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(71) Applicant: **BATTELLE ENERGY ALLIANCE, LLC** [US/US]; P.O. Box 1625, Idaho Falls, ID 83415-3899 (US).

(72) Inventors: **GINOSAR, Daniel, M.**; 915 Pescadero Place, Idaho Falls, ID 83404 (US). **WENDT, Daniel, S.**; 165 11th Street, Idaho Falls, ID 83404 (US).

(74) Agent: **BARZEE, Eric, M.**; Battelle Energy Alliance, LLC, P.O. Box 1625, Idaho Falls, ID 83415-3899 (US).

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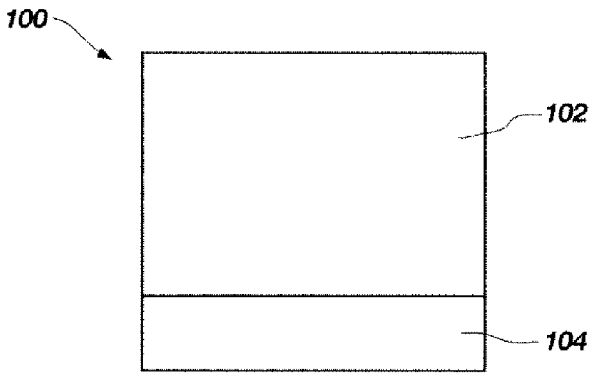


FIG. 1

(57) Abstract: A method of removing a polar solvent from a fluid volume contaminated with at least one polar impurity, such as a free fatty acid, is provided. The method comprises providing a fluid volume that includes at least one polar impurity dissolved in at least one solvent. The fluid volume is contacted with an expanding gas to remove the at least one solvent. The expanding gas may be dissolved into the at least one solvent in the fluid volume to form a gas-expanded solvent. The immiscibility of the polar impurities in the gas-expanded solvent enables separation of the polar impurities from the gas-expanded solvent. After separation of the polar impurities, at least one of the temperature and pressure may be reduced to separate the solvent from the expanding gas such that the clean solvent may be reused.

METHODS FOR RECOVERING A POLAR SOLVENT FROM A FLUID STREAM CONTAMINATED WITH AT LEAST ONE POLAR IMPURITY

RELATED APPLICATIONS

This application claims benefit of U.S. Non-provisional application No. 12/238,225, filed September 25, 2008, entitled METHODS FOR RECOVERING A POLAR SOLVENT FROM A FLUID STREAM CONTAMINATED WITH AT LEAST ONE POLAR IMPURITY, which is incorporated herein by reference in its entirety.

GOVERNMENT RIGHTS

This invention was made under a Cooperative Research and Development Agreement between Enviroquest Research Corporation and Battelle Energy Alliance, LLC under Contract No. DE AC051D14517, awarded by the U.S. Department of Energy. The U.S. Government has certain rights in the invention.

TECHNICAL FIELD

The present invention relates to a method of recovering a polar solvent contaminated with at least one polar impurity, such as a free fatty acid. More specifically, embodiments of the present invention relate to recovering the polar solvent using an expanding gas.

BACKGROUND

Biodiesel has been the subject of much investigation as an alternative for petroleum diesel fuel. As used herein, the term "biodiesel" refers to an ester-based fuel oxygenate that is derived from a biological source. The biodiesel fuel is used as an alternative for, or as an additive to, petroleum diesel fuel in automobiles or other vehicles. The biodiesel fuel is conventionally produced from a triglyceride starting material or a fatty acid starting material by a transesterification reaction or an esterification reaction, respectively. Generally, the triglyceride is reacted, or transesterified, with an alcohol to produce glycerol (also known as glycerin) and a corresponding alkyl ester of the triglyceride. Similarly, the fatty acid is reacted, or esterified, with an alcohol to produce a corresponding alkyl ester of the fatty acid. The triglyceride or fatty acid feedstock materials are available from various sources, such as from pure or used fats or oils. These fats or oils are typically hydrophobic and water-insoluble. In addition to including the triglyceride or fatty acid, the fats or oils include free fatty acids, phospholipids, sterols, water, dirt, detergents, polar compounds, or other

impurities. These sources of the fats or oils are too viscous and their freezing points too high to be used directly as the biodiesel fuel and, therefore, the triglycerides or fatty acids are transesterified or esterified to produce the corresponding alkyl ester, which has a lower viscosity than that of the source of the feedstock material. The transesterification of the triglyceride (or the esterification of the fatty acid) is conducted with an excess of the alcohol in the presence of a catalyst. As the reaction proceeds, two phases form. One phase includes the alkyl ester and the other phase includes the glycerol. The two phases are allowed sufficient time to settle before additional processing is conducted to purify the alkyl ester from the glycerol.

Currently, most biodiesel is made from soybean oil, methanol, and an alkaline catalyst. However, there are large amounts of waste fats and oils that are unsuitable for human consumption that could be converted to biodiesel at lower cost. The problem with processing these waste oils is that they often contain large amounts of free fatty acids that cannot be converted to biodiesel using an alkaline catalyst. These free fatty acids react with the alkaline catalyst to produce soaps that inhibit the separation of the biodiesel, glycerin, and wash water. An acid-catalyzed pretreatment with an alcohol, such as methanol, has been used to convert these high free fatty acid feedstocks to methyl esters which do not form soaps. However, this pretreatment leaves behind acid and water which interferes with the alkaline transesterification. The free fatty acids could first be extracted using a solvent, such as an alcohol, and the purified triglyceride would then undergo base-catalyzed transesterification. The fatty acid could be recovered from the solvent and then be esterified using an acid catalyst and methanol to produce the alkyl ester, sold, or simply discarded. Additionally, in some cases the biodiesel product contains unreacted free fatty acids which cause the product to be off spec. Again, these free fatty acids can be extracted using a solvent such as an alcohol.

Further, in food and chemical processes some fats and oils need to have impurities such as, for example, free fatty acids, sugars, and non-oil lipids, removed to improve their quality. This too can be accomplished by extracting the impurities with a solvent, such as an alcohol. The extraction process results in the formation of a waste product including the solvent contaminated with the impurities removed from the fat or oil

Removing the free fatty acids from a fat or oil results in additional complexity of recovering and recycling the solvent which has proven to be problematic. Particularly, the solvent is typically removed by distillation, evaporization, lyophilization, use of an inert gas, or use of a drying agent, such as a molecular sieve.

Because these conventional techniques consume considerable amounts of energy or use expensive and toxic compounds, efficient methods of recovering a solvent used to extract polar impurities, such as free fatty acids and water, from fat, oil, or other feedstock stream are desired.

BRIEF SUMMARY OF THE INVENTION

According to an embodiment, a method of recovering a polar solvent from a fluid volume is provided. The method may include extracting at least one polar impurity, such as a free fatty acid, from a feedstock volume into the polar solvent to form a fluid volume that includes the polar solvent and the at least one polar impurity. The fluid volume may be subjected to an expanding gas at a pressure at or near a critical point thereof such that polar solvent may become less polar, thus separating from the polar impurity, such as the at least one polar impurity. After the at least one polar impurity has been removed or separated, the pressure of the expanding gas may be modified to recover the polar solvent.

According to another embodiment, a method of removing at least one polar impurity from at least one polar solvent is provided. A fluid stream including at least one polar solvent and the at least one polar impurity, may be contacted with an expanding gas at or near a critical point thereof to form two substantially immiscible phases. The two substantially immiscible phases may be separated from one another by conventional techniques. After separation of phases, at least one of the temperature and pressure of the expanding gas may be modified such that the solvent separates from the expanding gas.

According to yet another embodiment, a method of recovering a polar solvent from a fluid volume, including methanol and at least one polar impurity, by exposing it to carbon dioxide is provided. At least one of a temperature and a pressure may be increased to form a gas-expanded solvent including the methanol and the carbon dioxide and a liquid phase including the polar impurity. The liquid phase may be removed from the gas-expanded solvent and the pressure of the gas-expanded solvent may be reduced by between about 20 psi to about 30 psi to separate the gas-expanded solvent into methanol and carbon dioxide.

According to another embodiment, a method of removing a polar impurity from a polar solvent is provided. The method may include contacting a fluid volume including the polar impurity and the polar solvent with carbon dioxide and adjusting at least one of a pressure and a temperature to greater than or equal to a critical point of the expanding gas to form one phase including the at least polar impurity and another phase including the solvent and the carbon dioxide. For example, the pressure may be increased to a range of from about 1110 psi

to about 1117 psi and a temperature in the range of from about 30°C to about 40°C to form a liquid phase and another phase including methanol and the carbon dioxide.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

FIGs. 1-4 are schematic illustrations of an embodiment of a method for recovering a solvent contaminated with a polar impurity;

FIG. 5 is a schematic illustration of an embodiment of a continuous flow process for removing polar impurities from a solvent;

FIGs. 6-9 are schematic illustration of an embodiment of a method for recovering methanol contaminated with oleic acid using carbon dioxide as an expanding gas; and

FIG. 10 is a plot showing fluid volumes as a function of pressure according to the embodiment shown in FIGs. 6-9.

DETAILED DESCRIPTION OF THE INVENTION

An expanding gas may be used to recover a polar solvent from a fluid volume contaminated with at least one polar impurity, such as a free fatty acid. As used herein, the term "expanding gas" means and includes a gas, liquid, or supercritical fluid capable of dissolving into a solvent at which point a volume occupied by the solvent increases. The expanding gas may alter the solubility of the polar impurity in the polar solvent, enabling recovery of the polar solvent. Recovering the polar solvent from the fluid volume using the expanding gas enables recycling of the polar solvent for use in the extraction of at least one polar impurity from, for example, high free fatty acid oils. While the fluid volume is described herein as a polar solvent contaminated with at least one polar impurity, such as at least one free fatty acid, produced as a product of the extraction process in biodiesel production, the expanding gas may be used to remove impurities from other impurity-containing feedstock volumes or product volumes. For instance, the expanding gas may be used to recover a polar solvent from an impurity-containing feedstock volume or product volume in the oil refining industry.

Biodiesel produced by the transesterification or esterification reaction may be an alkyl ester or mixtures thereof. An alkyl ester of a glyceride may be produced by a transesterification reaction in which an alcohol is reacted with a glyceride. Alternatively, an alkyl ester of a fatty acid may be produced by an esterification reaction in which an alcohol is reacted with a fatty acid. The chemical reaction for producing the alkyl ester from a glyceride is shown in Equation 1:

$$R_1COOR_2 + R_3OH \longrightarrow R_1COOR_3 + R_2OH \quad \text{(Equation 1).}$$

In the reaction, the organic ester, R_1COOR_2, is reacted with the alcohol, R_3OH, to produce the organic ester, R_1COOR_3, and the alcohol, R_2OH. R_1 may be an aliphatic hydrocarbon chain having from four to thirty-six carbon atoms. R_2 may be glycerol or another aliphatic hydrocarbon chain having from four to thirty-six carbon atoms. R_2 is linked to R_1 through an ester ("COO^-") linkage. R_1COOR_2 may be an acylglycerol, fat, oil, wax, or fatty acid. The acylglycerol may be mono-, di-, or tri-substituted including, but not limited to, a monoglyceride, diglyceride, or triglyceride. If R_1COOR_2 is a monoglyceride, diglyceride, triglyceride, fat, or oil, R_1 may be the aliphatic hydrocarbon (C_4 to C_{36}) chain and R_2 may be glycerol. If R_1COOR_2 is a fatty acid, R_1 may be the aliphatic hydrocarbon (C_4 to C_{36}) chain and R_2 may be hydrogen or a metal (*i.e.*, R_2 is the salt of the fatty acid ($R_1COO^-M^+$)). R_1COOR_2 may also include a free fatty acid (R_1COO^-). If R_1COOR_2 is a wax, R_1 may be an aliphatic hydrocarbon chain linked to R_2 through the ester linkage. In one embodiment, R_1COOR_2 is a triglyceride, such as an animal fat, animal oil, vegetable fat, vegetable oil, or mixtures thereof. Specific examples of triglycerides include, but are not limited to, peanut oil, rapeseed oil, sesame oil, soybean oil, corn oil, sunflower oil, palm oil, palm kernel oil, coconut oil, safflower oil, olive oil, linseed oil, cotton seed oil, tung oil, castor oil, beef fat, pork fat, fish oil, rendered fat, or mixtures thereof. The triglyceride may also be obtained from waste edible oils, such as restaurant grease, household grease, waste industrial frying oil, or mixtures thereof. In another embodiment, R_1COOR_2 is a fatty acid, such as a saturated fatty acid, an unsaturated fatty acid, or mixtures thereof. By way of non-limiting example fatty acids may include, but are not limited to, oleic acid, palmitic acid, stearic acid, linoleic acid, or mixtures thereof. R_3 may be a short-chain hydrocarbon group, which is attached to a hydroxyl group of the alcohol. R_3 may include, but is not limited to, a methyl, ethyl, propyl, or butyl group. The alcohol, R_3OH, may include, but is not limited to, methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, t-butanol, or mixtures thereof. The alcohol may be selected depending on the desired products of the reaction.

In the processing or refining of commercial oils, such as olive oil, corn oil, and soybean oil, impurities may be removed to reduce acidity and to provide improved aroma and flavor. Impurities such as free fatty acids, sugars, non-oil lipids, aflatoxin, and other components, may be extracted from the oil, for example, by a conventional liquid extraction process using an alcohol, such as ethanol.

The feedstock volume that is a source of the glyceride or fatty acid feedstock material may be a nonpolar liquid, such as a fat, oil, or mixtures thereof. The fat or oil may include, but is not limited to, an animal fat, animal oil, vegetable fat, vegetable oil, or mixtures thereof, such as rapeseed oil, sesame oil, soybean oil, corn oil, sunflower oil, peanut oil, palm oil, palm kernel oil, coconut oil, safflower oil, olive oil, linseed oil, cotton seed oil, tung oil, castor oil, beef fat, pork fat, chicken fat, fish oil, rendered fat, or mixtures thereof. The glyceride or fatty acid feedstock material may also be obtained from waste edible oils, such as restaurant grease, household grease, waste industrial frying oil, or mixtures thereof. In addition to the glyceride or fatty acid feedstock material, the feedstock volume may include other polar impurities, such as free fatty acids, phospholipids, sterols, water, dirt, detergents, or mixtures thereof. As a non-limiting example, the feedstock volume may include greater than or equal to about 5% by weight of free fatty acids, which are dispersed, dissolved, or emulsified in the feedstock volume. Conventional yellow grease may include greater than about 9% by weight free fatty acids, while conventional brown grease may include greater than about 25% by weight free fatty acids.

Polar impurities, such as free fatty acids, may be removed from the feedstock volume with a polar solvent, for example, before using the feedstock volume in the transesterification reaction to convert triglycerides to alkyl esters, or during processing of feedstock to produce commercially available oil. As a non-limiting example, the polar solvent may be methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, t-butanol, or mixtures thereof. The polar solvent may be selected such that it has an affinity to attract polar impurities from the nonpolar components, such as triglycerides, fats, and oils, in the feedstock volume. Thus, the polar solvent extracts the polar impurity from the feedstock volume forming a fluid volume that includes the polar solvent and the polar impurity. The removal of the polar impurities facilitates separation of the nonpolar components in the feedstock volume, such as separation of fatty acids for transesterification to form alkyl esters useful in the production of biodiesel.

The polar impurities and polar solvent in the fluid volume may be separated by treatment with the expanding gas. While the specific embodiments herein describe removing polar impurities from the polar solvent, the expanding gas may be similarly used to separate other polar compounds, as would be recognized by one of ordinary skill in the art. The fluid volume may be treated to recover the polar solvent by contacting the fluid stream with the expanding gas. Prior to treatment with the expanding gas, the fluid volume may be maintained at ambient temperature and pressure. The expanding gas may be a solvent that includes, by way of non-limiting example, carbon dioxide, methane, ethane, propane, butane,

pentane, isomers thereof (*i.e.*, n-butane, isobutane, t-butane, n-pentane, isopentane, etc.), propylene, butylene, pentene, or mixtures thereof. The expanding gas may be in a gas phase, a liquid phase, a near critical liquid phase, or a supercritical phase as the expanding gas contacts the contaminated polar solvent. The expanding gas may be selected so that it has a critical phase that is obtainable under moderate temperature and pressure conditions. In other words, a critical temperature ("T_c") and a critical pressure ("P_c") of the expanding gas may be moderate, which enables recovery of the polar solvent using low amounts of energy. For instance, the T_c may range from approximately -20°C to approximately 250°C and the P_c may range from approximately 200 pounds per square inch ("psi") to approximately 5000 psi. As used herein, the term "psi" is defined as gauge pressure, or psig. The expanding gas may be maintained at or near its T_c and P_c (*i.e.*, at or near a critical point of the expanding gas) to recover the polar solvent from the fluid volume including at least one polar impurity. For example, each of the temperature and pressure may be slightly below, at, or above the T_c and P_c. The T_c of the expanding gas is the temperature above which the expanding gas does not exhibit a distinct gas and liquid phase. The P_c of the expanding gas is the minimum pressure needed to liquefy the expanding gas at a temperature incrementally below its T_c. If the expanding gas is heated to a temperature above the T_c and pressurized to a pressure above the P_c, the expanding gas is in the supercritical phase and exhibits properties that are intermediate to those of a gas or a liquid. These properties include, but are not limited to, density, viscosity, surface tension, diffusivity, and solubility. The properties of the expanding gas in the supercritical phase may be different than the properties of the same solvent in either a liquid phase or a gas phase. For instance, in the supercritical phase, the expanding gas may exhibit a viscosity that is more similar to that of a gas and a density that is more similar to that of a liquid.

Due to its high density, low viscosity, and high diffusivity, the expanding gas may be used as a solvent or as a gas antisolvent. The expanding gas may function in either the solvent or gas antisolvent capacity depending on temperature and pressure conditions at which the expanding gas is used and the chemical nature of the solute. The concentration of the expanding gas may also affect whether the expanding gas functions as a solvent or gas antisolvent. In addition, the presence of a co-solvent(s) and its concentration may affect whether the expanding gas functions as a solvent or gas antisolvent. The expanding gas may also exhibit properties similar to its properties in the supercritical phase at temperatures and pressures that are near to the T_c and the P_c. For instance, the temperature and pressure conditions may be slightly below each of the T_c and P_c as long as the expanding gas exhibits

properties similar to those in the supercritical phase. As such, the term "expanding gas" as used herein also encompasses a near critical solvent having a temperature and pressure slightly below the T_c and P_c.

With expanding gas maintained at or near its T_c and P_c, as described above, the fluid volume and the expanding gas may be contacted, causing the expanding gas, such as carbon dioxide, to become substantially soluble in the polar solvent. As the fluid volume and the expanding gas come into contact, at least one of the temperature and pressure may be increased such that the expanding gas acts as a gas antisolvent. As the polar solvent volume increases by the expanding gas, a gas-expanded solvent may form that includes a mixture of the expanding gas and the polar solvent. As used herein, the term "gas-expanded solvent" means and includes a liquid in which a quantity of expanding gas is dissolved. The gas-expanded solvent may form at the interface of the expanding gas and the liquid phase. The gas-expanded solvent may be present in a liquid phase, a near critical liquid phase, or a supercritical phase. The gas-expanded solvent may begin to behave as a nonpolar solvent, such that the solubility of the polar impurities in the solvent is reduced causing the polar impurities to drop out of solution with the polar solvent, remaining in the fluid volume.

The gas-expanded solvent may become more nonpolar as at least one of the pressure and temperature is increased. By changing the solubility of the polar impurities in the solvent, two phases that are substantially immiscible may form. One of the phases may be a liquid phase that includes the polar impurities, while the other phase may include the expanding gas and the polar solvent. These two phases may subsequently be separated from one another by conventional techniques, such as by liquid-liquid separation, gas-liquid separation, gravity separation, or centrifugal separation. The liquid phase that includes the polar impurities may be heavier than the gas-expanded solvent, and may be easily separated or drained from the gas-expanded solvent. By way of non-limiting example, the polar impurities comprise at least one fatty acid and may be reacted with methanol in a separate, acid-catalyzed esterification reaction used for biodiesel production, while the polar solvent and the expanding gas may remain as a gas-expanded solvent.

After removing the liquid phase including the polar impurities, the polar solvent may be recovered by adjusting at least one of the pressure and temperature of the gas-expanded solvent such that the polar solvent and the expanding gas become substantially immiscible in one another. By decreasing at least one of the pressure and temperature of the gas-expanded solvent, the polar solvent drops out of the expanding gas as a liquid phase, while the expanding gas may exhibit a gas phase or as a non-polar liquid phase. These two phases may

subsequently be separated from one another by conventional techniques, such as by liquid-gas separation, liquid-liquid separation, gravity separation, or centrifugal separation. For example, the liquid phase that includes the polar solvent may be heavier than the gas phase that includes the expanding gas. As such, the liquid phase may be easily separated or drained from the gas phase and collected to be reused in extracting free fatty acids from feedstock volumes.

The expanding gas and the contaminated polar solvent may be contacted in a vessel. The vessel may be a batch separator or a continuous separator, and be suitably configured as a flask, a hemispherical or cylindrical vessel, a pipe, a static mixer, or an agitation vessel, as known in the art. The vessel may comprise glass, steel, stainless steel, nickel alloys, titanium alloys, glass-lined steel, polymer-lined steel, ceramic-lined steel, or mixtures thereof. As a non-limiting example, the vessel may be a cell configured to provide a closed system such that the contents of the vessel may be heated or pressurized. For instance, the vessel may be heated using a heat exchanger extending to the interior of the vessel, or by heating the vessel externally. The vessel may include a stir bar used to stir the mixture during recovery of the polar solvent. The vessel may also include a port or other opening to allow for easy separation of the two immiscible phases. Accordingly, the term "volume" as used herein encompasses a defined, contained volume of fluid as well as a flowing stream of fluid.

As shown in FIG. 1, a fluid volume 104 may be introduced into a vessel 100 at an ambient temperature and pressure. By way of non-limiting example, the fluid volume 104 may be in the liquid phase and may include one or more polar impurities dissolved in a solvent. The solvent may be a polar solvent such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, t-butanol, or mixtures thereof. The polar impurities may include, for example, free fatty acids, phospholipids, sterols, water, dirt, detergents, polar compounds, or other impurities, and may be present in the fluid volume 104, for example, in a range of from about 5% by weight to about 60% by weight, more specifically, from about 9% by weight to about 30% by weight. The temperature of the fluid volume 104 may be increased in a range of from about 30 °C to about 40°C, more particularly about 31 °C.

An expanding gas 102 may be introduced into the vessel 100 and contacted with the fluid volume 104. As a non-limiting example, the expanding gas may be carbon dioxide, methane, ethane, propane, butane, pentane, isomers thereof (*i.e.*, n-butane, isobutane, t-butane, n-pentane, isopentane, etc.), ethylene, propylene, butylene, pentene, or mixtures thereof. The vessel 100 may be initially maintained at ambient temperature and pressure conditions such that the fluid volume 104 and the expanding gas 102 remain in separate, immiscible phases. At least one of the pressure and temperature within the vessel 100 may be increased such that

the expanding gas 102 enters its liquid phase, near critical liquid phase, or supercritical phase. For example, the pressure within the vessel 100 may increase as the expanding gas 102 is introduced to the vessel 100 so that the expanding gas 102 is in its pressurized gas phase, near critical gas phase, or supercritical phase. An amount of expanding gas 102 sufficient to increase the pressure to greater than or equal to a critical pressure thereof may be introduced into the vessel 100. For example, the expanding gas 102 may be carbon dioxide and may be introduced to increase the pressure in the vessel 100 to at least about 1070 psi. As the pressure increases, the expanding gas 102 may dissolve into the solvent 104.

Referring to FIG. 2, as the pressure increases, the expanding gas 102′ may dissolve into the solvent forming a gas-expanded solvent 106. The gas-expanded solvent 106 may include a mixture of the expanding gas 102′, the solvent, and the one or more polar impurity and may be in its liquid phase, or near critical liquid phase. The expanding gas 102′ may be continuously introduced into the vessel 100 to maintain the expanding gas 102′ at or above a critical point thereof. By way of non-limiting example, to form the gas-expanded solvent 106, the pressure within the vessel 100 may be a range of from about 1070 psi to about 1090 psi and the temperature within the vessel 10 may be in the range of from about 30 ℃ to about 40 ℃, more specifically about 35 ℃.

Dissolving the expanding gas 102′ into the polar solvent may cause the gas-expanded solvent 106 to become increasingly nonpolar, decreasing the solubility of the polar impurity in the gas-expanded solvent 106. As the expanding gas 102′ dissolves into the gas-expanded solvent 106, the polarity of the gas-expanded solvent 106 decreases to the point where the polar impurities dissolved therein are no longer miscible with the decreased polarity solvent phase. The expanding gas 102′ may decrease the solubility of the polar impurities in the polar solvent by disrupting hydrogen bonding and electrostatic interactions in the polar solvent.

Referring to FIG. 3, as the expanding gas 102″ continues to dissolve into the gas-expanded solvent 106 (shown in FIG. 2), the gas-expanded solvent 106 becomes increasingly non-polar forming a solvent-rich fluid phase 108. By further increasing the pressure, the solvent may begin to dissolve from the gas-expanded solvent 106 (FIG. 2) into the expanding gas 102″ causing the solvent-rich fluid phase 108 and the expanding gas 102″ to form a single supercritical phase (not shown) in which the polar impurities are substantially immiscible. As the supercritical phase forms, the polar impurities drop out of solution forming a polar impurity-rich fluid volume 110.

By way of non-limiting example, to form the solvent-rich fluid phase 108, the pressure within the vessel 100 may be a range of from about 1090 psi to about 1120 psi, more

specifically about 1117 psi, and the temperature within the vessel 100 may be in the range of from about 30°C to about 40°C, more specifically about 35°C. The pressure may be increased by introducing additional expanding gas 102″ into the vessel 100. The solvent-rich fluid phase 106 may be in an expanded liquid phase, a near critical liquid phase, or a supercritical phase. The resulting polar impurity-rich fluid volume 110 may have a substantially increased concentration of polar impurities and a decreased solvent concentration. The polar impurity-rich fluid volume 110 including the polar impurities may be removed from the vessel 100 by conventional techniques such as by liquid-liquid separation or gravity separation. The concentrated polar impurities in the polar impurity-rich fluid volume 110 may be reacted with methanol in a separate, acid-catalyzed reaction to produce biodiesel. Additionally, the concentrated polar impurities may be discarded or sold as brown grease. The resulting gas-expanded solvent 108 may be substantially free of the polar impurities.

As shown in FIG. 4, after removal of the polar impurity-rich fluid volume 110, at least one of the pressure and the temperature within the vessel 10 may be decreased such that the solvent 112 and the expanding gas 102 become substantially immiscible in one another, causing them to separate into two phases. By way of non-limiting example, a decrease in pressure in a range of from about 10 psi to about 30 psi within the vessel 100 may cause the solvent 112 and the expanding gas 102 to separate into two substantially immiscible phases. For example, where the expanding gas 102 is carbon dioxide, the pressure may be reduced to a pressure of less than about 1117 psig at a temperature of at least about 35° C. The solvent 112 may form as a liquid phase and the expanding gas 102 may form as a gas phase. The polar solvent 112 may be substantially free of polar contaminates, such as free fatty acids. The polar solvent 112 may be removed from the vessel 100 by conventional techniques, such as by gravity separation. The substantially pure polar solvent 112 may be recycled for use in extracting polar impurities from a feedstock in biodiesel production.

Additionally, a decrease in temperature in a range of from about 5 to about 30 °C within the vessel 100 may cause the solvent 112 and the expanding gas 102 to separate into two substantially immiscible liquid phases. For example, where the expanding gas 102 is carbon dioxide, the temperature may be reduced to less than about 25°C at a pressure of about 1120 psi. The solvent 112 may be a polar solvent and may form as a polar liquid phase and the expanding gas 102 may form as a non-polar liquid phase or gas phase. The solvent 112 may be substantially free of polar contaminates, such as free fatty acids. The polar solvent 112 may be removed from the vessel 100 by conventional techniques, such as by gravity separation. The substantially pure solvent 112 may be recycled for use in extracting polar

impurities from a feedstock in biodiesel production and the expanding gas 102 may be recycled for use in separating polar impurities from the solvent.

FIG. 5 illustrates a continuous flow system 500 for recovering a solvent contaminated with at least one polar impurity. In the continuous flow system 500, a feedstock 501 may be combined with a solvent 503 to form a fluid stream 505 by way of a mixing device 506. The feedstock 501 may be, for example, a fat or oil including free fatty acids and triglycerides. Additionally, the polar impurity may be, for example, a phospholipid, a sterol, water, dirt, a detergent, or a mixture thereof. As a non-limiting example, the solvent 503 may be a polar solvent, such as methanol. The fluid stream 505 is passed into a vessel 507 wherein the polar impurities dissolve into the solvent from the feedstock volume to form a fluid stream 509 that may be removed from the first vessel using a conventional technique, such as gravity separation. The triglycerides remain in the feedstock 501′ and may be utilized in a transesterification reaction to convert triglycerides to alkyl esters.

The fluid stream 509 may be directed into a phase separating vessel 513a at a desired pressure by way of a pump 511a, or any other suitable device. An expanding gas 515 may be introduced into the vessel at desired pressure and temperature. The temperature of the fluid stream 509 and the expanding gas 515 may be adjusted prior to entering the phase separating vessel 513a or may be adjusted within the phase separating vessel 513a. The expanding gas 515 may be recycled from within the continuous flow system 500 by way of a pump 511b. By way of non-limiting example, a heat exchange device 519a may be utilized to heat the expanding gas 515 to a desired temperature prior to introducing the expanding gas 515 to the phase separating vessel 513a. Within the phase separating vessel 513a, the solvent from the fluid stream 509 may dissolve into the expanding gas 515 to form a gas-expanded solvent 517 with decreased polarity. Formation of the gas-expanded solvent 517 may result in immiscibility of the polar impurities therein. The polar impurities may drop out of solution forming a polar impurity-enriched stream 519 as a lower layer in the phase separating vessel 513a that may be continuously removed. The pressure and temperature may be increased so that the gas-expanded solvent 517 is near or above a critical point. As a non-limiting example, the expanding gas 515 may be carbon dioxide and the pressure within the phase separating vessel 513a may be at a range of from about 1090 psi to about 1120 psi, more specifically about 1117 psi, and the temperature within the phase separating vessel 513a may be in the range of from about 30°C to about 40°C, more specifically about 35°C. As a non-limiting example, free fatty acids in the polar impurity-enriched stream 519 may be reacted with

methanol in a separate, acid-catalyzed reaction to produce biodiesel or may be discarded or sold as brown grease (not shown).

The resulting gas-expanded solvent 517 may form as an upper layer and may be substantially free of polar impurities, such as free fatty acids. The gas-expanded solvent 517 may be directed to another phase separating vessel 513b. Another heat exchange device 519b may be employed to decrease, maintain, or increase the temperature of the gas expanding solvent 517. At least one of the temperature and pressure may be adjusted so that the solvent and the expanding gas become immiscible in one another, causing the expanding gas to come out of solution forming an upper layer including the expanding gas 515 and a lower layer including the solvent 503. By way of non-limiting example, a decrease in pressure in a range of from about 10 psi to about 30 psi within the vessel may cause the solvent 503 and the expanding gas 515 to separate into two substantially immiscible phases. For example, where the expanding gas 515 is carbon dioxide, the pressure may be reduced to a pressure of less than about 1117 psig at a temperature of at least about 35° C. Alternatively, by way of non-limiting example, a decrease in temperature in a range of from about 5 °C to about 30 °C within the another phase separating vessel 513b may cause the solvent 503 and the expanding gas 515 to separate into two substantially immiscible liquid phases. For example, where the expanding gas 515 is carbon dioxide, the temperature may be reduced to less than about 25°C at a pressure of about 1120 psi.

Where the solvent 503 is a polar solvent, such as methanol, the solvent 503 may form as a polar liquid phase and the expanding gas 515 may form as a gas, a supercritical fluid, or a non-polar liquid phase by modifying at least one of the pressure and temperature as previously discussed. The solvent 503 may be substantially free of polar contaminates, such as free fatty acids. The solvent 503 may be removed from the another phase separating vessel 513b by a conventional technique, such as by gravity separation. The substantially pure solvent 503 may be recycled for use in extracting the polar impurities, such as free fatty acids, from the feedstock 501 in continuous flow process 500.

The following example serves to illustrate embodiments of the present invention in more detail. This example is not to be construed as being exhaustive or exclusive as to the scope of this invention.

EXAMPLE

The separation of free fatty acids from a feedstock using polar solvent extraction followed by recovery of the polar solvent from the free fatty acids using a gas antisolvent was

performed. Methanol was used as the polar solvent to extract free fatty acids from the feedstock based on its affinity to attract polar free fatty acids from nonpolar triglycerides that make up the balance of the feedstock. Additionally, since methanol is conventionally used in biodiesel production reactions, methanol was used as the polar solvent to prevent the introduction of additional impurities into the biodiesel production process.

A high free fatty acid oil was simulated by mixing known quantities of soybean oil and oleic acid. The soybean oil has a high concentration of triglycerides, while oleic acid is a free fatty acid that would be found in degraded soybean oil. The soybean oil used in the extraction experiments was commercially obtained from ICN Biomedicals (Costa Mesa, CA), while oleic acid and methanol were commercially obtained from Sigma-Aldrich (St. Louis, MO).

Extraction was performed using a high free fatty acid oil mixture with a composition of 30% by volume oleic acid in soybean oil (29 wt% oleic acid in soybean oil). A series of extractions were performed in which methanol was used to extract oleic acid from the high free fatty acid oil mixture.

Expansion of a 50% by volume oleic acid in methanol (53 wt% oleic acid in methanol) solution was performed at a constant temperature of 35 °C. The experiment was performed in a constant volume 3 mL cell fitted with a quartz window to allow visual observation. Pressure of carbon dioxide introduced into the cell was controlled using an ISCO Model 100DX Syringe Pump controlled by an ISCO Series D Pump Controller, both commercially available from Isco, Inc. (Lincoln, NE) or an HiP Model 87-6-5 manually operated pressure generator, commercially available from High Pressure Equipment Company (Erie, PA). An oleic acid and methanol mixture volume of 0.5 mL was used.

FIGs. 6-9 illustrate the change in volume of the oleic acid and methanol mixture as the pressure within the cell 600 was increased. As shown in FIG. 6, following solvent extraction of oleic acid from a mixture of oleic acid in soybean oil using methanol, at a pressure of 1090 psi, carbon dioxide 602 is dissolved in the fluid volume 604 so that the fluid volume 604 has expanded substantially in comparison to when the cell 600 is at atmospheric pressure. When the system was at a pressure of 1090 psi, the carbon dioxide 602 and the fluid volume 604 were present in separate, immiscible phases.

Referring to FIG. 7, increasing the pressure within the cell 600 to about 1100 psig caused a methanol-rich phase 608 to form. The volume of the fluid volume 604′ was reduced as the methanol was expanded by the carbon dioxide 602. The methanol-rich phase 608 became more non-polar and increased in volume, while the fluid volume 604′ became increasingly concentrated with oleic acid.

Referring to FIG. 8, as the pressure within the cell 600 was increased to about 1109 psig, the methanol-rich phase 608 increased in volume and the fluid volume 604″ decreased in volume.

As shown in FIG. 9, at a pressure of 1117 psig, the carbon dioxide was substantially dissolved in the methanol and the gas-expanded solvent 608 substantially filled an upper portion of the cell 600. The oleic acid had dropped out of solution with the methanol such that an oleic acid rich fluid volume 604‴ was present in a lower portion of the cell 600. A plot of the fluid volume expansion as a function of cell pressure is provided in FIG. 10.

Samples of the gas-expanded solvent 608 and fluid volume 604‴ were taken at 1117 psig. The relative concentrations of oleic acid and methanol in the samples were determined using a conventional gas chromatography technique. Expansion of the oleic acid and methanol solution resulted in a fluid volume 604‴ with an oleic acid concentration of about 77 wt% and a methanol concentration of about 23 wt%. The presence of oleic acid in the polar solvent that has been exposed to the gas-expanded solvent process 608 was not detected using the gas chromatography technique, indicating that the solvent 608 was substantially free of oleic acid. Thus, a change of less than 20 psig in total system pressure resulted in decreased solubility of the oleic acid in the methanol, leading to the formation of two liquid phases; a concentrated oleic acid liquid phase and a substantially pure methanol liquid phase.

While the invention may be susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the drawings and have been described in detail herein. However, it should be understood that the invention is not intended to be limited to the particular forms disclosed. Rather, the invention encompasses all modifications, variations and alternatives falling within the scope of the invention as defined by the following appended claims and their legal equivalents.

CLAIMS

What is claimed is:

1. A method of recovering a solvent from a contaminated fluid volume, comprising:

extracting at least one polar impurity from a feedstock into a solvent to form a fluid volume comprising the solvent and the at least one polar impurity;

subjecting the fluid volume to an expanding gas at a pressure at or near a critical point thereof such that the solvent separates from the at least one polar impurity;

removing the at least one polar impurity; and

reducing at least one of the pressure and a temperature of the expanding gas to recover the solvent.

2. The method of claim 1, wherein extracting at least one polar impurity from the feedstock comprises extracting at least one free fatty acid from an animal fat, animal oil, vegetable fat, vegetable oil, restaurant grease, household grease, waste industrial frying oil, or any mixture thereof.

3. The method of claim 1, wherein extracting at least one polar impurity from the feedstock comprises extracting at least one polar impurity into at least one of methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, t-butanol, or mixtures thereof.

4. The method of claim 1, wherein subjecting the fluid volume to the expanding gas at a pressure at or near a critical point thereof comprises expanding the polar solvent with carbon dioxide to reduce the solubility of the polar impurities in the polar solvent.

5. The method of claim 1, wherein subjecting the fluid volume to the expanding gas at a pressure at or near a critical point thereof comprises expanding the solvent with carbon dioxide to reduce the solubility of the polar impurities in the solvent.

6. The method of claim 1, wherein reducing at least one of the pressure and a temperature of the expanding gas to recover the solvent comprises reducing the temperature of the expanding gas to less than or equal to a critical temperature thereof.

7. A method of removing at least one polar impurity from at least one polar solvent, comprising:

providing a fluid volume comprising at least one polar solvent and at least one polar impurity;

contacting the fluid volume with an expanding gas at or near a critical point thereof to form two substantially immiscible phases;

separating the two substantially immiscible phases; and

reducing at least one of a temperature and a pressure of the expanding gas such that the polar solvent separates from the expanding gas.

8. The method of claim 7, wherein subjecting the fluid volume to the expanding gas at a pressure at or near a critical point thereof comprises subjecting the fluid volume to carbon dioxide at a pressure in a range of from about 1090 psi to about 1117 psi and at a temperature of from about 31 °C to about 37 °C.

9. The method of claim 7, wherein contacting the fluid volume with the expanding gas at or near a critical point thereof comprises dissolving the expanding gas into the polar solvent to form a gas-expanded solvent comprising the expanding gas and the polar solvent and a liquid phase comprising the at least one polar impurity.

10. The method of claim 9, wherein dissolving the expanding gas into the polar solvent to form a gas-expanded solvent comprises forming a nonpolar gas-expanded solvent and a polar liquid phase.

11. The method of claim 7, wherein contacting the fluid volume with the expanding gas comprises contacting the expanding gas with carbon dioxide at a pressure in a range of from about 1070 psi to about 1117 psi.

12. The method of claim 7, wherein contacting the fluid volume with the expanding gas comprises using the expanding gas as a solvent or as a gas antisolvent.

13. The method of claim 7, wherein contacting the fluid volume with the expanding gas comprises disrupting hydrogen bonding and electrostatic interactions in the at least one polar solvent.

14. The method of claim 7, wherein removing the at least one polar component from the fluid volume comprises removing water from the fluid volume.

15. The method of claim 7, wherein reducing at least one of the temperature and the pressure of the expanding gas such that the polar solvent separates from the expanding gas comprises reducing the temperature to less than or equal to about 35 °C.

16. The method of claim 7, wherein reducing at least one of the temperature and the pressure of the expanding gas such that the polar solvent separates from the expanding gas comprises reducing the pressure of the gas-expanded solvent to less than about 1117 psi such that the polar solvent separates from carbon dioxide.

17. A method of recovering a solvent from a fluid volume comprising methanol at least one polar impurity, comprising:

exposing the fluid volume to carbon dioxide;

increasing at least one of a temperature and a pressure to form a gas-expanded solvent comprising the methanol and the carbon dioxide and a polar liquid phase comprising the at least one fatty acid;

removing the polar liquid phase from the gas-expanded solvent; and

reducing the pressure in a range of from about 20 psi and about 30 psi to separate the solvent and the carbon dioxide from the gas expanding solvent.

18. The method of claim 17, wherein increasing at least one of a temperature and a pressure within the closed system comprises increasing the temperature in a range of from about 31 °C to about 37 °C and maintaining the pressure in a range of from about 1070 psi to about 1120 psi.

19. The method of claim 17, wherein increasing at least one of a temperature and a pressure within the closed system comprises increasing the pressure within the closed system to about 1117 psi at a temperature of about 35 °C.

20. The method of claim 17, wherein reducing the pressure within the closed system by about 20 psi to recover the methanol from the gas expanding solvent comprises reducing the pressure within the closed system to less than or equal to about 1090 psi at a temperature of about 35 °C

21. A method of removing at least one impurity from a polar solvent, comprising:

contacting a fluid volume comprising the at least one impurity and the polar solvent with carbon dioxide in a closed system; and

adjusting conditions in the closed system to a pressure in a range of from about 1110 psi to about 1117 psi and a temperature in the range of from about 30°C to about 40°C to form a liquid phase comprising the at least one impurity and another phase comprising the polar solvent and the carbon dioxide.

22. The method of claim 21, further comprising removing the liquid phase from the closed system.

23. The method of claim 21, further comprising reducing the pressure within the closed system to less than about 1117 psi to render the polar solvent and the carbon dioxide substantially immiscible.

24. The method of claim 23, further comprising separating the polar solvent from the carbon dioxide.

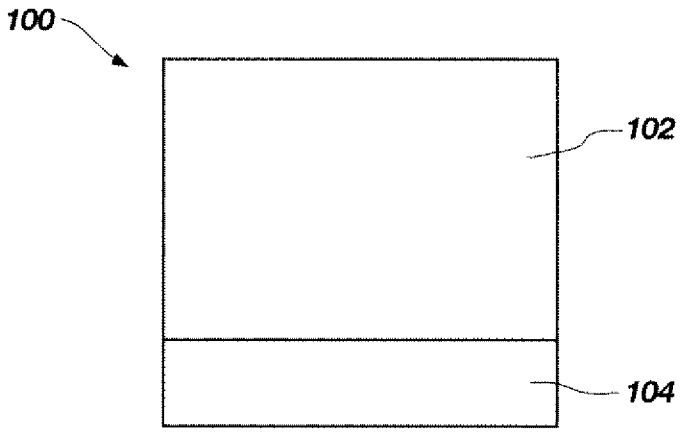


FIG. 1

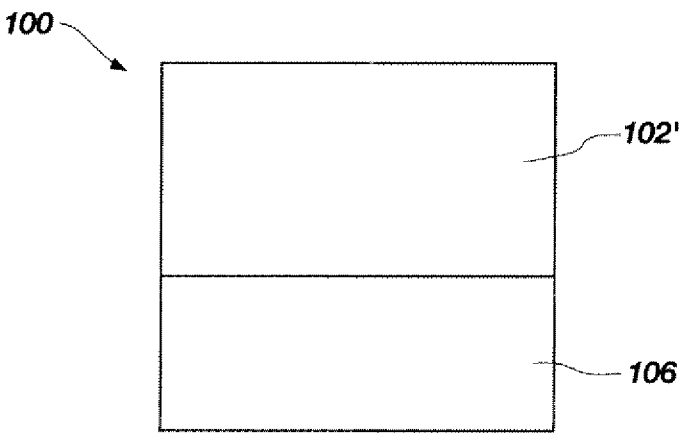


FIG. 2

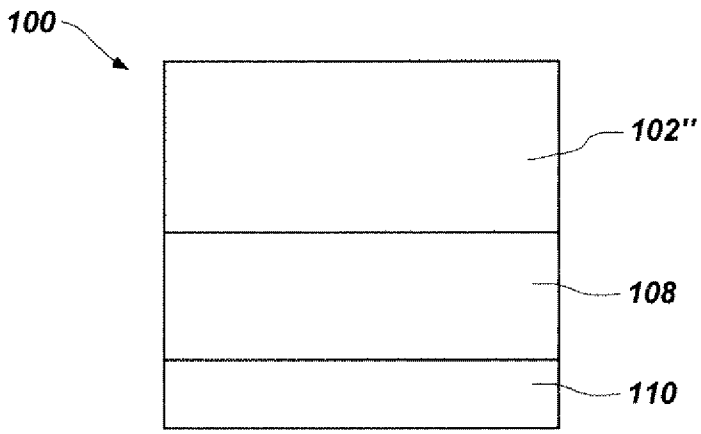


FIG. 3

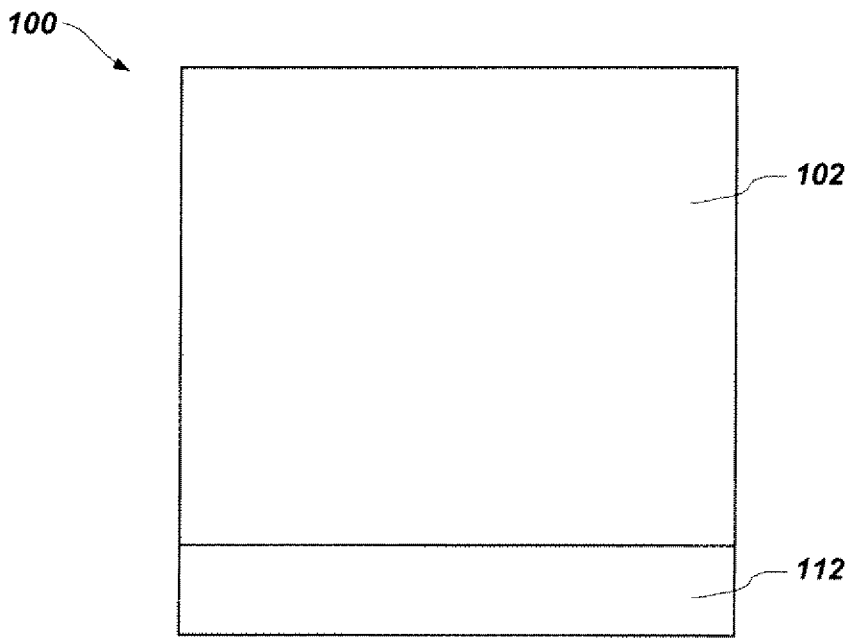


FIG. 4

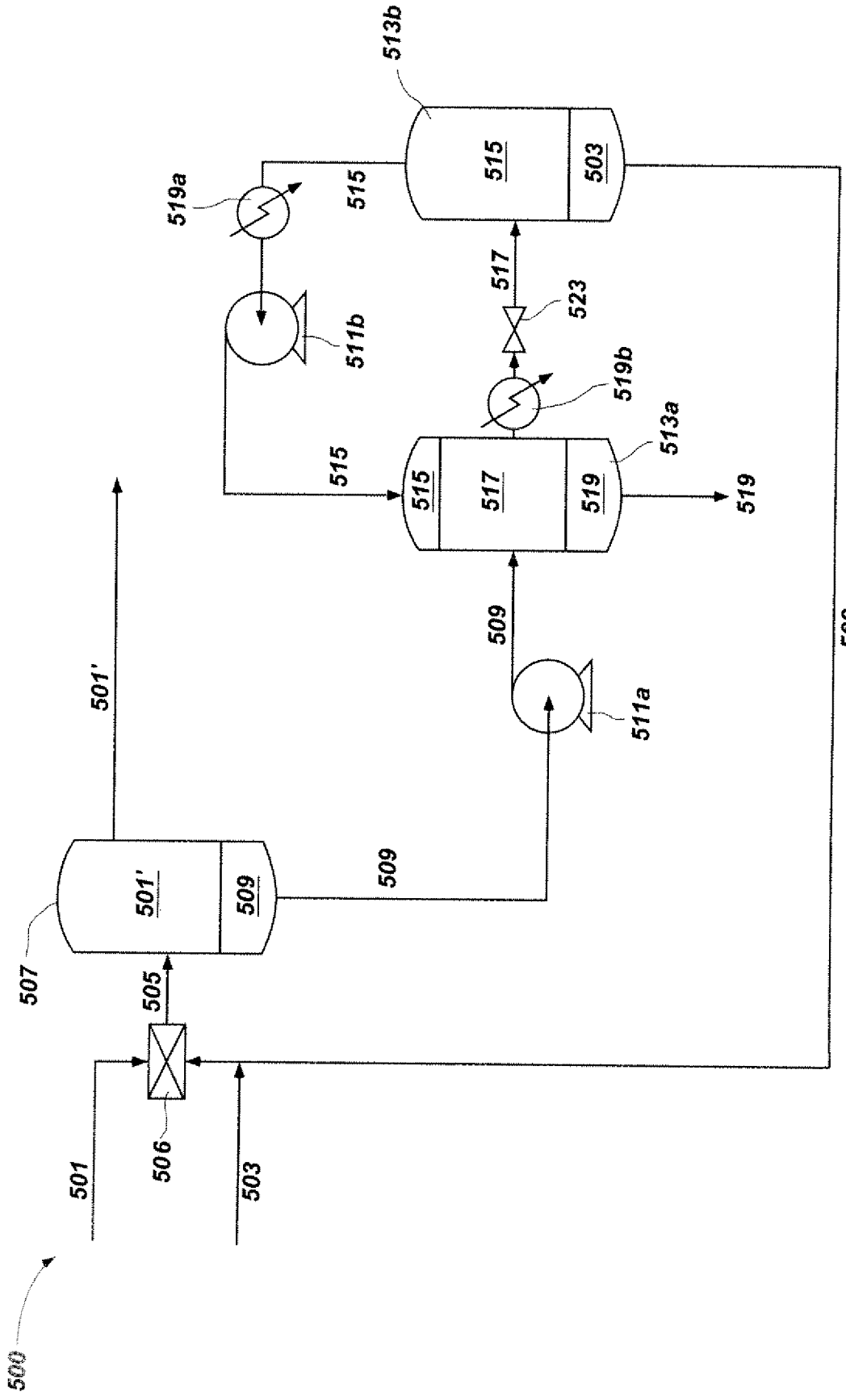

500
501
503
506
505
507
501'
509
511a
511b
513a
513b
515
517
519
519a
519b
523

FIG. 5

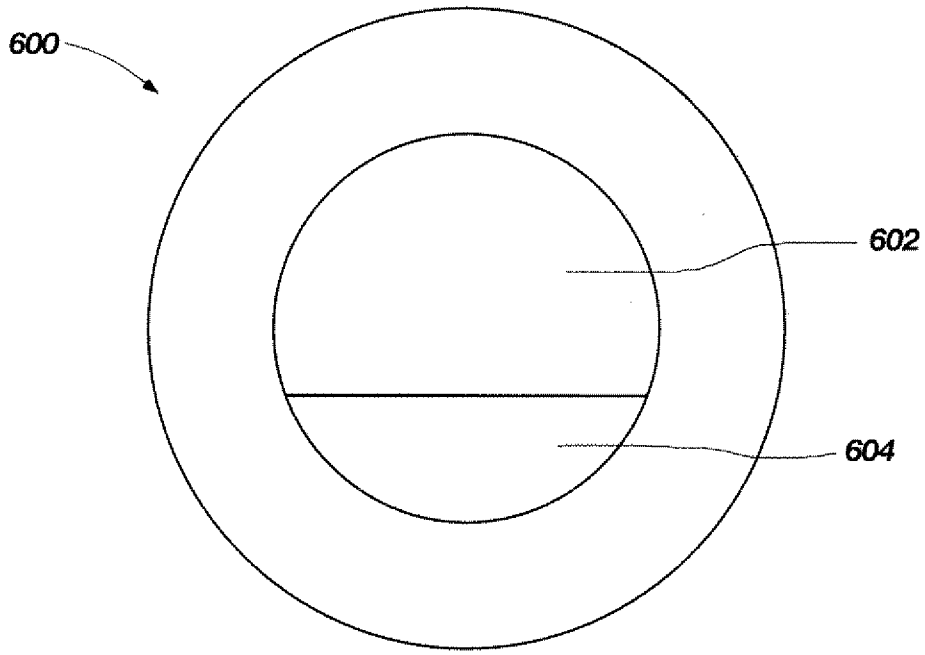


FIG. 6

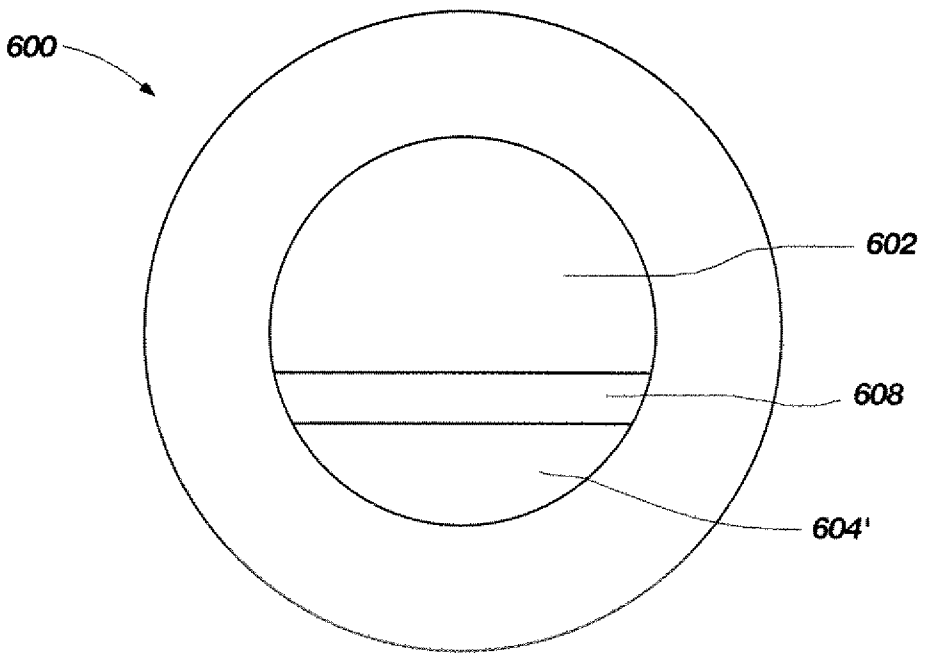


FIG. 7

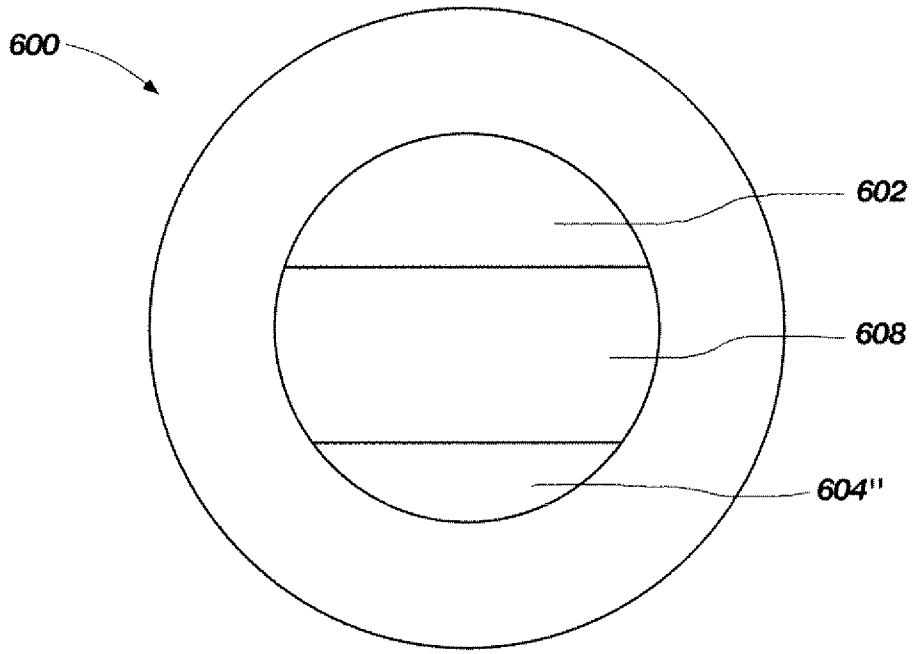


FIG. 8

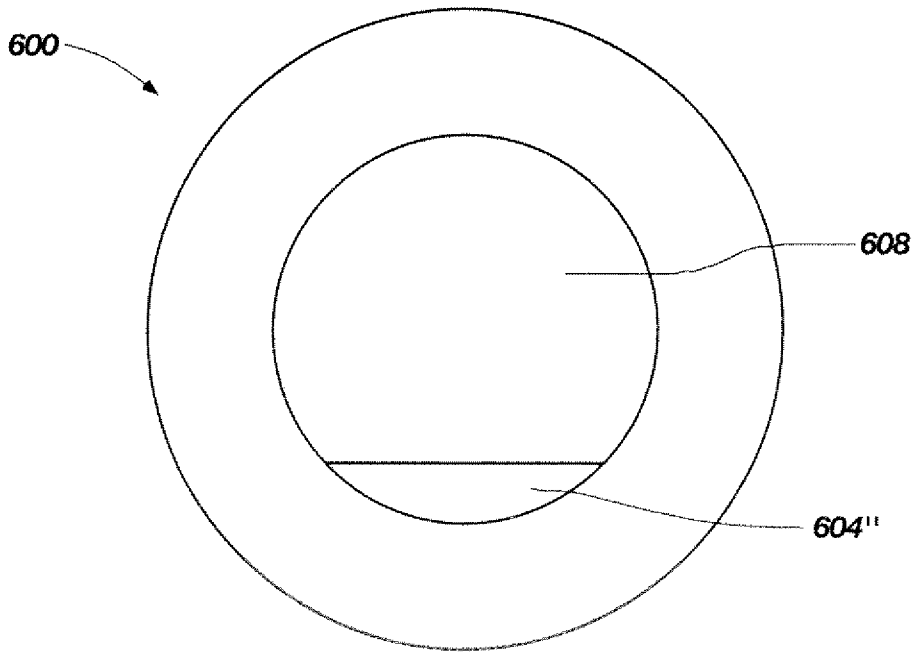


FIG. 9

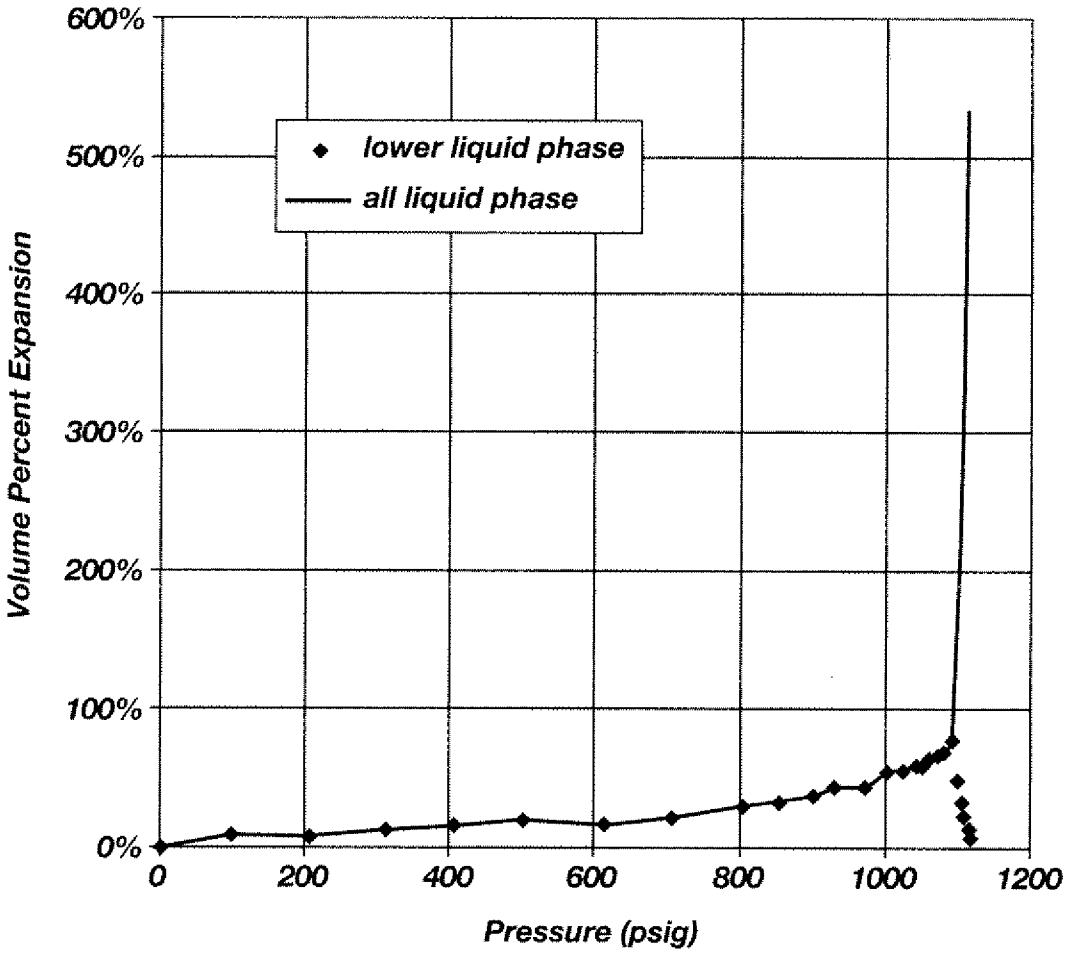

600%
500%
400%
300%
200%
100%
0%
Volume Percent Expansion
lower liquid phase
all liquid phase
0
200
400
600
800
1000
1200
Pressure (psig)

FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 09/57188

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01D 17/02 (2009.01)
USPC - 210/702, 704, 799, 902
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)
US: 210/702, 704, 799, 902

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
IPC: B01D 17/02 (2009.01)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST (PGPB, USPT, USOC, EPAB, JPAB); GOOGLE Scholar; GOOGLE Patents for ginosar, Daniel, polar, solvent, methanol, fat$, wendt, fatty, acid, carbon, dioxide, co2, biodiesel, critical, temperature, pressure, hydrogen, bond$.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2006/0252950 A1 (GINOSAR et al.) 09 November 2006 (09.11.2006); para [0002], [0012]-[0025].	1-12, 15-24 --- 13,14
Y	US 2007/0012621 A1 (GINOSAR et al.) 18 January 2007 (18.01.2007); para [0008], [0009], [0013], [0016], [0022]).	13,14
A	US 2007/0282119 A1 (MATSON et al.) 06 December 2007 (06.12.2007); entire document.	1-24

☐ Further documents are listed in the continuation of Box C. ☐

* 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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"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	Date of mailing of the international search report
21 November 2008 (21.11.2009)	30 NOV 2009
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (April 2007)