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(54) **INCORPORATION OF BIOLOGICALLY
DERIVED CARBON INTO PETROLEUM
PRODUCTS**

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(57) **ABSTRACT**

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Petroleum products comprising biologically based carbon are provided. A biologically based surfactant is added to petroleum and an emulsion composition having lower viscosity than the petroleum is formed. The petroleum is subjected to processing and the surfactant is co-processed with the petroleum to provide petroleum products comprising biologically based carbon.

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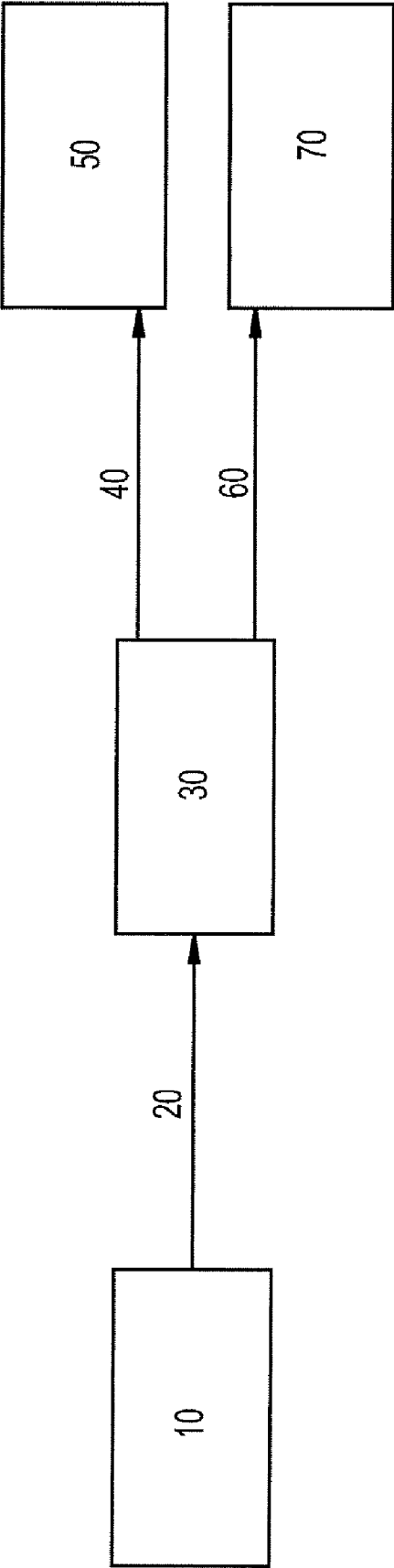


Fig. 1

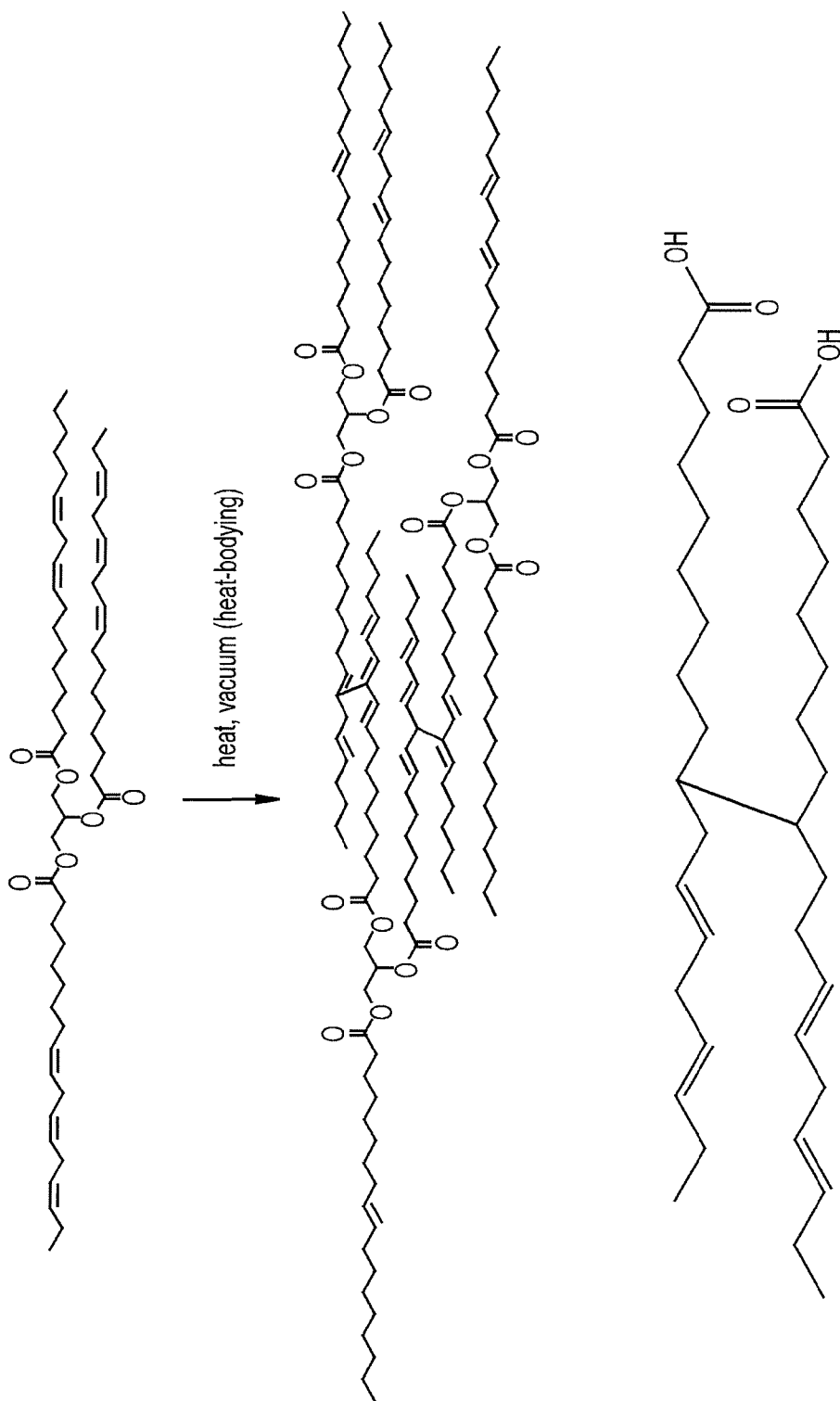


Fig. 2

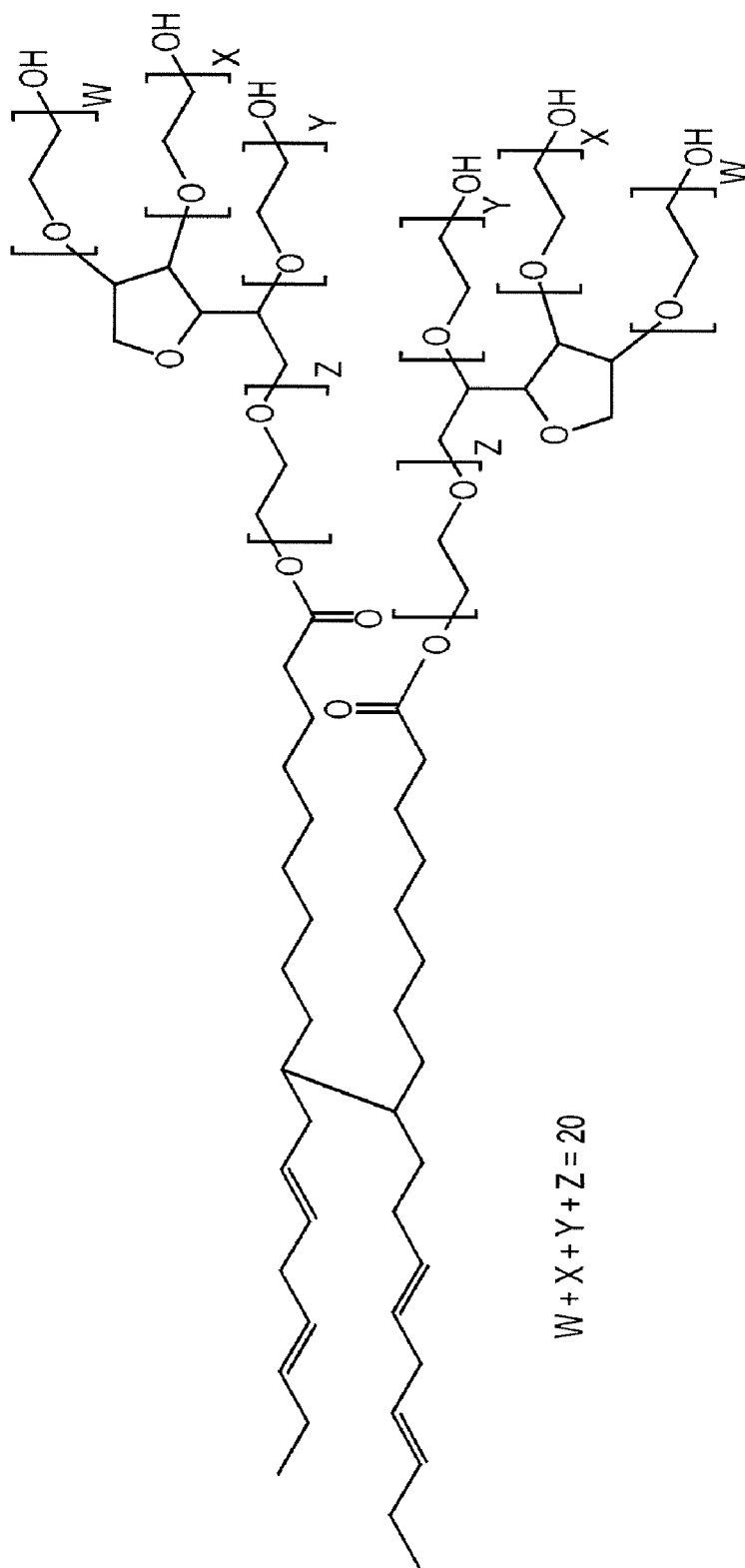


Fig. 3

INCORPORATION OF BIOLOGICALLY DERIVED CARBON INTO PETROLEUM PRODUCTS

[0001] A common problem encountered in the production and transport of petroleum from a source of supply to a location where the petroleum is to be further processed or used is that the petroleum is often too viscous for transportation by conventional pipelines or other methods, such as tanker ships, barges, rail cars, and trucks. The viscosity of crude petroleum oil or other heavy petroleum materials encountered in other contexts must be reduced so they can be pumped. The addition to these materials of a highly miscible petroleum liquid, such as a light petroleum fraction, light weight hydrocarbons, kerosene, condensates, or diesel fuel, may reduce their viscosity but generally requires subsequent separation of the light petroleum fraction, usually by distillation.

[0002] Another method for reducing the viscosity involves the formation of an emulsion of petroleum and water. To accomplish emulsification, amphiphilic surfactant molecules (emulsifiers) and energy are added to a mixture of water and immiscible petroleum. The resulting emulsion has lower viscosity than the original petroleum material, and the emulsion is pumped to a collection point or a processing facility. In order to reduce costs, after transport the emulsion is broken and the emulsifiers recovered, either as a separate phase or as part of the aqueous phase. The emulsifier and aqueous phase may be recycled for reuse with further crude petroleum.

[0003] However, in recent years especially, a growing consensus has developed in petroleum importing countries that alternatives to petroleum must be developed. Alternative fuels and chemicals derived from biological, rather than fossil sources, have attracted a significant amount of interest as the replacement of petrochemicals and petroleum derived products with products and/or feedstocks derived from biological sources (i.e., biobased products) offers many advantages. For example, products and feedstocks from biological sources are typically a renewable resource, and as such provide a fundamentally more dependable and manageable source of supply. Oil exporting countries sometimes have foreign policies and political interests that are at odds with the interests of importing countries, and the continuing flow of funds to oil exporting countries from the importing countries has been viewed as counter to national and international security interests. Finally, as easily extracted petroleum continues to be depleted, the cost of obtaining petroleum from any source tends to cause the cost of conventional fossil-based petrochemicals and petroleum derived products as a whole to be higher compared to biobased products. In addition, companies may benefit from the marketing advantages associated with biobased products or biologically derived carbon from renewable resources in the view of a public becoming more concerned with the supply of petroleum.

[0004] Against this background, the present invention advantageously provides materials and methods for incorporating biologically derived carbon into petroleum products, in particular through providing materials and methods for reducing the viscosity of petroleum materials as these are transported or processed into petroleum products. Biobased surfactants added to petroleum materials enable the formation of an emulsion of lower viscosity than the petroleum material. When the petroleum is processed, the biobased sur-

factant is co-processed with the petroleum material so that biobased carbon from the surfactant is incorporated into the petroleum product. Biobased surfactants include AB type and ABA type surfactants formed from biobased starting materials.

[0005] The present invention can be better understood by reference to the accompanying drawings, wherein:

[0006] FIG. 1 schematically depicts a system for transporting petroleum which makes use of the present invention;

[0007] FIG. 2 shows i) a route for synthesis of a (cross-linked) branched-chain dicarboxylic acid depicting idealized carbon-carbon bond formation between fatty acids of two triacylglycerols in polymerization of triacylglycerols by blowing or heat-bodying and ii) an idealized (cross-linked) branched-chain dicarboxylic acid formed by hydrolysis of triacylglycerols polymerized by heat-bodying; and

[0008] FIG. 3 shows one embodiment of a biobased ABA surfactant from polymerized fatty acids, useful in the present invention

[0009] In one preferred application of the principles of the present invention, an emulsion is formed which comprises crude petroleum and one or more biobased surfactants. After transport through a pipeline or in a container vessel of some kind, for example, a tanker ship, railcar, barge or truck, the emulsion is broken into an aqueous phase and an oil phase and the aqueous phase is recycled or discarded. The one or more biobased surfactants, however, remain substantially with the oil phase and so become incorporated into the crude petroleum. The crude petroleum containing the biobased surfactant is then subjected to one or more further processing steps to provide processed petroleum products containing biologically derived carbon resulting from the co-processing of the one or more biobased surfactants.

[0010] By way of further background to the problems solved by the present invention, crude petroleum is a highly complex mixture and includes hydrocarbons with some sulfur, nitrogen, oxygen, minerals and metals. The appearance and characteristics of crude petroleum differ, depending on the oil field and the specific well from which they were obtained. Crude petroleum oils are available by several routes, including but not limited to drilling into subterranean reservoirs, and from tar sands, oil sands, oil shales, gas-to-liquid processes, and coal-to-liquid processes.

[0011] “Crude petroleum”, “petroleum” and/or “petroleum materials” as used interchangeably herein are thus to be understood as embracing petroleum materials as obtained from any of these sources or by any of these means, and so may comprise crude petroleum oil recovered from subterranean reservoirs or formations by drilling, tar sand crude petroleum, oil shale crude petroleum, crude petroleum oil obtained in a gas-to-liquid process or crude petroleum oil obtained in a coal-to-liquid process. “Crude petroleum”, “petroleum” and/or “petroleum materials” should also be understood as encompassing a petroleum fraction or a petroleum product resulting directly from a physical or chemical processing of the petroleum materials from any of these various sources or obtained by these various means, as well as combinations of such fractions or products with the petroleum oils so sourced or obtained.

[0012] As used herein, the term “petroleum product” refers to a material resulting from subjecting an emulsion of petroleum and one or more biobased surfactants made according to the present invention, to one or more unit operations. As used herein, the term “unit operation” refers to processing opera-

tions, including but not limited to of hydrolytic emulsion splitting, separation, fractionation, distillation, hydrolysis, hydrotreating, hydrocracking, decarboxylation, hydrogenation, steam cracking, thermal cracking, naphtha cracking, fluid catalytic cracking, catalytic reforming, steam reforming, metathesis, alkylation, dimerization, isomerization, coking, and combinations of any of the foregoing.

[0013] A better understanding of the present invention may be gained by considering the use of biologically derived fuel to supplement or replace traditional, fossil-based petroleum diesel fuels in diesel combustion engines. Biodiesel fuel is defined as a fuel comprising monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats that meets the requirements of ASTM D6751. Biodiesel fuel may be blended with traditional fossil-based petroleum diesel fuel, and the resulting blend is designated by an indicator such as B2, B20, B100, etc. wherein the number portion of the indicator informs the reader of the content, in percent, of biodiesel in petroleum diesel. "Green diesel fuel" (or "green diesel") refers to a fuel that meets applicable ASTM specifications for diesel fuel and has been produced from non-fossil renewable resources, including but not limited to agricultural or silvicultural plants, animal fats, residue and waste generated from the production, processing, and marketing of agricultural products, silvicultural products, and other renewable resources. Green diesel thus also contains biologically derived carbon from biobased materials, as determined by the conventionally known methods described below.

[0014] Biobased materials may be differentiated from petroleum derived materials, for example, by their carbon isotope ratios using ASTM International Radioisotope Standard Method D 6866, the disclosure of which is incorporated by reference in its entirety. Method D 6866 is based upon the fact that isotopic ratios of the isotopes of carbon within any given material, such as the $^{13}\text{C}/^{12}\text{C}$ carbon isotopic ratio or the $^{14}\text{C}/^{12}\text{C}$ carbon isotopic ratio, can be determined using certain established analytical methods, such as isotope ratio mass spectrometry, with a high degree of precision.

[0015] ASTM Method D6866, similar to radiocarbon dating, compares how much of a decaying carbon isotope remains in a sample to how much would be in the same sample if it were made of entirely recently grown materials. The percentage is called the biobased content of the product. Samples are combusted in a quartz sample tube and the gaseous combustion products are transferred to a borosilicate break seal tube. In one method, liquid scintillation is used to count the relative amounts of carbon isotopes in the carbon dioxide in the gaseous combustion products. In a second method, $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$ isotope ratios are counted (^{14}C) and measured ($^{13}\text{C}/^{12}\text{C}$) using accelerator mass spectrometry. Zero percent ^{14}C indicates the entire lack of ^{14}C atoms in a material, thus indicating a fossil (for example, petroleum based) carbon source. One hundred percent ^{14}C , after correction for the post-1950 bomb injection of ^{14}C into the atmosphere, indicates a modern carbon source. ASTM D 6866 effectively distinguishes between biobased materials and petroleum derived materials in part because isotopic fractionation due to physiological processes, such as, for example, carbon dioxide transport within plants during photosynthesis, leads to specific isotopic ratios in natural or biobased compounds. By contrast, the $^{13}\text{C}/^{12}\text{C}$ carbon isotopic ratio of petroleum and petroleum derived products is different from the isotopic ratios in natural or bioderived compounds due to different chemical processes and isotopic fractionation

during the generation of petroleum. In addition, radioactive decay of the unstable ^{14}C carbon radioisotope leads to different isotope ratios in biobased products compared to petroleum products. As used herein, "biologically derived", "bioderived", and "biobased" will be understood to refer to materials whose carbon content is shown by ASTM D 6866, in whole or in significant part (for example, at least about 20 percent or more), to be derived from or based upon biological products or renewable agricultural materials (including but not limited to plant, animal and marine materials) or forestry materials.

[0016] The present disclosure teaches methods for incorporating biologically derived carbon into a petroleum product, and provides biobased materials for accomplishing these methods. The biologically derived carbon is incorporated into a surfactant, which is used to form an emulsion with water for transporting petroleum. The petroleum comprising a biobased surfactant is subjected to at least one further processing step so that the petroleum is processed into a petroleum product and the biobased surfactant is co-processed with the petroleum. At least part of the biologically derived carbon of the surfactant is incorporated into the petroleum product. When the petroleum is processed into finished petroleum products, the biologically sourced carbon is co-processed with the petroleum through one or more unit operations, to yield at least one petroleum product comprising biologically sourced carbon from the co-processed biobased surfactant.

[0017] Surfactants (emulsifiers) comprise at least one hydrophilic portion and one hydrophobic portion. In the current disclosure, either or both portions may be biobased. Biobased surfactants (natural surfactants) containing biologically derived carbon include, without limitation, glycosides of fatty acids and alcohols, polyether glycosidic ionophores, macrocyclic glycosides, carotenoid glycosides, isoprenoid glycosides, fatty acid amide glycosides and analogues and derivatives thereof, glycosides of aromatic metabolites, alkaloid glycosides, hemiterpenoid glycosides, monoterpene glycosides, phospholipids, lysophospholipids, ceramides, gangliosides, sphingolipids, fatty acid amides, alkylpolyglucosides, polyol alkyl ethoxylates, anhydrohexitol alkyl ethoxylates, and combinations of any thereof. In an embodiment of the present invention, a surfactant comprising an anhydrohexitol alkyl ethoxylate containing biologically derived carbon is used. In a further embodiment of the present invention, a surfactant comprising a polyol alkyl ethoxylate containing biologically derived carbon is used.

[0018] In some embodiments, the hydrophilic portions of surfactants useful in the present invention include, without limitation, a polyol alkyl ethoxylate containing biobased carbon (bioderived polyol alkyl ethoxylate). The polyol portions of polyol alkyl ethoxylates may be biologically derived polyols from biological or botanical sources. Biobased polyols suitable as a starting material for polyols suitable for use in polyol alkyl ethoxylates include, but are not limited to, anhydrohexitols, saccharides, such as monosaccharides including but not limited to dioses, such as glycolaldehyde, trioses, such as glyceraldehyde and dihydroxyacetone, tetroses, such as erythrose and threose, aldo-pentoses such as arabinose, lyxose, ribose, deoxyribose, xylose, keto-pentoses, such as ribulose and xylulose, aldo-hexoses such as allose, altrose, galactose, glucose (dextrose), gulose, idose, mannose, talose, ketohexoses, such as fructose, psicose, sorbose, tagatose, heptoses, such as mannoheptulose and sedoheptulose, octoses, such as octulose and 2-keto-3-deoxy-manno-octo-

nate, and nonoses, such as sialose, disaccharides including but not limited to sucrose (table sugar, cane sugar, saccharose, or beet sugar), lactose (milk sugar), maltose, trehalose, cellobiose, oligosaccharides, such as raffinose (melitose), stachyose, and verbascose, sorbitol, glycerol, sorbitan, isosorbide, polyglycerols, hexoses, pentoses, polyols, hydrogenated sugars, hydroxymethylfurfural, refined sugars, crude sugars, products of the breakdown of cellulose, products of the breakdown of hemicellulose, products of the breakdown of lignin, plant fiber hydrolyzates, fermented plant fiber hydrolyzates, carbohydrate hydrogenolyzates, and combinations of any thereof.

[0019] According to other embodiments, the bioderived polyol feedstock may be a side product or co-product from the synthesis of biodiesel or the saponification of vegetable oils and/or animal fats (i.e., triacylglycerols), such as glycerol.

[0020] According to further embodiments, the polyol portion of polyol alkyl ethoxylate containing biobased carbon may be derived from polyol feedstocks obtained as mixed polyols from hydrolyzed natural (biobased) fibers. Natural fibers may be hydrolyzed (producing a hydrolyzate) to provide bioderived polyol feedstock comprising plant fiber hydrolyzate, such as mixtures of polyols. Fibers suitable for this purpose include, without limitation, corn fiber from corn wet mills, dry corn gluten feed which may contain corn fiber from wet mills, wet corn gluten feed from wet corn mills, distiller dry grains solubles (DDGS) and Distiller's Grain Solubles (DGS) from dry corn mills, canola hulls, rapeseed hulls, peanut shells, soybean hulls, cottonseed hulls, cocoa hulls, barley hulls, oat hulls, wheat straw, corn stover, rice hulls, starch streams from wheat processing, fiber streams from corn mesa plants, edible bean molasses, edible bean fiber, and mixtures of any thereof. Plant fiber hydrolyzates, such as hydrolyzed corn fiber, may be enriched in bioderived polyol compositions suitable for use as a feedstock in the hydrogenation reaction described herein, including, but not limited to, arabinose, xylose, sucrose, maltose, isomaltose, fructose, mannose, galactose, glucose, and mixtures of any thereof.

[0021] According to other embodiments, the bioderived emulsifiers/surfactants may be derived from a polyol feed-

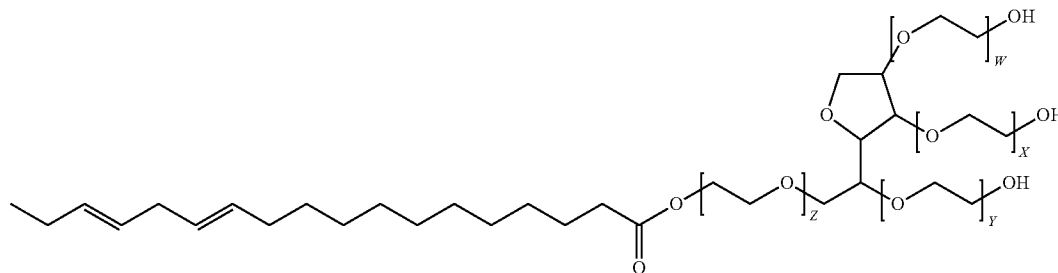
stock of polysaccharides or polyols can be recovered and/or concentrated from the fermentation broth to provide a bio-based polyol feedstock suitable for use as a starting material for polyols suitable for use in polyol alkyl ethoxylates, as described herein.

[0022] In some embodiments, the anhydrohexitol portion of the anhydrohexitol alkyl ethoxylate comprises an anhydrohexitol selected from the group consisting of monoanhydrohexitols, dianhydrohexitols, isomannide, sorbitan, and combinations of any thereof.

[0023] In still further embodiments, bioderived 6-carbon sugars (hexoses), such as mannose, can be converted to mannitol, which can be converted to mannitan, which can be converted to isomannide for use in polyol alkyl ethoxylates.

[0024] In certain embodiments, biobased emulsifiers may contain portions derived from hydrogenolysis of biobased polyol feed stocks, such as a carbohydrate having been subjected to hydrogenolysis, where the carbonyl group (aldehyde or ketone) of the carbohydrate has been reduced to a primary or secondary hydroxyl group to provide a carbohydrate hydrogenolyzate.

[0025] In an embodiment, the anhydrohexitol portion of anhydrohexitol alkyl ethoxylates may be derived from sorbitan. Sorbitan (IUPAC name (3S)-2-(1,2-Dihydroxyethyl) tetrahydrofuran-3,4-diol) may comprise a mixture of chemical compounds derived from the dehydration of sorbitol. The sorbitan mixture can vary, but may include, without limitation, 1,4-anhydrosorbitol, 1,5-anhydrosorbitol and 1, 4, 3, 6-dianhydrosorbitol. Sorbitan is used in the production of surfactants such as polysorbates. In an embodiment, a non-ionic sorbitan fatty acid ethoxylate may be employed (Structure 1). The molecular weight of structure 1 is approximately 1404; the molecular weight of the bioderived alkyl (oleic acid) portion is approximately 282.5; thus, the fatty acid portion of sorbitan fatty acid ethoxylate of structure 1 comprises approximately 20.1% of the sorbitan fatty acid ethoxylate. The anhydrohexitol alkyl ethoxylate of structure 1 is an AB type surfactant, with the polar ethoxylate chains represented by A and the nonpolar fatty acid alkyl chain represented by B.



$$W + X + Y + Z = 20$$

stock obtained from biobased fibers which have been hydrolyzed and subjected to fermentation. The fermentation of plant fiber hydrolyzates may provide new biobased polyol feedstocks, or may alter the amounts of residues of polysaccharides or polyols obtained from hydrolyzed fibers. After fermentation, a fermentation broth may be obtained and resi-

Structure 1. Sorbitan fatty acid ethoxylate. Double bonds are cis or trans.

[0026] In other embodiments, AB type polyol alkyl ethoxylate surfactants are used, with the sorbitan and polar polyol ethoxylate chains represented by A and the nonpolar fatty acid alkyl chain represented by B.

[0027] In other embodiments, the alkyl portion of polyol alkyl ethoxylates may be derived from biologically derived fatty acids or biobased fatty alcohols. Natural carboxylic acids may include, without limitation, animal or vegetable fatty acids selected from the group consisting of butyric acid, caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, behenic acid, lignoceric acid, hexacosanoic acid, octacosanoic acid, triacontanoic acid and n-dotriacontanoic acid, fatty acids having an odd number of carbon atoms, such as propionic acid, n-valeric acid, enanthic acid, pelargonic acid, hendecanoic acid, tridecanoic acid, pentadecanoic acid, heptadecanoic acid, nonadecanoic acid, heneicosanoic acid, tricosanoic acid, pentacosanoic acid, heptacosanoic acid, branched fatty acids such as isobutyric acid, isocaproic acid, isocaprylic acid, isocapric acid, isolauric acid, 11-methyldodecanoic acid, isomyristic acid, 13-methyl-tetradecanoic acid, isopalmitic acid, 15-methyl-hexadecanoic acid, isostearic acid, 17-methyloctadecanoic acid, isoarachic acid, 19-methyl-eicosanoic acid, α -ethyl-hexanoic acid, α -hexyldecanoic acid, α -heptylundecanoic acid, 2-decyltetradecanoic acid, 2-undecyltetradecanoic acid, 2-decylpentadecanoic acid, 2-undecylpentadecanoic acid, 6-methyl-octanoic acid, 8-methyl-decanoic acid, 10-methyl-dodecanoic acid, 12-methyl-tetradecanoic acid, 14-methyl-hexadecanoic acid, 16-methyl-octadecanoic acid, 18-methyl-eicosanoic acid, 20-methyl-docosanoic acid, 22-methyl-tetracosanoic acid, 24-methyl-hexacosanoic, 26-methyloctacosanoic acid, unsaturated fatty acids, such as 4-decenoic acid, caproic acid, 4-dodecenoic acid, 5-dodecenoic acid, lauroleic acid, 4-tetradecenoic acid, 5-tetradecenoic acid, 9-tetradecenoic acid, palmitoleic acid, 6-octadecenoic acid, oleic acid, 9-octadecenoic acid, 11-octadecenoic acid, 9-eicosenoic acid, cis-11-eicosenoic acid, cetoleic acid, 13-docosenoic acid, 15-tetracosenoic acid, 17-hexacosenoic acid, 6,9,12,15-hexadecatetraenoic acid, linoleic acid, linolenic acid (18:3 n3), gamma linolenic acid (18:3 n6), α -eleostearic acid, gadoleic acid (20:1), α -eleostearic acid, puniceic acid, 6,9,12,15-octadecatetraenoic acid, parinaric acid, 5,8,11,14-eicosatetraenoic acid, erucic acid, 5,8,11,14,17-eicosapentaenoic acid (EPA), 7,10,13,16,19-docosapentaenoic acid, 4,7,10,13,16,19-docosahexaenoic acid (DHA), hydroxylated fatty acids, such as α -hydroxylauric acid, α -hydroxymyristic acid, α -hydroxypalmitic acid, α -hydroxystearic acid, ω -hydroxylauric acid, α -hydroxyarachic acid, 9-hydroxy-12-octadecenoic acid, ricinoleic acid, α -hydroxybehenic acid, 9-hydroxy-trans-10,12-octadecadienic acid, kamolenic acid, ipurolic acid, 9,10-dihydroxystearic acid, 12-hydroxystearic acid, the corresponding alcohol of any thereof, derivatives of any thereof, and combinations of any thereof. In other embodiments, these fatty acids may be reduced to their corresponding fatty alcohols.

[0028] In still another embodiment, the alkyl portion of the polyol alkyl ethoxylate comprises a fatty acid alkyl portion derived from a biological source, such as from the group consisting of animal oil, vegetable oil, biodiesel, triacylglycerols, diacylglycerols, monoacylglycerols, fatty acids, fatty alcohols, branched dicarboxylic acids, dicarboxylic acid ethers, phospholipids, soapstock, deodorizer distillate, acid oil, polymerized oil, heat-bodied oil, blown oil, derivatives of any thereof, and combinations of any thereof. In other embodiments, fatty acids comprise a mixture of fatty acids derived from a biological source, such as from the group consisting of animal fat, beef tallow, biodiesel, borneo tallow,

butterfat, camelina oil, candlefish oil, canola oil, castor oil, ceramides, cocoa butter, cocoa butter substitutes, coconut oil, cod-liver oil, coriander oil, corn oil, cottonseed oil, diacylglycerols, flax oil, float grease from wastewater treatment facilities, hazelnut oil, hempseed oil, herring oil, illipe fat, jatropha oil, kokum butter, lanolin, lard, linseed oil, mango kernel oil, marine oils, meadowfoam oil, menhaden oil, milk fat, monoacylglycerols, mowrah fat, mustard oil, mutton tallow, neat's foot oil, olive oil, orange roughy oil, palm oil, palm kernel oil, palm kernel olein, palm kernel stearin, palm olein, palm stearin, peanut oil, phospholipids, phulwara butter, pile herd oil, pork lard, rapeseed oil, rice bran oil, safflower oil, sal fat, sardine oil, sasanqua oil, shea fat, shea butter, soybean oil, sphingolipids, sunflower seed oil, tall oil, tallow, tsukaki oil, tung oil, triacylglycerols, triolein, used cooking oil, vegetable oil, whale oil, white grease, yellow grease, and derivatives, conjugated derivatives, genetically-modified derivatives, and mixtures of any thereof. In an embodiment, biobased fatty acids from biodiesel are provided incorporated into the surfactant to provide a polyol biodieselate ethoxylate.

[0029] In other embodiments, the alkyl portion of the polyol alkyl ethoxylate comprises a branched dicarboxylic acid. Branched dicarboxylic acids may be obtained by subjecting fatty acid-containing compositions containing one or more double bonds to cross-linking, such as by industrial processes including but not limited to heat bodying, oxidation, polymerization, and blowing. For example, soybean oil may be cross-linked by blowing, wherein polymerization is carried out by bubbling air through a triacylglycerol oil while heating to temperatures of about 110° C. Typical oils include but are not limited to, drying oils, such as linseed oil, and semi-drying oils, such as soybean oil.

[0030] In an embodiment, carbon-carbon and ether cross-linkages are formed between fatty acids of fatty acid-containing compositions during the blowing process of a fatty acid-containing composition containing unsaturated fatty acids as depicted in FIG. 2. FIG. 2 shows a route for synthesis of a (cross-linked) branched-chain dicarboxylic acid depicting idealized carbon-carbon bond formation between fatty acids of two triacylglycerols in polymerization of triacylglycerols by blowing or heat-bodying, and an idealized (cross-linked) branched-chain dicarboxylic acid formed by hydrolysis of triacylglycerols polymerized by heat-bodying. Double bonds in the cross-linked molecule may be cis or trans double bonds, or may become single bonds in the blowing process. The carbon-carbon and ether linkages formed as a result of the blowing process polymerize a portion of the monounsaturated fatty acids, such as oleic acid, and/or a portion of the polyunsaturated fatty acids, such as linoleic acid and linolenic acid, cross-linking the fatty acid-containing compositions. In the case of triacylglycerol oils, dimers or polymers of fatty acid alkyl chains linked to glycerol molecules are formed. The heat-bodying of fatty acid-containing compositions also forms cross linkages but tends to form more carbon-carbon linkages and fewer ether linkages.

[0031] When one or more of the resulting cross-linked fatty acids is joined to one or more alcohols through an ester bond, the ester bonds can be broken to form cross-linked acids having two carboxylic acid groups. For example, hydrolysis of the ester bonds of a cross-linked triacylglycerol oil results in breaking the ester bonds holding each of the three fatty acids to the glycerol backbone of the triacylglycerol units, while cross-linkages between the fatty acids remain intact. Hydrolysis can be carried out with heat and pressure, and

under conditions which minimize the isomerization of remaining cis double bonds to trans double bonds, for example as described in U.S. Pat. No. 7,126,019 issued Oct. 24, 2006. Hydrolysis of the ester bonds of the cross-linked triacylglycerols yields a mixture of dicarboxylic acids and cross-linked dicarboxylic ethers. Selection of suitable starting fatty acid-containing compositions and cross-linking reaction designs will allow a portion of double bonds to remain in the cross-linked fatty acids (FIG. 2).

[0032] The dicarboxylic acids and dicarboxylic ethers are biobased and can be reacted to form ABA type surfactants, wherein the polar anhydrohexitol and ethoxylate chains are represented by A and the nonpolar cross-linked alkyl chain are represented by B. Because the melting points of branched-chain fatty acids are lower than the straight-chain counterparts, these branched B fatty acid chains of the surfactant molecules should crystallize at lower temperatures than the non-cross-linked counterparts. Thus, they may provide crude petroleum emulsion better viscosity reduction benefits at lower temperatures than more conventional polyol alkyl ethoxylates at low temperatures, better enabling low-temperature emulsion transport of petroleum. In an embodiment, dicarboxylic acids or cross-linked dicarboxylic ethers can be used to form AB type surfactants. In another embodiment, blends of AB and ABA surfactants may be synthesized from dicarboxylic acids, cross-linked dicarboxylic ethers, mixtures of dicarboxylic acids and unsaturated fatty acids, or mixtures of any thereof.

[0033] In an embodiment, an ABA type surfactant comprises at least one polyol, at least one ethoxylate group, and at least one dicarboxylic acid derived from cross-linked fatty acids. In another embodiment, an ABA type surfactant comprises at least two polyols, at least two ethoxylate groups, and at least one cross-linked dicarboxylic acid derived from polymerized fatty acids. In another embodiment, an ABA type surfactant comprises at least two polyols, at least two ethoxylate groups, and at least one cross-linked dicarboxylic acid ether derived from polymerized fatty acids.

[0034] In some embodiments, a biobased surfactant is a polyol alkyl ethoxylate containing biologically derived carbon.

[0035] In other embodiments, the one or more biobased surfactants (emulsifiers) may be combined with a petroleum fraction. In some embodiments, the petroleum fraction is selected from the group consisting of a separated crude petroleum phase, bitumen, naphtha, condensed refinery gases, gasoline, petrol, kerosene, diesel fuel, jet aircraft fuel, lubricating oils, base oils, vacuum gas oil, condensate, raffinate, reformat, light naphtha, residue, heavy gas oil, wax, tar, petroleum coke, asphalt base, heating oil, liquefied petroleum gas, fuel oil, paraffins, aromatics, naphthenes, cycloalkanes, olefins, cyclic hydrocarbons, alkenes, dienes, alkynes, burner fuel, fuel gas, light cycle oil, cat slurry, distillate, fuel, heavy fuel oil, reformat, alkylate, isomerate, resid, untreated distillate, treated distillate, middle distillate, and combinations of any thereof. The composition comprising a petroleum fraction and one or more biobased surfactants may be subjected to further processing to obtain a composition comprising a processed petroleum fraction and a co-processed biobased surfactant.

[0036] In an embodiment, crude petroleum is combined with one or more biobased surfactants and an aqueous phase, which may be or include seawater, in the context of reducing the viscosity of crude petroleum recovered offshore, for

example. Energy, such as heat or agitation, is supplied to the mixture as needed to cause an emulsion to form. After a suitable incubation, during which the emulsion may be transported, the emulsion is broken to form an aqueous phase and a petroleum phase composition. The petroleum phase composition comprises petroleum and a partitioned biobased surfactant or surfactants. A partitioned biobased surfactant includes one that has partitioned out of a petroleum/water emulsion or water/petroleum emulsion into the petroleum phase on phase splitting. The petroleum phase containing biobased surfactant may then be subjected to a further unit operation typical of petroleum processing, such as hydrolytic emulsion splitting, separation, fractionation, distillation, hydrolysis, hydrotreating, hydrocracking, decarboxylation, hydrogenation, steam cracking, thermal cracking, naphtha cracking, fluid catalytic cracking, catalytic reforming, steam reforming, metathesis, alkylation, dimerization, isomerization, coking, and combinations of any thereof to yield a composition comprising a petroleum product and a co-processed biobased surfactant or surfactants.

[0037] In another embodiment, crude petroleum is combined with at least one biobased surfactant and an aqueous phase, which again may be or include seawater as may be desirable in certain contexts. Energy, such as heat or agitation, is supplied to the mixture as needed to cause an emulsion to form. After a suitable incubation, during which the emulsion may be transported, the emulsion is broken by hydrolysis of the surfactant to form an aqueous phase and a petroleum phase composition. The petroleum phase composition comprises petroleum and biologically derived carbon from part of the hydrolyzed biobased surfactant. The petroleum phase containing biologically derived carbon may be subjected to a unit operation typical of petroleum processing, including but not limited to hydrolytic emulsion splitting, separation, fractionation, distillation, hydrolysis, hydrotreating, hydrocracking, decarboxylation, hydrogenation, steam cracking, thermal cracking, naphtha cracking, fluid catalytic cracking, catalytic reforming, steam reforming, metathesis, alkylation, dimerization, isomerization, coking, and combinations of any thereof to yield a composition comprising a petroleum product containing biologically derived carbon.

[0038] In certain embodiments, this petroleum product containing biologically derived carbon will be in the form of petroleum diesel fuel from the crude petroleum and biologically derived carbon from the co-processed biobased surfactant. The biologically derived carbon from the co-processed biobased surfactant or surfactants may in some embodiments take the form of a biodiesel fuel from the reaction of a biobased surfactant. In some embodiments, the reaction is selected from the group consisting of hydrolytic emulsion splitting, hydrolysis, hydrotreating, hydrocracking, decarboxylation, hydrogenation, steam cracking, thermal cracking, naphtha cracking, fluid catalytic cracking, catalytic reforming, steam reforming, metathesis, alkylation, dimerization, isomerization, coking, and combinations of any thereof to yield a composition comprising a petroleum fraction and a biobased surfactant having been subjected to a unit operation. Hydrolytic emulsion splitting refers to a reaction in which a surfactant in an emulsion is at least partially hydrolyzed, resulting in a decrease in emulsion stability and at least partial separation into two or more phases.

[0039] In another embodiment, petroleum products are produced by mixing a biobased surfactant and water with petroleum to provide a composition, transporting the compo-

sition, separating water from the composition to provide a petroleum phase comprising biobased surfactant and separated petroleum, and then processing the petroleum phase and co-processing the biobased surfactant into at least one petroleum product, wherein the petroleum product comprises at least one of a co-processed biobased surfactant and a biobased surfactant having been subjected to a unit operation. In some embodiments a biobased surfactant comprises biobased polyol biodieselate ethoxylate, wherein the alkyl portions of the surfactant are derived in whole or in part from biodiesel. **[0040]** In an embodiment illustrated schematically in FIG. 1, a system for transporting petroleum comprises a first conduit **20** for transporting a mixture **10** comprising petroleum, an aqueous phase, and a biobased surfactant. The first conduit is fluidly connected with a separator **30**. The separator is fluidly connected with a second conduit **40** containing a mixture of petroleum and a biobased surfactant **50**; and with a third conduit **60** comprising an aqueous phase **70**.

[0041] In still another embodiment, a method for incorporating biologically derived carbon into a petroleum fraction is described. The method comprises incorporating a biobased surfactant and water into petroleum to form an emulsion, transporting the emulsion of petroleum, incorporated biobased surfactant, and incorporated water; and subjecting the transported emulsion to a unit operation to obtain a petroleum fraction, wherein the content of biologically derived carbon in the petroleum fraction is greater than the content of biologically derived carbon in the petroleum. In an embodiment, the biobased surfactant is hydrolyzed during co-processing with petroleum, and biologically derived carbon from the hydrolyzed surfactant is incorporated into a processed petroleum product.

[0042] The present invention is more particularly illustrated by the following examples, which should be taken as illustrative only and not limiting of the invention as claimed hereafter:

EXAMPLE 1

[0043] Crude petroleum oil (Sour crude oil) was obtained from ConocoPhillips (Houston, Tex.). The specific gravity of the crude petroleum was 0.7-1.03 at 60° F., the flash point was 100° F. and the content of volatility was greater than 50%. The crude petroleum oil was analyzed by proton NMR, which confirmed the absence of ethoxylated protons (chemical shift near 3.8 ppm), and by GC-MS, which confirmed the absence of fatty acids.

[0044] Sea water substitute was prepared as an aqueous phase according to ASTM D 1141, and nonionic surfactant containing biologically derived carbon in the alkyl portion (sorbitan monooleate ethoxylate, Toximul SEE 341, Stepan Co., Northfield, Ill.) having a POE (polyoxyethylene number) of 20 (structure 1), was added to the sea water substitute in various proportions at room temperature and dispersed gently to form a series of clear surfactant solutions. These clear solutions of water and surfactant were added to the amounts of crude petroleum oil as indicated in Table 1. The mixtures of water, biobased surfactant solution and crude petroleum oil were each agitated at room temperature for 3 minutes at 6000 RPM using a high shear homogenizer to provide crude petroleum oil emulsions. Emulsions of various compositions were prepared as outlined in Table 1. The viscosity behavior of the crude petroleum oil and the crude petroleum oil emulsion were determined by measuring the viscosity at room temperature using a Brookfield L viscometer. Good viscosity was

viscosity of 350-400 cPs. The stability behavior was determined by checking the appearance of each emulsion every day for 21 days. A good emulsion was one that remained as a single phase for 21 days at room temperature, while a poor emulsion separated into two or more phases before 21 days. Emulsion #1, the 70:27:3 (crude petroleum oil:sea water substitute:Toximul SEE341) emulsion, showed good viscosity reduction and good stability after 21 days.

TABLE 1

Composition, viscosity rating, and stability rating of crude petroleum oil emulsions.					
#	Crude petroleum oil (g)	Sea water substitute (g)	Toximul SEE341 (g)	Viscosity	Stability
1	70	27	3	Good	Good
2	80	18	2	Too high	ND
3	70	28.5	1.5	ND	Good
4	80	19	1	Too high	ND
5	70	29	1	ND	Poor
6	70	27.9	2.1	ND	Poor
7	70	27.6	2.4	ND	Poor
8	70	27.3	2.7	ND	Good
9	70	26	4	Too high	Good
10	70	25	5	Too high	Good
11	70	24	6	Too high	Good

ND = not determined.

[0045] A Rheolyst AR1000-N rheometer from TA Instruments was then employed to determine the viscosity behavior of crude oil and two 70:27:3 emulsions at various shear rates at 10-25° C. using a parallel plate configuration with a gap setting of 0.5 mm together with a cone and plate sensor with a cone angle of 2°, cone diameter of 40 mm and a 0.137 mm gap at the cone tip. The desired viscosity range was 350-400 cPs, which was obtained in the emulsion of crude petroleum oil and seawater substitute using Toximul SEE341 surfactant (Table 2).

[0046] The crude petroleum oil showed Newtonian shear thinning with temperature, with a temperature-dependent decrease in viscosity from about 10,000 cps at 10° C. to about 1,300 cps at 30° C. (Table 2). However, the emulsions of crude petroleum oil showed non-Newtonian shear thinning behavior at lower shear rate (about 500 cps) than the crude petroleum oil.

TABLE 2

Temperature-dependent viscosity changes in crude petroleum oil and emulsions (shear rate: 15.8/sec)					
Sample	10° C.	15° C.	20° C.	25° C.	30° C.
Crude Petroleum oil	10050	5600	3400.3	2100	1362
Emulsion 70:30 (crude petroleum oil:distilled water)	692	601	536	520	502
Emulsion 70:30 (crude petroleum oil:sea water)	488	404	372	349	332

EXAMPLE 2

[0047] One hundred grams of a crude petroleum oil emulsion with water and sorbitan fatty acid ethoxylate comprising biologically derived carbon was prepared. The emulsion had the composition of emulsion #1 in Example 1 and was pre-

pared substantially as in Example 1, except that the surfactant solution was mixed into the crude petroleum oil by agitation at 3000 rpm for 2 minutes. A composition comprising a stable emulsion containing 27 grams of water, 3 grams of Toximul SEE341 and 70 grams of crude petroleum oil formed. The emulsion was processed by adding 30 grams of a 5% (weight/volume) solution of sodium hydroxide and heating the mixture to 70° C. for one minute in a separator. Under these conditions, the surfactant was co-processed by hydrolytic cleavage of the ester bonds, releasing the nonpolar (fatty acid alkyl) portion of the biobased surfactant from the polar (anhydrohexitol ethoxylate) portion. A petroleum product phase was collected.

[0048] The polar (anhydrohexitol ethoxylate) portion of the surfactant would naturally partition into the aqueous phase; proton NMR testing showed the presence of ethoxylated protons in the separated petroleum phase, confirming the presence of co-processed biobased surfactant in the processed petroleum product, by a chemical shift peak around 3.8 ppm characteristic of the ethoxylated protons.

[0049] GC-MS analysis of the aqueous phase showed a complete absence of the fatty acid alkyl portion of the surfactant. However, the presence of fatty acids containing biologically derived carbon from co-processed biobased surfactant in the processed petroleum product was confirmed by GC-MS. The separated processed petroleum phase contained 0.6% biobased alkyl groups originating from the biologically derived fatty acid portions of the co-processed biobased surfactant molecule, indicating a composition comprising a petroleum product and biobased carbon from the co-processed biobased surfactant. The biobased alkyl fatty acid contribution to the composition of Toximul SEE341 is 20% by weight; the processed petroleum product phase contained 100% of the biobased alkyl portions of the co-processed surfactant contained in the original 100 grams of emulsion.

EXAMPLE 3

[0050] One hundred grams of a crude petroleum oil emulsion with sorbitan fatty acid ethoxylate (containing biobased carbon) having the composition of emulsion #1 in Example 1 was prepared substantially as in Example 1 except that the biobased surfactant solution was mixed into the crude petroleum oil by agitation at 3000 rpm for 2 minutes. After formation of a stable emulsion containing 3 grams of Toximul SEE341, the crude petroleum oil emulsion was processed in an emulsion breaking (hydrolysis) unit operation by adding 30 grams of sea water substitute and heating to 80° C. for 5 minutes. The surfactant was co-processed with the petroleum oil. After this unit operation, the processed emulsion was allowed to cool. The processed emulsion separated cleanly into a separated processed petroleum product and an aqueous phase with no interfacial layer. The processed petroleum product comprising co-processed surfactant (petroleum oil phase) and the separate aqueous phase were collected and analyzed to determine the content of alkyl portions (fatty acid) of emulsifier in each of the phases.

[0051] The presence of ethoxylated protons in the separated crude petroleum oil phase, indicating the presence of co-processed surfactant in the processed petroleum product phase, was confirmed by proton NMR, which showed a chemical shift peak around 3.8 ppm characteristic of the ethoxylated protons.

[0052] GC-MS analysis of the aqueous phase showed that the aqueous phase was substantially free from alkyl portions

of the surfactant, containing 0.065% of alkyl portion (fatty acid) of the surfactant. The processed petroleum product phase contained 0.31% of the alkyl (biologically derived fatty acid) portion of the surfactant molecule. The alkyl fatty acid contribution to the composition of Toximul SEE341 is 20% by weight; thus, of the surfactant contained in the original 100 grams of emulsion, the processed petroleum product phase contained 50% of the biobased fatty acid alkyl portions in the form of free fatty acids. The absence of fatty acids in the aqueous phase indicated that the remaining co-processed biobased surfactant was dissolved in the petroleum product (oil phase).

EXAMPLE 4

[0053] Anhydrohexitol surfactant molecule is synthesized from 100% biobased material. Anhydrohexitol (sorbitan) is produced from corn fructose, ethoxy groups are produced from ethanol, and fatty acid groups from biodiesel are used to synthesize an anhydrohexitol biodieselate ethoxylate comprising 100% biobased carbon. An emulsion is formed and processed as in Example 3. After processing, half (1.5 grams) of intact partitioned biobased surfactant is incorporated into 70 grams of separated crude petroleum oil (processed petroleum product) phase. An additional 0.31% of fatty acids from hydrolyzed biobased alkyl fatty acid portions of the surfactant molecule are incorporated into the separated crude petroleum oil phase to provide 71.81 grams of a separated crude petroleum oil phase containing 1.81 grams of biologically derived carbon from the co-processed biobased emulsifier (2.5% by weight of the separated petroleum oil phase).

EXAMPLE 5

[0054] A polyol surfactant molecule is synthesized from 100% biobased material. A mixture of polyols is produced by hydrolysis of corn stover, ethoxy groups are produced from ethanol, and fatty acid groups are produced from biodiesel. From these, an ethoxylated polyol biodieselate surfactant is synthesized to yield a polyol biodieselate ethoxylate. An emulsion is formed and processed with this surfactant in the manner of Example 3. Half (1.5 grams) of intact partitioned biobased surfactant is incorporated into 70 grams of separated crude petroleum oil (processed petroleum product) phase as in Example 4. An additional 0.31% of fatty acids from hydrolyzed biobased alkyl fatty acid portions of the surfactant molecule are incorporated into the separated crude petroleum phase as in Example 4 to provide 71.81 grams of a separated crude petroleum phase containing 1.81 grams of biologically derived carbon from biobased emulsifier (2.5% of the separated petroleum phase).

EXAMPLE 6

[0055] An anhydrohexitol alkyl ethoxylate surfactant molecule is synthesized from materials containing 100% biologically derived carbon. Anhydrohexitol (sorbitan) is produced from corn fructose, ethoxy groups are produced from ethanol, and the alkyl group is produced as a cross-linked dicarboxylic acid from polymerized triacylglycerol vegetable oil. Polymerized vegetable oil is prepared by polymerization and heating soybean oil to temperatures of about 300° C. under vacuum. Then, glycerol-fatty acid linkages of the polymerized oil are hydrolyzed by the application of heat and pressure substantially as described in U.S. Pat. No. 7,126,019 issued Oct. 24, 2006 to yield a fraction enriched in cross-linked

dicarboxylic acids comprising one or more double bonds. These are reacted with anhydrohexitol from corn fructose and ethoxy groups produced from ethanol to produce a biobased ABA type surfactant. Processing of petroleum crude oil with 100% biobased surfactant is carried out as in Example 3. When the surfactant is co-processed with the petroleum, half (1.5 grams) of intact partitioned biobased surfactant is incorporated into 70 grams the processed petroleum phase as in Example 3. An additional 0.31% of fatty acids from hydrolyzed biobased alkyl fatty acid portions of the surfactant molecule are incorporated into the processed petroleum phase as in Example 4 to provide 71.81 grams of a processed petroleum product containing 1.81 grams of carbon from co-processed biobased ABA type emulsifier (2.5% of the separated petroleum phase).

EXAMPLE 7

[0056] Processed petroleum product containing biologically derived carbon from the 2.5% co-processed biobased emulsifier contained in the separated petroleum phase is obtained substantially as in Example 7. The petroleum product containing biologically derived carbon from the 2.5% co-processed biobased emulsifier is further processed into diesel fuel, thus providing petroleum diesel fuel containing biobased diesel fuel, wherein the biobased diesel fuel comprises a product of co-processing a biobased surfactant.

[0057] This invention has been described with reference to certain exemplary embodiments. However, it will be recognized by those of ordinary skill in the art that various substitutions, modifications or combinations of any of the exemplary embodiments may be made without departing from the spirit and scope of the invention, as more particularly defined by the claims below.

1. A composition comprising:
 - a processed petroleum product; and,
 - a co-processed biobased surfactant.
2. The composition of claim 1, wherein the processed petroleum product is the resultant material from processing
 - (i) one or more of separated crude petroleum oil phase, bitumen, naphtha, condensed refinery gases, gasoline, petrol, kerosene, diesel fuel, jet aircraft fuel, lubricating oils, base oils, vacuum gas oil, condensate, raffinate, reformate, light naphtha, residue, heavy gas oil, wax, tar, petroleum coke, asphalt base, heating oil, liquefied petroleum gas, fuel oil, paraffins, aromatics, naphthenes, cycloalkanes, olefins, cyclic hydrocarbons, alkenes, dienes, alkynes, burner fuel, fuel gas, light cycle oil, cat slurry, distillate, fuel, heavy fuel oil, reformate, alkylate, isomerate, resid, untreated distillate, treated distillate, middle distillate, and combinations of any thereof,
 - via (ii) one or more unit operations selected from hydrolytic emulsion splitting, separation, fractionation, distillation, hydrolysis, hydrotreating, hydrocracking, decarboxylation, hydrogenation, steam cracking, thermal cracking, naphtha cracking, fluid catalytic cracking, catalytic reforming, steam reforming, metathesis, alkylation, dimerization, isomerization, coking, and combinations of any thereof.
3. The composition of claim 2, wherein the co-processed biobased surfactant results from combining a biobased surfactant with the petroleum material (i) and then processing the combined biobased surfactant and petroleum material (i) via the one or more unit operations (ii).

4. The composition of claim 1, further comprising biodiesel.

5. The composition of claim 1, wherein the co-processed biobased surfactant comprises a polyol alkyl ethoxylate containing biologically derived carbon.

6. The composition of claim 5, wherein the polyol portion of the polyol alkyl ethoxylate is derived from compounds selected from the group consisting of anhydrohexitols, saccharides, monosaccharides, dioses, glycolaldehyde, trioses, glyceraldehydes, dihydroxyacetone, tetroses, erythrose, threose, aldo-pentoses, arabinose, lyxose, ribose, deoxyribose, xylose, keto-pentoses, ribulose, xylulose, aldo-hexoses, allose, altrose, galactose, glucose, dextrose, gulose, idose, mannose, talose, keto-hexoses, fructose, psicose, sorbose, tagatose, heptoses, mannoheptulose, sedoheptulose, octoses, octulose, 2-keto-3-deoxy-manno-octonate, nonoses, sialose, disaccharides, sucrose, table sugar, cane sugar, saccharose, beet sugar, lactose, milk sugar, maltose, trehalose, cellobiose, oligosaccharides, raffinose, melitose, stachyose, verbascose, sorbitol, glycerol, sorbitan, isosorbide, polyglycerols, hexoses, pentoses, polyols, hydrogenated sugars, hydroxymethylfurfural, refined sugars, crude sugars, products of the breakdown of cellulose, products of the breakdown of hemicellulose, products of the breakdown of lignin, plant fiber hydrolyzates, fermented plant fiber hydrolyzates, carbohydrate hydrogenolizates, and combinations of any thereof.

7. The composition of claim 5, wherein the polyol portion of the polyol alkyl ethoxylate comprises a polyol selected from the group consisting of monoanhydrohexitols, dianhydrohexitols, isomannide, sorbitan, and any combinations thereof.

8. The composition of claim 5, wherein the alkyl portion of the polyol alkyl ethoxylate comprises an alkyl portion derived from the group consisting of animal oil, vegetable oil, biodiesel, triacylglycerols, diacylglycerols, monoacylglycerols, fatty acids, fatty alcohols, branched dicarboxylic acids, dicarboxylic acid ethers, phospholipids, soapstock, deodorizer distillate, acid oil, polymerized oil, heat-bodied oil, blown oil, and combinations of any thereof.

9. The composition of claim 5, wherein the surfactant is selected from the group consisting of an AB type surfactant, an ABA type surfactant, and combinations thereof.

10. A surfactant comprising:

- at least one polyol;
- at least one ethoxylate group; and,
- at least one branched dicarboxylic acid derived from polymerized fatty acids.

11. The surfactant of claim 10, wherein at least one of the polyol, ethoxylate group, and the branched dicarboxylic acid derived from polymerized fatty acids contains biologically derived carbon.

12. The surfactant of claim 11, wherein the surfactant is of the ABA type.

13. A process for producing a petroleum product comprising:

- separating water from a composition comprising the water, a biobased surfactant and petroleum, thus producing a separated petroleum phase comprising biobased surfactant and petroleum; and,

processing the petroleum phase into at least one petroleum product, by performing at least one of hydrolytic emulsion splitting, separation, fractionation, distillation, hydrolysis, hydrotreating, hydrocracking, decarboxylation, hydrogenation, steam cracking, thermal cracking,

naphtha cracking, fluid catalytic cracking, catalytic reforming, steam reforming, metathesis, alkylation, dimerization, isomerization, coking, and combinations of any thereof.

14. A process for reducing the viscosity of a petroleum through the use of a biobased surfactant, comprising:

mixing a biobased surfactant with petroleum and water, thus producing a composition;

transporting the composition through a pipeline;

separating water from the composition, thus producing an oil phase comprising biobased surfactant and petroleum; and,

processing the oil phase into at least one petroleum product.

15. The process of claim **14**, wherein the biobased surfactant comprises polyol biodieselate ethoxylate.

16. The process of claim **14**, wherein the biobased surfactant comprises an ABA type surfactant.

17. The process of claim **16**, wherein the ABA type surfactant is derived from a dicarboxylic acid comprising cross-linked alkyl groups.

18. A process of incorporating biologically derived carbon content into a petroleum product, comprising:

mixing a biobased surfactant comprising biobased carbon, water, and petroleum, thus producing a composition;

separating water from the composition, thus producing an oil phase comprising the biobased surfactant and the petroleum; and,

processing the oil phase into at least one petroleum product.

19. The process of claim **18**, wherein producing the composition involves forming a water-in-oil emulsion and wherein separating water from the composition involves breaking the emulsion.

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