans-esterification reaction, the organic group of the ester is exchanged for that of the alcohol,
30 which, in the case of triglycerides, results in the formation of alkyl ester and crude glycerol. As such, in the production of biodiesel, significant amounts of a waste stream, that can include glycerin, water, salts of fatty acids and/or free fatty acids, methanol, free glycerol,

soap, unconverted monoglycerides and diglycerides, and/or other polar compounds, is produced, requiring additional separation/processing steps to obtain usable biodiesel products, while also creating disposal issues with regard to the waste stream. As defined herein, the term "crude biodiesel product" includes the immediate product of a trans-
5 esterification reaction (e.g., a product that has not been subjected to substantial modification and/or separation processes).

Chemically, triglycerides consist of three long-chain fatty acid molecules joined by a glycerine molecule. The biodiesel process uses a sodium hydroxide or potassium hydroxide catalyst (lye) to break off the glycerine molecule and combine each
10 of the three fatty-acid chains with a molecule of methanol, creating mono-alkyl esters, or Fatty Acid Methyl Esters (FAME) - biodiesel. The glycerol by-product sinks to the bottom and is removed. The process is called transesterification.

The common international standard for biodiesel is EN 14214.

There are additional national specifications. ASTM D 6751 is the most
15 common standard referenced in the United States and Canada. In Germany, the requirements for biodiesel are fixed in the DIN EN 14214 standard and in the UK the requirements for biodiesel is fixed in the BS EN 14214 standard, although these last two standards are essentially the same as EN 14214 and are just prefixed with the respective national standards institution codes.

20 There are standards for three different varieties of biodiesel, which are made of different oils:

ME (rapeseed methyl ester, according to DIN E 51606)

PME (vegetable methyl ester, purely vegetable products, according to DIN E
51606)

25 FME (fat methyl ester, vegetable and animal products, according to DIN V 51606)

The standards ensure that the following important factors in the fuel production process are satisfied:

- Complete reaction.
- 30 - Removal of glycerin.
- Removal of catalyst
- Removal of alcohol.

- Absence of free fatty acids.
- Low sulfur content.

In some embodiments of a liquid biofuel as described herein, the liquid biodiesel composition is based on esterified fat and/or oil originating from a group comprising animal, plant, fungi or algae.

In some embodiments of a liquid biofuel as described herein, the liquid biodiesel composition comprises one or more esterified fatty acids, wherein the one or more fatty acids are selected in a group comprising lauric acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, arachidic acid, gadoleic acid, behenic acid, erucic acid, lignoceric acid and nervonic acid.

In some embodiments of a liquid biofuel as described herein, the liquid biodiesel composition comprises, as the mainly represented esterified fatty acids, those selected in a group comprising oleic acid, linoleic acid, linolenic acid, palmitic acid, stearic acid and gadoleic acid.

In some embodiments of a liquid biofuel as described herein, the liquid biodiesel composition is based on esterified oil originating from a group comprising soybean oil, sunflower oil, rapeseed oil, olive oil, canola oil and palm oil.

In some embodiments of a liquid biofuel as described herein, the liquid biodiesel composition comprises, or even consists essentially of, esterified palm oil.

In some embodiments, the starting liquid biodiesel composition comprises triglycerides, advantageously at a final concentration complying with biodiesel standards, which encompasses a final concentration complying with the European standard EN14214.

In some embodiments, the starting liquid biodiesel composition comprises a triglyceride content of at most 0.2 % by weight of the total weight of the said starting liquid biodiesel composition.

In some embodiments, the triglycerides contained in the starting liquid biodiesel comprise one or more triglyceride compounds having fatty acid chains which may be identical or distinct, i.e. two fatty acid chains are identical and the third fatty acid chain is distinct from the two others, or the three fatty acid chains are distinct.

In some embodiments of the triglyceride compounds, the fatty acid chains having a number of carbon atoms ranging from 4 to 26, advantageously a number of

carbon atoms ranging from 8 to 22, which encompasses a number of carbon atoms ranging from 8 to 18.

In some embodiments of the triglyceride compounds, the fatty acid chains contained therein comprise saturated fatty acid chains.

5 In some embodiments of the triglyceride compounds, the fatty acid chains contained therein comprise unsaturated fatty acid chains, which encompasses mono-unsaturated fatty acid chains and poly-unsaturated fatty acid chains, advantageously poly-unsaturated fatty acid chains having a number of double bonds ranging from 1 to 3, and preferably poly-unsaturated fatty acid chains having a number of double bonds ranging
10 from 1 to 2.

In some embodiments, the starting liquid biodiesel composition comprises free fatty acids, notably free fatty acids having a number of carbon atoms ranging from 7 to 13.

In some embodiments, the starting liquid biodiesel composition results from the mixture of two or more biodiesel compositions, which means that the said starting
15 liquid biodiesel consists of a blend composition.

In some embodiments, the starting liquid biodiesel composition results from the blending of two or more biodiesel compositions selected in a group comprising (i) a biodiesel composition derived from palm stearin, preferably derived from refined bleached and deodorized (RBD) palm oil, (ii) a biodiesel composition derived from waste cooking
20 oil and (iii) a biodiesel composition derived from palm oil methyl ester.

Advantageously, the starting liquid biodiesel composition comprises a biodiesel composition derived from waste cooking oil.

According to these embodiments, the final content of waste cooking oil in the starting liquid biodiesel composition ranges from 20% by weight to 100% by weight, based
25 on the total weight of the said starting liquid biodiesel composition, which encompasses a final content of waste cooking oil ranging from 50% by weight to 100% by weight, based on the total weight of the said starting liquid biodiesel composition.

These embodiments include a weight content of waste cooking oil of at least 20%, 21%, 22%, 23%, 24%, 25%, 26%, 27%, 28%, 29%, 30%, 32%, 33%, 34%, 35%,
30 36%, 37%, 38%, 39%, 40%, 41%, 42%, 43%, 44%, 45%, 46%, 47%, 48%, 49%, 50%, 51%, 52%, 53%, 54%, 55%, 56%, 57%, 58%, 59%, 60%, 61%, 61%, 63%, 64%, 65%, 66%, 67%, 68%, 69%, 70%, 71%, 72%, 73%, 74%, 75%, 76%, 77%, 78%, 79%, 80%,

81%, 82%, 83%, 84%, 85%, 86%, 87%, 88%, 89%, 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98% and 99%, based on the total weight of the starting liquid biodiesel composition.

Without wishing to be bound by any particular theory, the inventors believe
5 that the presence of waste cooking oil in the starting liquid biodiesel composition contributes to the property of the liquid biofuel composition as described herein of remaining stable during a long time period.

An illustrative well known liquid biodiesel composition comprising waste cooking oil is the Malaysian biodiesel, that has been used in the examples herein. The said
10 Malaysian liquid biodiesel composition comprises a biodiesel composition derived from palm stearin, a biodiesel composition derived from palm oil methylester and a biodiesel composition derived from waste cooking oil.

As used herein, the expression "biodiesel composition derived from" means that the said biodiesel composition does not necessarily consist of a raw material but
15 instead consists of a processed raw material, typically a biodiesel composition resulting from a process of a raw composition comprising at least one or more steps selected in a group comprising refining, bleaching or deodorizing the said raw material. In some embodiments, the raw material comprises fatty acids which are processed at least by trans-esterification for obtaining a liquid biodiesel composition which may be used for preparing
20 a biofuel composition as described herein.

Carbonaceous material

As used in this specification, the term "carbonaceous" refers to a carbon-containing material.

25 The carbon content of carbonaceous material particles useful for the present invention typically exceeds 30 wt.%, based on the total weight of the carbonaceous material particles; it is often above 40 wt. %. It is preferably above 45 wt.%, and more preferably above 50 wt.%, based on the total weight of the carbonaceous material particles. On the other hand, it is typically of at most 90 wt.%, and often of at most 80 wt.%, based
30 on the total weight of the carbonaceous materials particles. It can be of at most 70 wt.% or even of at most 60 wt.%, based on the total weight of the carbonaceous material particles. Certain useful ranges for the carbon content of carbonaceous material particles useful for

the present invention are either from about 40 wt.% to about 80 wt.%, or from about 45 wt.% to about 75 wt.%, based on the total weight of the carbonaceous material particles. The carbon content of the carbonaceous material particles can be determined by any method known to the skilled person. For example, it can be determined by drying the carbonaceous material particles for 12 h at 100°C in an oven (to remove water and other volatiles), then keeping the dried particles in a dessicator (to avoid water pickup), then burning the carbonaceous material particles in a burning oven under conditions capable of converting essentially the whole (when not, the whole) carbon content of the carbonaceous material particles into carbon dioxide, then quantifying the C content (through the CO₂ formed by the combustion) by infrared detection.

The carbon-containing material includes, by way of illustration and not limitation, coal, coke, graphite, char, biocoal such as charcoal or torrefied biomass, notably torrefied wood and the like. In general, any carbonaceous fuel can be used as the solid carbonaceous material in the invention.

In one preferred embodiment, the carbonaceous material is coal. By way of illustration, anthracite, semi-anthracite, medium and high-volatile bituminous, sub-bituminous, and lignite coals can advantageously be used to practice this invention.

The coal for use in the invention can be obtained in a dry or wet form and mixed with fluid to form a coal-fluid mixture.

In view of the manner in which coal fractures during milling, coal particles will have irregular shapes which, however, are of a body (or maximum side-to-side thickness) such that the sub-sieve sized discrete particles will pass through a specified mesh of a sieve. The size of the discrete particle can be expressed in terms of a spherical diameter comprised between 1 µm to 5000 µm; through which a coal particle from a sample of coal or coal-water slurry will pass. For particles finer than 10 µm, the size of the particles can be determined by means of a sieve, or a sedimentometer, or a scanning electron microscope (SEM), or the like.

In certain embodiments, the particle size values, as well as the size distribution of the particles, is measured by the mean of laser diffraction by dry dispersion, respecting the principles and basic rules set out in ISO 13320:2009 (E).

In practice, the analysis is preferably performed using a Helos H1302 laser diffraction sensor (Sympatec, Germany).

The detector of the focal length is selected so that its pass band covers the size range of the carbonaceous material particles to be analysed.

For example, when analysing a milled torrefied biomass, R4 detector (0.5 μm to 350 μm) is particularly well adapted.

5 The carbonaceous material particles are dispersed in a stream of dry nitrogen under pressure using a dry dispersing unit (Rodas, Sympatec, Germany).

 The optimum operating conditions are sought experimentally to obtain a good dispersion of particles, without crushing in the ejector. In practice, when analysing carbonaceous material particles in the form of ground torrefied biomass, the nitrogen
10 pressure is about 100 kPa (1 bar) and the depression represents about 4 kPa (40 mbar).

 The carbonaceous material particles are fed using a vibrating chute. The feed rate is adjusted so as to obtain an optical concentration between 2% and 10%.

 In practice the total mass of the sample containing the carbonaceous material particles to be analysed ranges from about 1g to about 10g, preferably about 5 g.

15 Laser diffraction data were acquired and analysed using the Windox 5 software (Sympatec, Germany).

 In some embodiments, the carbonaceous solid material is coke. Coke is the solid, cellular, infusible material remaining after the carbonization of coal, pitch, petroleum residues, and certain other carbonaceous materials. The varieties of coke, other than those
20 from coal, generally as identified by prefixing a word to indicate the source, e.g., "petroleum coke". To indicate the process by which a coke is manufactured, a prefix also is often used, e.g., "beehive coke".

 By way of illustration and not limitation, petroleum coke can be used in this invention. There are at least two types of petroleum coke: delayed coke, and fluid coke.
25 Delayed coke generally contains from about 8 to about 18 weight percent of volatile matter, has a grindability index of from about 40 to about 60, and has a true density of from about 1.28 to about 1.42 grams per milliliter. Fluid coke generally contains from about 3.7 to about 7 weight percent of volatile matter, has a grindability index of from about 20 to about 30, and has a true density of from about 1.5 to about 1.6 grams per milliliter.

30 Other carbonaceous materials which can be used in this invention include, .e.g., high temperature coke, foundry coke, low temperature coke, medium temperature coke, pitch coke, char, charcoal, solvent refined coal, and mixtures of one or more of said

carbonaceous materials with coal and/or petroleum coke. Mixtures of coal and petroleum coke can be used in this invention.

Most preferably, carbonaceous material according to the present invention may also be a biocoal such as torrefied biomass, such as torrefied wood. Biocoal is a solid fuel made from biomass by heating it in an inert atmosphere. The result is either charcoal, or if the process temperature is mild, a product called torrefied wood. Indeed biomass may be transformed by heat in a low oxygen environment, by a process known as torrefaction, into a hydrophobic, decay-resistant material that may be used as a fuel (e.g., as a coal fuel substitute, a feedstock for entrained-flow gasification, or other fuel), a soil additive, a long-term carbon storage mechanism, or for other suitable use. In particular, torrefied biomass may be used in existing fuel-burning power plants (e.g., coal-burning power plants), thus facilitating the use of renewable fuels with existing fuel-burning infrastructure to generate electricity.

Torrefaction of biomass may be described as a mild form of pyrolysis at temperatures typically ranging between 230-320°C. During torrefaction, water present in the biomass may evaporate and biopolymers such as cellulose, hemicellulose and lignin, of the biomass may partially decompose, giving off various types of volatile organic compounds referred to as "torgas", resulting in a loss of mass, usually between approximately 30% and approximately 40% and chemical energy between approximately 10% and approximately 20% in the gas phase. Torrefaction results in energy densification, yielding a solid product with lower moisture content and higher energy content compared to untreated biomass. The resulting product may be solid, dry, dark brown or blackened material which is referred to as "torrefied wood", "torrefied biomass," "biocoal," or "renewable coal replacement fuel" ("RCRF").

Preferred embodiments of carbonaceous material particles are torrefied wood particles. The inventors have shown that very good results are obtained when preparing the liquid biofuel as described herein with torrefied wood particles. Notably, it has been shown that torrefied wood particles suspended in a liquid biodiesel composition are easily dispersible, which further increases the workability, including the pumpability, of the said liquid biofuel.

Without wishing to be bound by any particular theory, the inventors believe that because the torrefied wood particles possess a hydrophobic surface, as compared to

other carbonaceous material particles, the said torrefied wood particles are, notably, endowed with better dispersible properties.

Unless otherwise stated in this specification, the weight of carbonaceous material is on a moisture-free or "dry basis" herein. Thus, as used herein, the term "dry basis" refers to carbonaceous material which is substantially free of carrier liquid. Carbonaceous material is considered to be dry after it has been air dried by being exposed to air at a temperature of at least 20°C and a relative humidity of less than 50 percent for at least 24 hours.

The carbonaceous materials particles of the present invention are referred as solid particles; referring then to particles that are in the solid state, not the liquid or molten state. However, as may be appreciated by one skilled in the art, solid particles can have varying degrees of hardness depending upon factors such as exposure to atmosphere, for instance.

The carbonaceous material particles preferably provide an average diameter D_{50} ranging from 0.1 μm to 200 μm .

In some embodiments, the carbonaceous material particles have a size distribution defined by a D_{50} ranging from 1 μm to 50 μm , and most preferably ranging 8 μm to 25 μm .

In some embodiments, the carbonaceous material particles preferably provide the size distribution as follows:

- D_{10} comprise between 1 and 50 μm ,
- D_{50} comprise between 0.1 and 100 μm , preferably between 3 and 20 μm , and
- D_{90} comprise between 50 and 500 μm .

Such an average diameter may be obtained by wet or dry grinding, notably in a grinding mill, for instance a tumbling mill, which can be done in either a batch or continuous mode. A tumbling mill is any horizontally mounted cylindrical mill which tumbles its contents when rotating. The preferred tumbling mill used in this invention is the ball mill.

Particle size distribution of carbonaceous materials and notably the average diameter D_{50} , may be determined by the use of laser diffraction sensors, sedimentometer or a scanning electron microscope (SEM).

In some embodiments the liquid biofuel, the carbonaceous material particles content is of at least 10% w/w of the said biofuel, preferably of at least 20% w/w of the said biofuel, and most preferably of at least 30% w/w of the said biofuel.

As shown in the examples herein, a liquid biofuel comprising a content of carbonaceous material particles of more than 50% w/w may be prepared, while maintaining dispensability of the said particles and maintaining the rheological properties of a shear thinning liquid.

As intended herein, a carbonaceous material particle content of at least 10% w/w encompasses at least 15% w/w, 20% w/w, 25% w/w, 30% w/w, 35% w/w, 40% w/w, 45% w/w, 50% w/w, 55% w/w, 60% w/w, and 60% w/w, based on the total weight of the said liquid biofuel.

The carbonaceous material particle content of the liquid biofuel is preferably of less than 80% w/w, so as to avoid manufacturing a biofuel liquid having a too much high viscosity.

In some embodiments, the liquid biofuel as described herein may comprise from 10 to 80 % by weight of carbonaceous material particles, which encompasses from 40 to 60 % by weight.

Further features of the liquid biofuel

In some embodiments, the liquid biofuel as described herein further comprises water, preferably in an amount of 0.5% w/w or more and 20% w/w or less, based on the total weight of the said liquid biofuel.

As used herein, an amount of water of 0.5% w/w or more encompasses at least 0.5% w/w, 1% w/w, 2% w/w, 3% w/w, 4% w/w, 5% w/w, 6% w/w, 7% w/w, 8% w/w, 9% w/w, 10% w/w, 11% w/w, 12% w/w, 13% w/w, 14% w/w, 15% w/w, 16% w/w, 17% w/w, 18% w/w and 19% w/w, based on the total weight of the said liquid biofuel.

In the embodiments of the liquid biofuel wherein the said biofuel comprises water, the said liquid biofuel may be in a form of an oil-in-water(O/W) emulsion. Such a O/W emulsion may be prepared by simply mixing the liquid composition comprising (i) the suspension of carbonaceous material particles in a liquid biodiesel composition and (ii) the water.

The inventors have shown that in the embodiments wherein the liquid biofuel consists of a W/O emulsion, the carbonaceous material particles, e.g. the torrefied wood particles, are located in the continuous phase. In these embodiments, the inventors have shown that the carbonaceous material particles, e.g. the torrefied wood particles, get caught
5 between the droplets in the continuous phase, which prevent them for settling. At the same time, the carbonaceous material particles may act as emulsifying agents, preventing the coalescence of the droplets.

Without wishing to be bound with any particular theory, the inventors believe that O/W emulsions are successfully prepared when the liquid biofuel as described herein
10 comprises water because of the possible presence of non-esterified or des-esterified fatty acid and/or alcohol molecules, which molecules behave as polar molecules having a surfactant effect.

These results explain why there is no requirement for an added emulsifying agent, an added dispersing agent, an added humectant agent, an added wetting agent, an
15 added surfactant agent, nor a viscosity controlling agent for obtaining an appropriate liquid biofuel as described herein.

Hence, in some preferred embodiments, the liquid biofuel is free, is essentially free or contains less than 0.1 wt.%, based on the total weight of the liquid biofuel, of any non ionic emulsifying agent, such as an alkoxylated fatty carboxylic acid, an alkoxylated
20 fatty alcohol, an alkoxylated octyl- or nonylphenol, an alkoxylated fatty amine, an alkoxylated fatty amide (wherein "fatty" wherever used herein denotes usually a C₈-C₂₄ compound) or a mixture thereof.

In some other preferred embodiments, the liquid biofuel is free, is essentially free or contains less than 0.1 wt.%, based on the total weight of the liquid biofuel, of any
25 ionic emulsifying agent, such as a sodium C₈-C₂₄ alkyl sulfate, sodium dodecylbenzene sulfonate, sodium dioctyl sulfosuccinate, ammonium myristate, cetyl pyridinium chloride, an alkali metal salt of a naphthalene sulfonic acid and an alkali metal of a lignosulfonate and the like.

In still some other preferred embodiments, the liquid biofuel is free, is
30 essentially free or contains less than 0.1 wt.%, based on the total weight of the liquid biofuel, of any dispersing agent, such as a polyvinyl alcohol having a hydrolysis ratio of from about 25% to about 100% (notably commercially available as "POVAL" dispersants).

In still some other preferred embodiments, the liquid biofuel is free, is essentially free or contains less than 0.1 wt.%, based on the total weight of the liquid biofuel, of any humectant agent.

5 In still some other preferred embodiments, the liquid biofuel is free, is essentially free or contains less than 0.1 wt.%, based on the total weight of the liquid biofuel, of any wetting agent.

In still some other preferred embodiments, the liquid biofuel is free, is essentially free or contains less than 0.1 wt.%, based on the total weight of the liquid biofuel, of any surfactant agent.

10 In still some other preferred embodiments, the liquid biofuel is free, is essentially free or contains less than 0.1 wt.%, based on the total weight of the liquid biofuel, of any viscosity agent, such as a clay powder or gel, a hydrogenated castor oil and a mix thereof.

15 In some particularly surprising embodiments of the liquid biofuel as described herein, the liquid biofuel contains less than 1000 ppm, based on the total weight of the biofuel, of any added compound capable of exerting an emulsifying or a stabilizing effect. In particular, the liquid biofuel can be essentially free or can be free of any added compound capable of exerting an emulsifying or a stabilizing effect.

20 In some other particularly surprising embodiments of the liquid biofuel as described herein, the said liquid biofuel does not contain any added emulsifying agent, any added surfactant agent, any added dispersing agent, any added humectant agent, any added wetting agent, nor any added rheology additive. As used herein, the term "surfactant" means an amphiphilic compound that comprises a hydrophilic moiety and a hydrophobic moiety and that, when present in water, lowers the surface tension of the water.

25 In some embodiments, a liquid biofuel as described herein may also comprise one or several possible additives usually known in this technical field, such as for instance antioxidant agents, Cold Flow Improvers (CFI), corrosion inhibitors, foam inhibitors, and biocidal preservatives.

Characteristics of the final suspension

30 The liquid biofuel as described herein may provide a viscosity comprised between 0.1 and 10 000 Pa.s, at a temperature of 70°C.

Further, it is also shown in the examples that the viscosity of a liquid biofuel as described herein decreases when it is subjected to increasing shear rate values. These rheological properties of the said liquid biofuel show that the said liquid biofuel is easily workable, and is especially easily pumpable.

5 The rheological properties of the suspensions may be measured using a rheometer under controlled shear rate conditions.

Preparation of the liquid biofuel

10 A liquid biofuel as described herein may be obtained by several known methods; notably by simply mixing the carbonaceous material particles in the liquid biodiesel composition.

15 It is notably possible to produce the suspension by milling under wet conditions, which can be done in either a batch or continuous mode. It is perfectly possible to add the carbonaceous material, the liquid phase and the additives together in advance of the milling operation to provide a composition of exactly desired concentration or alternatively the carbonaceous material content may be intentionally set a low level during milling and increased to the desired level afterwards by a dewatering process. The milling processes described here are presented by way of example and are not intended to be limiting inasmuch as there are numerous methods of milling carbonaceous materials into a
20 composition, including dry methods using a ball mill, or any of a number of other mills such as those cited earlier. If any dry milling method is employed, the washing step may preferably be conducted after the dry milling to avoid a dewatering and drying procedure prior to the milling.

25 It is also possible to proceed to a wet or dried milling of the carbonaceous material to reach the desired size distribution, and notably afterward blend the carbonaceous material with the liquid phase and the additives with a classical agitation blade/counter blade.

30 The present invention also pertains to the use of carbonaceous material particles having a D_{50} ranging from 0.1 μm to 200 μm for preparing a biodiesel-based liquid biofuel.

 The present invention also concerns a method for generating power comprising combustion of the liquid biofuel as described herein.

The following examples are included to illustrate embodiments of the invention. Needless to say, the invention is not limited to the described examples.

EXAMPLES

5 Compounds used in the following examples are as follows:

Torrefied wood chips: 28GJ/Ton , 10% RH, feedstock origin, from New Biomass Energy LLC

Palm oil-based Malaysian biofuel

Specified additives

10

Example 1: preparation of torrefied wood particles

The torrefied wood chips obtained from a torrefactor process and having cm scale was first grinded by dry grinding process to obtain 300 μm to 1mm particle size. Then, this powder is dried milled by Retsch ZM200 dry miller with the following characteristics: grid 120 μm , speed 18000 rpm, 25°C, nitrogen purge, 80 g per batch in 10 min; to obtain particle size distribution centered at 25 μm as followed:

$$D_{10} = 6 \mu\text{m}$$

$$D_{50} = 23 \mu\text{m}$$

$$D_{90} = 60 \mu\text{m}$$

20

These size distributions are measured with Sympatec laser diffraction sensors.

Example 2 : Liquid biofuel preparation

Slurries were prepared by mixing 70% w/w liquid biodiesel (Malaysian biodiesel) and 30% w/w particles of torrefied wood.

25

The Malaysian biodiesel-based liquid biofuel with no additive is stable during a visual check at 2 days and 2 weeks periods.

Example 3 : Liquid biofuel emulsion preparation

30

In Example 3, two liquid biodiesel compositions were used for preparing liquid biofuels, (i) the Malaysian biofuel used in Example 2 and (ii) a LOF biodiesel comprising a

mixture of palm oil ester, palm oil stearin, palm oil mill sludge (POME) and palm oil methyl ester.

Both biofuel (Malaysian and LOF) were used with different water and torrefied wood particles (TWP) content. The results indicated that 10% of water could stabilize the slurry for up to 40% w/w of torrefied wood particles. Further, the addition of water increases the viscosity of the liquid biofuel.

The following liquid biofuel based on Malaysian biodiesel were prepared :
(i):50%/TWP 30%/water 20%, (ii) Malaysian biofuel 50%/TWP 40%/water 20%,

The following liquid biofuel based on LOF biodiesel were prepared: (i) 50%/TWP 40%/water 10%, (ii) LOF biofuel 50%/TWP 30%/water 20% (from left to right) at 2 weeks.

Viscosity of a biofuel of water/biodiesel/TWP is shown in figure 1. The shear thinning behavior of the resulting liquid biofuel is quite obvious. With more water, the viscosity decreased.

As shown in Figure 1, the Malaysian biodiesel-based biofuel has a higher viscosity than the LOF biodiesel-based biofuel, at all shear rate values.

This method was also tested on a liquid biofuel prepared from a Colza biodiesel.

The following liquid biofuel based on Colza biodiesel were prepared: 0%/TWP 30%/water 0%, Colza biodiesel 50%/TWP 40%/water 10%, Colza biodiesel 50%/TWP 30%/water 20% and Colza biodiesel 60%/TWP 30%/water 10% (from left to right) at 48 h.

With a liquid biofuel comprising a suspension of torrefied wood particles suspended in a Colza biodiesel in the presence of water, the same rheological behavior than with the Malaysian biodiesel is observed. The addition of water stabilizes the slurry, for which no torrefied wood particles settlement was observed at Day 2.

CLAIMS

1. A liquid biofuel comprising carbonaceous material particles having a D_{50} ranging from 0.1 μm to 200 μm suspended in a liquid biodiesel composition.

5

2. The liquid biofuel according to claim 1, wherein the carbonaceous material particles content is of at least 10% w/w of the said biofuel, preferably of at least 20% w/w of the said biofuel, and most preferably of at least 30% w/w of the said biofuel.

10

3. The liquid biofuel according to any one of claims 1 and 2, wherein the carbonaceous material particles have a size distribution defined by a D_{50} ranging from 1 μm to 50 μm , and most preferably ranging 8 μm to 25 μm .

4. The liquid biofuel according to any one of claims 1 to 3, wherein carbonaceous material particles provide the size distribution as follows:

15

- D_{10} comprise between 1 and 50 μm , and
- D_{90} comprise between 50 and 500 μm .

5. The liquid biofuel according to any one of claims 1 to 4, wherein the carbonaceous material particles are selected in a group comprising a vegetal biomass, a coal, a coke, a graphite, a char, a biocoal and a combination thereof.

20

6. The liquid biofuel according to any one of claims 1 to 5, wherein the carbonaceous material particles consist of a torrefied biomass, preferably torrefied wood particles.

25

7. The liquid biofuel according to any one of claims 1 to 6, wherein the liquid biodiesel is based on esterified fat and/or oil originating from a group comprising animal, plant, fungi or algae.

30

8. The liquid biofuel according to any one of claims 1 to 7, wherein the liquid biodiesel comprises esterified palm oil.

9. The liquid biofuel according to any one of claims 1 to 8, comprising further water in an amount ranging from 0.5% w/w to 25% w/w.

5 10. The liquid biofuel according to any one of claims 1 to 9, which does not comprise any added emulsifying agent or any surfactant compound.

11. The use of carbonaceous material particles having a D_{50} ranging from 0.1 μm to 200 μm for preparing a biodiesel-based liquid biofuel.

1/1

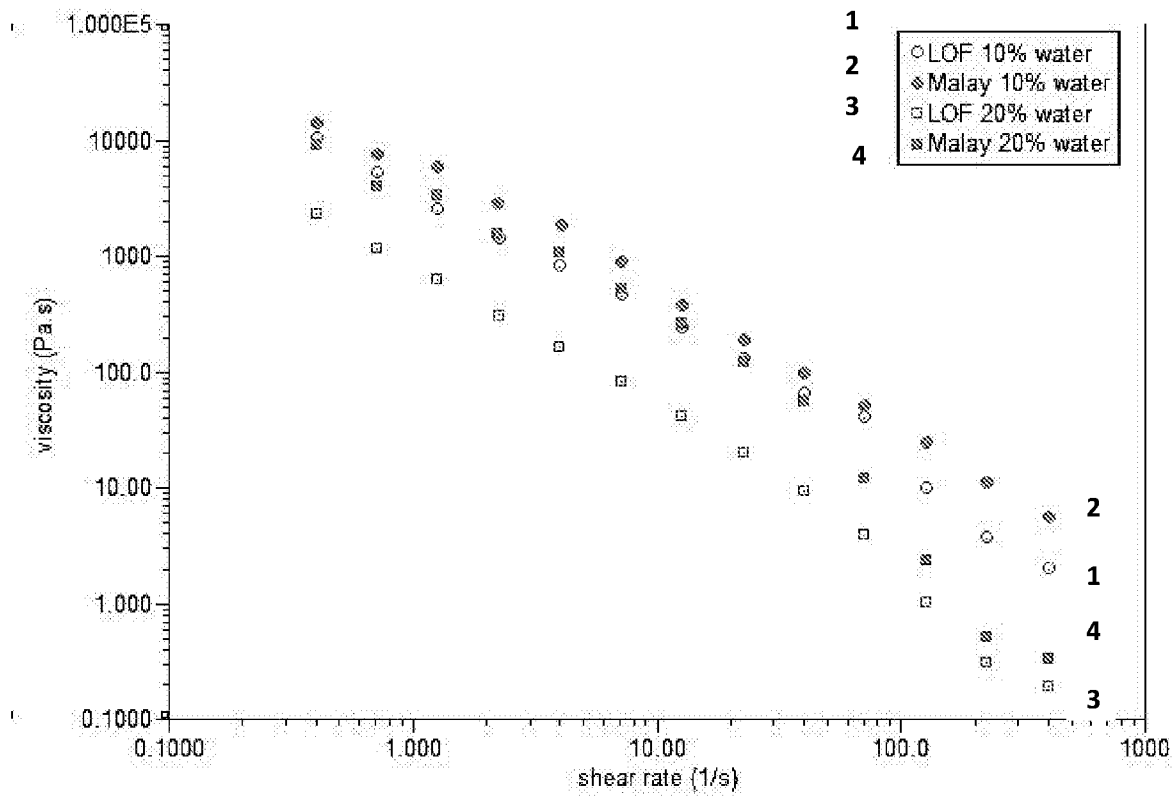


FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/094577

A. CLASSIFICATION OF SUBJECT MATTER

C10L 1/02(2006.01)i

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)

C10L 1/-

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)

CNPAT,WPI,EPODOC,CNKI:BIODIESEL, particle, oil, COAL, CARBONACEOUS, FAT, biofuel, liquid

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012060961 A1 (KIOR INC.ET AL.) 10 May 2012 (2012-05-10) description, paragraphs [0006] to [0039]	1-11
X	WO 2012092644 A1 (LICELLA PTY LTD ET AL.) 12 July 2012 (2012-07-12) description, page 3, line 1 to page 19, line 18	1-11
A	US 4355999 A (ATLANTIC RICHFIELD CO) 26 October 1982 (1982-10-26) claims 1-11	1-11
A	CN 101092578 A (YAN, CHUNXIA) 26 December 2007 (2007-12-26) claims 1-10	1-11



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

“E” earlier application or patent but published on or after the international filing date

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“O” document referring to an oral disclosure, use, exhibition or other means

“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

24 August 2015

Date of mailing of the international search report

22 September 2015

Name and mailing address of the ISA/CN

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2014/094577

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