Title: BIODIESEL PRODUCTION WITH REDUCED WATER EMISSIONS

Abstract: Waste water emissions from a biodiesel production facility are substantially reduced by recovering water from a spent water stream used in a water washing step in the refining of crude biodiesel which has a concentration of lower alkanol below about 5000 parts per million by mass. The water washing removes glycerin from the crude biodiesel. The water is recovered from the spent water stream and is concentrated to provide an aqueous fraction which can be recycled for the water washing and an aqueous glycerin-containing fraction that preferably contains at least about 10 mass percent glycerin.
BIODIESEL PRODUCTION WITH REDUCED WATER EMISSIONS

Field of the Invention

[0001] This invention pertains to processes for the synthesis of biodiesel from fats and oils by base catalyzed transesterification with lower alkanol, and particularly to such processes characterized by low water emissions.

Background to the Invention

[0002] Biodiesel is being used as an alternative or supplement to petroleum-derived diesel fuel. Biodiesel can be made from various bio-generated oils and fats from vegetable and animal sources.

[0003] One process involves the transesterification of triglycerides in the oils or fats with a lower alkanol in the presence of a catalyst, acidic or basic, to produce alkyl ester useful as biodiesel and a glycerin co-product. In this process, the alkyl ester and glycerin are separated, usually by a phase separation, and the lighter phase containing crude biodiesel is refined. Typically refining operations include the removal of residual alkanol, glycerin and other impurities present in the crude biodiesel. One of the refining unit operations conventionally used is a water washing to remove salts, lower alkanol and residual glycerin.

[0004] The spent water from this washing, which is contaminated with lower alkanol, residual glycerin and other organic impurities, is usually sent to sewer. The oxygen demand for the degradation of the organics contained in the water is not insignificant. The biochemical oxygen demand may be in excess of 0.01 kilograms of oxygen per liter of biodiesel produced. This biochemical oxygen demand can require a biodiesel production facility to install a waste water treatment facility or otherwise procure waste water disposal services.

[0005] One type of process for reducing waste water emissions from a biodiesel plant is described by Van Gerpen, et al., "Building a Successful Biodiesel Business", Second Edition, Biodiesel Basics, (2006) pages 133 to 145. They disclose combining the spent wash water from the biodiesel wash columns with glycerin by-product from the transesterification, acidifying the mixture to split the soaps and neutralize catalyst, flashing the water and alcohol from the mixture and then distilling the alcohol and water fraction. One of the difficulties faced using such a process is that the glycerin by-product, which otherwise could be relatively water free, contains enough water to require its separation
from the alkanol. Accordingly, using the glycerin by-product still to handle the spent wash water adds not only to the heat duty to remove alcohol from the glycerin, but also the need for an alcohol and water separation.

Accordingly, biodiesel production processes are sought that generate a minimum of waste water from water washing of the crude biodiesel while minimizing energy consumption.

Summary of the Invention

By this invention, processes for making biodiesel are provided that have substantially reduced waste water emissions without undue additional costs in energy consumption. The preferred processes of this invention do not require the facilities in a biodiesel plant to distill alkanol from the spent glycerin by-product of the transesterification. In accordance with the processes of this invention, the concentration of lower alkanol in the crude biodiesel is reduced to below about 5000 parts per million by mass (ppm-m) prior to washing with water. Especially where the alkanol concentration is reduced to below about 2000 ppm-m, the water washing is not required to remove lower alkanol for the biodiesel to be of merchantable quality. Moreover, due to the low alkanol concentration in the crude biodiesel to be washed, any drying unit operation subsequent to the water washing will contain relatively little alkanol in the off gases, thereby minimizing any potential volatile organic emissions. The additional costs to reduce alkanol to low concentrations in the crude biodiesel are in part offset by the increased recovery of alkanol which can be recycled to the transesterification. Further, as the crude biodiesel contains very little water, the recovered alkanol is typically sufficiently dry that it can be recycled without effecting an additional water and alkanol fractionation.

Because the crude biodiesel has a very low concentration of alkanol prior to water washing, the water used for the washing of crude biodiesel to remove glycerin (spent water) can be subjected to a concentration unit operation, e.g., membrane separation or fractionation by distillation, to provide an aqueous, glycerin-containing fraction that contains at least 10 mass percent glycerin, and an aqueous fraction having a reduced concentration of glycerin that can be recycled as a portion of the water for washing the crude biodiesel. The aqueous fraction recycled as a portion of the water for the washing of the crude biodiesel contains alkanol. However, as the water washing need not effect
Further alkanol removal, the recycle is not detrimental to the quality of the biodiesel product.

[0009] As the aqueous, glycerin containing fraction has a low concentration of alkanol, further processing of this fraction to recover additional alkanol is not usually economically justifiable. However, if the interest is in recovering a glycerin product, such additional processing may be desired. As the aqueous, glycerin-containing fraction is concentrated in glycerin, or glycerin and soaps, if present, it is more suitable for admixing with the heavier, glycerin-containing layer from the phase separation of the transesterification reaction product. Since the aqueous, glycerin-containing fraction from the concentration is often less than about 5, and preferably less than about 3, mass percent of the glycerin-containing layer from the product phase separation, the size of the distillation equipment and the heat duty are not materially changed from that needed to only process the glycerin layer from the transesterification. Hence, the processes of this invention are useful for retrofit applications where a refined glycerin by-product is desired.

[0010] In its broad aspects, the processes of this invention comprise washing a crude biodiesel stream containing alkyl esters of fatty acids ("alkyl esters"), lower alkanol, and glycerin and often also soaps of fatty acids ("soaps") or free fatty acids, depending upon the degree of acidulation with water for a time sufficient to remove at least a portion of the glycerin therein to provide an alkyl ester stream of increased purity and a spent water stream. As free fatty acids are soluble in the crude biodiesel, they are not significantly removed by the water washing. Soaps, being water soluble, are readily removed by the water washing. The concentration of glycerin in the crude biodiesel is often below about 1 mass percent, say, between about 0.1 and 0.8, mass percent. Preferably the concentration of the lower alkanol in the crude biodiesel stream is less than about 500ppm-m and often is in the range of between about 1 or 5 to 500 ppm-m, most preferably less than about 200 ppm-m, e.g., between about 5 to 100 or 200 ppm-m, and sometimes less than 10 ppm-m. The preferred lower alkanols are methanol, ethanol and isopropanol with methanol being the most preferred.

[0011] The spent water stream is subjected to a concentration unit operation such as distillation or membrane separation. Adjuvants may be added to the spent water stream, e.g., pH adjusters, buffers, anti-foam agents, and the like. Nevertheless, the stream subjected to concentration typically contains at least about 90 mass percent water. The
concentration provides an aqueous fraction (vapor fractionation overhead or permeate) comprising water and an aqueous, glycerin-containing fraction. The aqueous fraction preferably contains less than about 5, more preferably less than 2, and sometimes less than about 0.5, mass percent of the total glycerin in the spent water stream. At least a portion of the aqueous fraction is recycled as water for washing crude biodiesel. The concentration provides an aqueous, glycerin-containing fraction that contains less than about 70 mass percent water. The concentration of soaps (if present during the washing) and glycerin in the aqueous, glycerin-containing fraction are often in the range of about 30 to 90 mass percent. The concentration of glycerin in the aqueous, glycerin-containing fraction will depend upon whether soaps are also present, and if so, the mass ratio of soaps to glycerin in the crude biodiesel. The concentration of glycerin in the aqueous, glycerin-containing fraction is often in the range of at least about 30 to 70 or 90, preferably between about 30 and 60, mass percent in the absence of soaps. Where soaps are present, the concentration of glycerin in the aqueous, glycerin-containing fraction is often at least about 10, say, about 15 to 70, mass percent. The concentration of water in the aqueous, glycerin-containing fraction is at least about 10, preferably at least about 15, mass percent.

[0012] The aqueous fraction from the concentration contains little, if any, i.e., preferably less than about 5 mass percent, and preferably less than about 2 mass percent, of the total glycerin and soaps or free fatty acids, if present, in the spent water stream. Often the concentration of total glycerin and soaps or free fatty acids in the lower boiling fraction is less than about 0.5, preferably less than about 0.1, mass percent. Advantageously, since significant amounts of water can be acceptable in the higher boiling fraction, the distillation technique can be simple and require minimal heat duty. Due to the significant difference in boiling points between glycerin and water, adequate separation can often be achieved by evaporation. If desired, however, a vapor liquid separation using packing or trays can be used, with or without reflux.

[0013] In accordance with this invention, lower alkanol may be contained in both the aqueous fraction and the aqueous, glycerin-containing fraction from the concentration, e.g., by membrane separation or distillation, of the spent water stream.

[0014] Although the aqueous fraction contains less organic than the spent water stream from the concentration and thus may be sent to sewer with less biochemical oxygen demand than the spent wash water, most preferably all, of the aqueous fraction is recycled
as part of the water for washing the crude biodiesel. Even though the aqueous fraction may contain some glycerin and lower alkanol, the efficacy of aqueous fraction for removal of glycerin from the crude biodiesel is not significantly hindered due to the much higher solubility of these components in water as compared to alkyl esters in the biodiesel being refined. Hence, for a retrofit, the processes of this invention do not unduly adversely affect the capacity of existing equipment to achieve the water washing yet still provide for the environmental benefits of this invention.

[0015] In preferred aspects, the processes also pertain to the base catalyzed transesterification of glycerides with lower alkanol. These processes comprise:

a. contacting a glyceride-containing feed and lower alkanol under transesterification conditions comprising the presence of a transesterification catalyst, wherein the molar ratio of lower alkanol to glyceride is at least about 3:1 to provide a crude biodiesel containing alkyl esters of fatty acids, glycerin, and lower alkanol, said contacting being for a time sufficient to convert at least about 90 mass percent of the glycerides in the glyceride-containing feed;
b. separating by phase separation said crude biodiesel to provide a heavier glycerin-containing layer and a lighter alkyl ester-containing layer, wherein a portion of the glycerin is contained in each of the heavier and lighter layer;
c. subjecting the lighter layer to vapor fractionation conditions to provide a lower boiling fraction containing lower alkanol and a higher boiling fraction containing alkyl ester and glycerin and lower alkanol; and
d. water washing the higher boiling fraction containing alkyl ester to provide a biodiesel of increased purity and a spent water stream,

the improvement comprising conducting step (c) to provide a higher boiling fraction containing less than about 5000, preferably less than about 2000, parts per million by mass of lower alkanol; in step (d) concentrating the spent water stream to provide an aqueous fraction and an aqueous, glycerin-containing fraction and providing at least a portion of the aqueous fraction as a portion of the water for step (d). In preferred aspects of this
invention, step (c) is conducted to provide a higher boiling fraction containing less than 500, and sometimes less than 200, ppm-m of lower alkanol. In this preferred aspect of the invention, the vapor from any subsequent drying will contain a very low concentration of lower alkanol.

[0016] The transesterification may be acid or base catalyzed. In one preferred aspect, step (a) of the processes is a base-catalyzed transesterification of glycerides. With base catalyzed transesterification, the formation of soaps can occur. Preferably, the pH of the higher boiling fraction to be washed in step (d) is adjusted to less than about 5 or 6, most preferably between about 3 and 5. At these acidities, soaps present can be converted to free fatty acids, thus facilitating the water washing. However, the free fatty acids are preferentially soluble in the biodiesel. If it is desired to reduce the free fatty acid content of the biodiesel, one or more of the water wash stages may be conducted under conditions where the soaps are maintained and are preferentially removed in the aqueous phase. Where soaps are maintained, it is generally preferred to operate the wash under sufficiently alkaline conditions that undue emulsions are not formed, e.g., at a pH of at least about 8, and often in the range of between about 9 and 10.5 or 11.

[0017] Often the transesterification comprises at least two sequential stages, each of which is fed lower alkanol, and between stages, glycerin is separated by phase separation. Step (b) may thus be performed by phase separation between stages or by phase separation between stages and after the final stage. Additional lower alkanol and catalyst may be added, if desired, to the lighter layer passing to a subsequent reaction zone. In one embodiment, at least about 50 mass percent of the glyceride fed to a preceding reactor is reacted in the preceding reactor, a glycerin-containing phase is separated from the transesterification product of the first reaction zone and a glyceride and alkyl ester-containing layer is fed to a subsequent reaction zone for substantial completion of the transesterification. The transesterification product from the subsequent reaction zone may be subjected to another phase separation to recover glycerin. In another embodiment, the preceding reaction zone effects at least about 90, preferably between about 92 to 98, percent of the conversion of the glyceride; a phase separation of a glycerin-containing layer is effected and substantial completion of the conversion of the glyceride is effected in the subsequent reaction zone and the transalkylation product from the subsequent transalkylation zone is subjected to step (c) without an intervening phase separation unit.
operation. Where more than one transalkylation reaction zone is used, the ratio of alkanol to glyceride may be the same or different in each zone.

[0018] In preferred processes of this invention, the heavier glycerin-containing layer is subjected to fractionation by distillation to provide an alkanol-containing overhead fraction that is recycled to step (a) and a glycerin-containing higher boiling fraction that contains a minor amount of water, often less than about 5, preferably less than about 3, mass percent.

[0019] In other preferred processes of this invention, the heavier glycerin-containing layer is contacted with glyceride-containing feed prior to step (a) under conditions such that alkanol is reacted with glyceride and alkanol is extracted into the glyceride-containing feed to provide a pretreated glyceride-containing feed. The pretreated glyceride-containing feed is phase separated from the glycerin-containing layer and at least a portion of the pretreated glyceride-containing feed is passed to step (a).

Brief Description of the Drawings

[0020] Figure 1 is a schematic depiction of a biodiesel facility using the processes of this invention.

[0021] Figure 2 is a schematic depiction of another biodiesel facility using the processes of this invention.

[0022] Figure 3 is a schematic depiction of a two stage washing apparatus that can be used in the practice of the processes of this invention.

Detailed Discussion

[0023] The following discussion is in reference to the facility depicted in the Figures. The Figures are not intended to be in limitation of this invention.

[0024] The biodiesel facility of Figure 1 includes an acid-catalyzed esterification section, a pretreatment section, a transesterification section and a refining section. One or more of these sections can be used.

Acid Treatment

[0025] As shown in Figure 1, glycerides can be provided to facility 100 via line 102 for pretreatment by acid. While esterification of glycerides can be effected by acid catalyzed esterification, the more severe conditions used in acid catalyzed esterification are generally only used where the glycerides also contains significant amounts of free fatty
acid. Line 104 is provided in the event that more than one feed is desired to be processed in the acid treatment section.

[0026] The feed may be directly introduced into acid treatment reactor 106, or as shown, is subjected to a contact with an alkanol laden stream of glycerin to strip alkanol from the glycerin into the oil-containing feed phase. This contact will be described later.

[0027] For purposes of this discussion, the feed will contain both free fatty acids and phospholipids, and acid treatment reactor 106 serves both to convert free fatty acid to esters and to facilitate removal of phospholipids. Broadly, esterification is conducted with alkanol, which may be a diol, but preferably is a monoalkanol, having a primary –OH, under esterification conditions. The preferred alkanols are lower alkanols, especially those having 1 to 3 carbons, although butanol and isobutanol and higher alkanols are operable. Most preferably the alkanol is methanol.

[0028] Esterification conditions include the presence of acidic catalyst, elevated temperature, e.g., at least about 40°C and sometimes as high as 200°C or more, and especially where the reaction menstruum is to be in the liquid phase, such high temperatures may be accompanied with the use of superatmospheric pressures sufficient to maintain the liquid phase. Preferably an inerting gas such as nitrogen, hydrocarbon gas such as methane or carbon dioxide is used during the acid treatment.

[0029] The preferred conditions for the acid treatment will depend upon the nature of the feed, the type of acid treatment sought, and the apparatus. Reactor 106 may comprise one or more stages or vessels and separation unit operations may be located between each stage or vessel. Where reactor 106 is staged, it is often desirable to remove water and any glycerin between stages to enhance conversion of free fatty acid to esters. Glycerin, if present, will be contained in the removed water fraction. Reactor 106 may be a vessel or a length of pipe. But preferably other types of vessels are used such as mechanical and sonically agitated reactors, and reactors with static mixing such as reactors containing contact structures such as trays, packing, baffles, orifices, venturi nozzles, tortuous flow path, and other impingement structures. Suitable reactors include those providing high intensity mixing, including high shear.

[0030] The molar ratio of alkanol to free fatty acid in the feed will vary depending upon the reactivity of the alkanol and the extent of esterification sought. The esterification reaction is an equilibrium limited reaction and hence an excess of alkanol may be used to
drive the reaction to the desired degree of completion. As will be discussed later, any unreacted free fatty acid can be recovered elsewhere in the process and returned to acid treatment reactor 106. Often, the alkanol and the residence time in reactor 106 is sufficient to convert at least about 30 mole percent, and preferably at least about 50 mole percent, and sometimes at least about 75 mole percent to essentially all, the free fatty acid to ester. Where less than all the free fatty acid is converted to fatty ester, it is preferred that the oil phase from the acid treatment section of facility 100 contain less than about 3, most preferably less than about 2, mass percent free fatty acid. Where esterification is sought, the molar ratio of alkanol to free fatty acid is generally between about 0:5:1 to 20:1, and preferably between about 0.9:1 to 10:1, and most preferably between about 3:1 to 9:1.

[0031] In one preferred embodiment where the feed contains free fatty acids, the oil phase from the acid treatment section of facility 100 contains at least about 0.5, say between about 0.5 and 2 or 3, mass percent free fatty acid. This free fatty acid serves to neutralize at least a portion of the base catalyst contained in a spent glycerin stream produced in the transesterification and base pretreatment sections of facility 100. Preferably, the molar ratio of free fatty acid in the oil phase from the acid treatment to mole of base in the glycerin phase introduced into base reactor 134 as discussed below will be at least about 0.3:1, often at least about 0.7:1 up to about 1:1. The use of ratios of free fatty acid to base catalyst of greater than 1:1 can adversely affect the performance of the base pretreatment.

[0032] The acid catalyst can be heterogeneous or homogeneous. Where heterogeneous, it may be a solid or a highly dispersed second liquid phase. As shown, liquid catalyst is provided via line 114 to acid treatment reactor 106. Any suitable acid catalyst (Bronsted acid or Lewis acid) for the esterification of free fatty acids can be used including homogeneous and heterogeneous catalysts. The preferred acid catalysts are mineral acids such as hydrochloric acid, sulfurous acid, sulfuric acid, phosphoric acid, and phosphorous acid. However other strong acids including organic and inorganic acids can be used. Examples of strong organic acids include alkyl sulfonic acids such as methylsulfonic acid; alkylbenzene sulfonic acids such as toluene sulfonic acid; naphthalenesulfonic acid; and trichloroacetic acid. Solid acid catalysts include NAFION® resins. Sulfuric acid and phosphoric acid are preferred due to non-volatility and low cost with sulfuric acid being most often used due to its availability and strong acidity. Sulfuric
acid may be provided in any suitable grade including, but not limited to highly concentrated, e.g., 98 percent, sulfuric acid, or in concentrated aqueous solutions, e.g., at least 30 percent, sulfuric acid. For the purposes of discussion in connection with facility 100, sulfuric acid is used as the acid.

[0033] The amount of acid catalyst provided can vary over a wide range. Typically the catalyst is provided in a catalytically effective amount of at least about 0.1 mass percent based upon the feed. Where soaps are present, the amount of acid should be sufficient to convert them to free fatty acids. Often the acid is present in an amount of at least about 0.2 to 5, say, 0.25 to 2, mass percent based upon the feed above that required to convert any soaps to free fatty acids.

[0034] The residence time for the acid treatment will depend upon the amounts of phospholipids and free fatty acid present, the conversion sought, the type and amount of catalyst used, the reactivity and amount of alkanol as well as the temperature of the process, and the type of reactor and extent of mixing. Residence times thus can range from less than 1 minute to over 1000 minutes. The residence times frequently are in the range of about 5 minutes to 120 minutes, preferably in the range of about 10 minutes to 90 minutes.

[0035] Acid treatment temperatures are generally between about 30°C and 200°C. High temperatures are often unnecessary to achieve high conversions and thus temperatures in the range of about 30°C or 40°C to 150°C, and sometimes, 60°C or 85°C to 120°C, provide sufficient conversions of fatty acids and phospholipids with relatively short residence times. Preferred esterification temperatures are below about 90°C, more preferably below about 85°C, to attenuate the reaction rate of water with ester. The reaction pressure can be any suitable pressure, e.g., from about 10 to 5000, preferably from about 90 to 1000, kPa absolute.

[0036] During the acid treatment in reactor 106 some conversion of glycerides to esters may occur. If no base catalyzed transesterification is to be used, then the sought conversion should be relatively high, e.g., at least about 90 mass percent. Where only a partial conversion of glycerides to esters is desired, the esters, triglycerides, diglycerides and monoglycerides essentially remain in the oil phase. Some glycerin will be produced as a result of the transesterification of the glycerides in the feed. The extent of such conversion is not critical but does result in lesser requirements of alkanol and catalyst in the transesterification section per unit of biodiesel produced as well as enabling increased
performance such as rate of conversion and extent of conversion to be obtained. Generally up to about 20 mass percent, say, between about 0.1 to 15, and sometimes between 5 to 10, mass percent of the glyceride-containing feed is transesterified during acid esterification.

[0037] The acid treatment reaction product from reactor 106 is passed via line 108 to phase separator 110. Phase separator 110 is optional depending upon whether or not two phases exist. In some instances, an oil layer containing glycerides and fatty ester and a water-containing layer form. The water-containing layer can contain more polar components such as glycerin, water-soluble catalyst, alkanol, and water-soluble phosphorus compounds. As shown, a neutralized spent glycerin stream from the base pretreatment section is provided via line 170A and contacted with the acid treatment product. The spent glycerin aids in the extraction of water and water-soluble phosphorus compounds. Additionally, the glycerin assists in making the phase separation. In this embodiment, the amount of glycerin added can vary widely. As relatively small amounts of water are produced during the acid esterification of free fatty acids, beneficial results can be achieved with relatively little spent glycerin being added. Often the spent glycerin added is less than about 20, preferably between about 0.5 and 10, mass percent of the stream from acid treatment reactor 106.

[0038] Phase separator 110 may be of any suitable design including a decanter, a phase separation facilitated decanter that contains coalescing sites, and a centrifuge. The lower, water-containing fraction exits separator 110 via line 112. This fraction contains some alkanol, water, water-soluble catalyst and water-soluble phosphorus compounds.

[0039] The oil fraction of separator 110 contains virtually no sulfuric acid, often some alkanol, relatively little water, unreacted free fatty acids, if any, fatty ester and glycerides. The fraction is passed via line 118 from separator 110 to fractionation column 120 to provide an overhead fraction containing alkanol and a bottoms stream containing oil. The overhead from column 120 can be recycled to acid treatment reactor 106 via line 122. Make up alkanol is provided via line 124.

[0040] The fractionation column may be of any suitable design including a flash column, stripping column, falling film evaporator, or trayed or packed column. If desired, more than one fractionation column can be used with one effecting separation of water from alkanol. Similarly a side draw 116 may be taken from fractionation column 120 for the removal of water, and fractionation column 120 may be a divided wall column to
enhance such separation. In an embodiment, a substantial portion of the water is removed by the phase separation in phase separator 110, and fractionation column 120 does not separately recover water. Water will be contained in both the overhead and bottoms stream from column 120. However, the relatively small amount of water in the overhead can be recycled with alkanol via line 122 to reactor 106 without undue adverse effect. Water contained in the bottoms passes to the base pretreatment section and is removed from the oil phase therein.

[0041] In another embodiment, only a portion of the alkanol is removed by fractionation in column 120. The alkanol remaining in the oil phase is passed to the base pretreatment section. In the base pretreatment section described later alkanol can be reacted with glyceride to form esters and can be recovered in the spent glycerin phase for recycle to the acid treatment section. Thus, the capital and operating costs for fractionation column 120 can be reduced. Often the bottoms stream from fractionation column 120 contains between about 0.1 to 10, say, between about 0.5 and 5, e.g., 0.5 to 2, mass percent alkanol.

[0042] While shown as processing the oil phase from separator 110, fractionation column 120 may be positioned between acid treatment reactor 106 and separator 110 and serve to recover alkanol from the acid treatment product exiting reactor 106. Alternatively the alkanol can be left in the oil and the oil feed to the pretreatment section and the portion of alkanol lost to the glycerin purge from the first pretreatment decanter can be stripped to recover the alkanol.

[0043] Numerous options exist for use of the oil phase from the acid treatment. If it contains little phospholipids and free fatty acids, preferably less than 0.1, more preferably less than 0.05, mass percent of each based on the oil phase, it can be directly passed to the transesterification component of the facility, i.e., to line 200. Alternatively, the oil phase can be passed to the base pretreatment component.

**Pretreatment by Base**

[0044] The base pretreatment uses glycerin produced in facility 100 to treat feed. The base pretreatment serves to recover alkanol contained in the glycerin phase from the transesterification section. Hence, the spent glycerin from the base pretreatment section may contain relatively little alkanol. Base pretreatment also serves to partially convert glycerides in the feed to fatty acid esters and mono- and di-glycerides. Thus, the amount of
alkanol required to transesterify the pretreated feed will be less than had no base pretreatment occurred. Base pretreatment can also serve to remove phospholipids as glycerin-soluble components. Base pretreatment further removes free fatty acids from the glyceride-containing feed by saponification to glycerin-soluble soaps.

[0045] A glyceride-containing feed stream is provided by line 132 to base reactor 134. If desired, the glyceride-containing feedstock can be first introduced in line 132. The feed stream may comprise a fresh glyceride-containing feed. Alternatively or in addition, the feed stream may comprise the oil phase from the acid treatment provided via lines 126 and 130. To base reactor 134 is also provided a glycerin and base catalyst-containing stream via line 142 which will be further discussed below. Preferably a non-acidic inerting gas such as nitrogen and hydrocarbon gas such as methane is used during base pretreatment.

[0046] In base reactor 134, free fatty acids contained in the feed stream are reacted with base catalyst to form soaps. If the free fatty acid content of the feed stream requires more than the amount of base catalyst introduced via line 142 for the desired degree of saponification, additional base can be added via line 133. The additional base may be the same or different from that comprising the catalyst, and may be one or more of alkali metal hydroxides or alkoxides and alkaline earth metal hydroxides, oxides or alkoxides, including by way of examples and not in limitation, sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide, calcium hydroxide, calcium oxide and calcium methoxide.

[0047] To the extent that phospholipids are present in the feed stream to base reactor 134, at least a portion is chemically reacted, e.g., by a hydration or by a salt formation, to provide chemical compounds preferentially soluble in glycerin.

[0048] Base reactor 134 is maintained under base reaction conditions, which for free fatty acid-containing feed streams is that sufficient to react basic catalyst and free fatty acids to soaps and water, and for phospholipids-containing feed streams is that sufficient to react basic catalyst and phospholipids to chemical compounds preferentially soluble in a glycerin phase. Typical base reaction conditions include a temperature of at least about 10°C, say, 35°C to 150°C, and most frequently between about 40°C and 80°C. Pressure is not critical and subatmospheric, atmospheric and super atmospheric pressures may be used, e.g., between about 1 and 5000, preferably from about 90 to 1000, kPa absolute. The
residence time is sufficient to provide the sought degree of saponification of fatty free acids and reaction of phospholipids. The residence time in base reactor 134 may range from about 1 minute to 10 hours.

[0049] Base reactor 134 may be of any suitable design. Reactor 134 may be a vessel or a length of pipe. But preferably other types of vessels are used such as mechanical and sonically agitated reactors, and reactors with static mixing such as reactors containing contact structures such as trays, packing, baffles, orifices, venturi nozzles, tortuous flow path, and other impingement structures. Suitable reactors include those providing high intensity mixing, including high shear.

[0050] The base reaction product from reactor 134 contains glycerin, glycerides, soaps, water, reacted phospholipids and often fatty acid ester and is passed via line 136 to separator 128. Separator 128 serves to separate the less dense oil layer from the more dense glycerin layer. The soaps and reacted phospholipids preferentially pass to the glycerin layer as does most of the water. The oil layer preferably contains less than about 0.5 mass percent soaps and less than about 500, preferably less than about 300, ppm-m phosphorus (calculated as elemental phosphorus). However if the feedstock oil has higher levels of free fatty acids and additional base is added through line 133 the additional soaps formed will preferentially be removed from the system through line 137 and it will contain higher levels of soaps. Phase separator 128 may be of any suitable design including a decanter, a phase separation facilitated decanter that contains coalescing sites, and, if needed, a centrifuge.

[0051] The glycerin phase is withdrawn from separator 128 via line 137 and may be sent to glycerin recovery or another application. If the glycerin layer contains significant amounts of soaps, it may be desirable to recycle the soaps to acid treatment reactor 106 for conversion to fatty esters. As shown, a portion or all of the glycerin phase may be passed via line 170 to acidification reactor 172 where soaps are converted to free fatty acids. At least a portion of this glycerin phase is passed via line 170A to provide the glycerin to assist in the separation of water, water-soluble catalyst (or salts thereof) and phosphorus-containing species from the acid treatment product in phase separator 110. The glycerin-containing phase from separator 110 is passed via line 112 to line 170. Also as shown, a portion of the glycerin phase in line 170 is recycled to reactor 134 via line 170B. The recycle can serve several purposes. For instance, hydrated phospholipids are
returned to reactor 134 where they may undergo transesterification to recover additional fatty acid ester. Also, any base contained in the recycled glycerin stream is available for saponification of free fatty acids.

[0052] Unless acid contained in the acid treatment effluent of line 108 is neutralized prior to being passed to separator 110, the glycerin-containing phase from separator 110 will contain water-soluble acid which can be used as acid for acidification reactor 172. Acid can also be provided via line 174. Acidification reactor 172 may be one or more vessels of any suitable design including a length of pipe and other types of vessels such as mechanical and sonically agitated reactors, and reactors with static mixing such as reactors containing contact structures such as trays, packing, baffles, orifices, venturi nozzles, tortuous flow path, and other impingement structures. Suitable reactors include those providing high intensity mixing, including high shear. The acidification conditions usually encompass a temperature in the range of about 20°C to 150°C, a pressure from about 1 to 5000, preferably 90 to 1000, kPa absolute, and a residence time of from about 1 second to 5 hours. Suitable acids include mineral acids and organic acids, but typically a readily available acid such as sulfuric or phosphoric acid is used. The amount of acid is usually sufficient to convert substantially all the soaps to free fatty acid. The use of excess acid is not deleterious to the formation of the free fatty acids, but can entail additional expense. Accordingly the molar ratio of acidifying acid function to soaps is in the range of about 1:1 to 1.5:1. Generally the pH of the glycerin stream is less than about 6, say, between about 3 and 5. The acidity of the glycerin stream is determined by diluting the glycerin stream to 50 volume percent water and measuring the pH.

[0053] The glycerin stream from acidification reactor 172 is passed via line 176 to contact vessel 178 into which glyceride-containing feed is provided via line 102. In contact vessel 178 the glycerin stream is contacted with fresh feed which serves to extract a portion of the alkanol from the glycerin phase. The contact with the glycerin also serves to remove water from the feed. Removal of water assists in the esterification of free fatty acids in acid treatment reactor 106 as the esterification is an equilibrium-limited reaction affected by water concentration.

[0054] Contact vessel 178 may be of any suitable design including a length of pipe and other types of vessels such as mechanical and sonically agitated reactors, and reactors with static mixing such as reactors containing contact structures such as trays, packing,
baffles, orifices, venturi nozzles, tortuous flow path, and other impingement structures. Suitable reactors include those providing high intensity mixing, including high shear. The contact conditions usually encompass a temperature in the range of about 20°C to 150°C, a pressure from about 1 to 5000 kPa absolute, and a residence time of from about 1 second to 5 hours. Often at least about 50 mass percent of the alkanol in the glycerin stream passes to the oil phase as do essentially all of the free fatty acids. The amount of alkanol recovered from the glycerin will depend upon the alkanol content of the glycerin, the ratio of glycerin to fresh feed, and the contacting conditions. Frequently the mass ratio of glycerin to oil is in the range of between about 1:5 to 1:20, say 1:8 to 1:15, and at least about 30, and sometimes between about 50 and 99, mass percent of the alkanol in the glycerin phase passes to the oil phase.

[0055] The fluid mixture from contact vessel 178 is passed via line 180 to phase separator 182. In phase separator 182, a glyceride and free fatty acid oil layer is produced that is passed via line 184 to acid treatment reactor 106. A glycerin-containing layer is discharged via line 186. Separator 182 may be of any suitable design including a decanter, a phase separation facilitated decanter that contains coalescing sites, and, if necessary, a centrifuge. Contact vessel 178 and decanter 182 may be a single vessel, including but not limited to, a countercurrent extraction column.

[0056] If the acid treatment product from acid treatment reactor 106 has a sufficiently low free fatty acid content and low phospholipids content, another option is to eliminate separator 110 and fractionation column 120 and provide the acid treatment product in line 108 directly to separator 128 or base reactor 134.

[0057] Returning to separator 128, the oil phase is withdrawn and passed via line 138 to second pretreatment reactor 139. Second pretreatment reactor 139 and third pretreatment reactor 148 are adapted to recover alkanol contained in the glycerin from the transesterification component of facility 100 through reaction, e.g., transesterification and extraction into the glyceride-containing phase. A base transesterification process is used in these pretreatment reactors. While two reactors are shown, the number of reactors will depend upon the sought consumption of the alkanol as well as the efficiency of the reactors. Hence one, two, or three or more pretreatment reactors may be used. Also, the pretreatment reactor can comprise a number of stages in a single vessel which could be a countercurrent contact vessel. Advantageously, the feed stream to the alkanol consumption
pretreatment reactors is relatively free from free fatty acids so as to prevent undue consumption of the base catalyst. Typically the pretreatment reactors provide a glycerin stream from which most of the alkanol has been removed. Often, the alkanol content of the glycerin discharged from base reactor 134 is less than about 5, and preferably less than about 2, mass percent.

[0058] In an alternative mode of operation, a significant portion of the alkanol is contained in line 126 (or line 108 if separator 110 and distillation column 120 are not used) and passed to separator 128. The concentration of alkanol in the glycerin-containing stream in line 170 may be higher than 5 mass percent, and alkanol is recovered by partitioning to the glyceride-containing feed in contact vessel 178. The alkanol content of the glycerin may be sufficiently low that no distillation is required to recover alkanol yet the overall process to make biodiesel can still exhibit high efficiencies.

[0059] Second pretreatment reactor 139 also receives the glycerin phase from third pretreatment reactor 148. This glycerin phase contains glycerin, base catalyst, and alkanol. Second pretreatment reactor 139 is maintained under base transesterification conditions including the presence of base catalyst provided by the glycerin phase feed and elevated temperatures, often between about 30°C and 220°C, preferably between about 30°C and 80°C to provide a second pretreatment product. The pressure is typically in the range of between about 90 to 1000 kPa (absolute) although higher and lower pressures can be used.

The reactor is typically batch, semi-batch, plug flow or continuous flow tank. Preferably other types of vessels are used such as mechanical and sonically agitated reactors, and reactors with static mixing such as reactors containing contact structures such as trays, packing, baffles, orifices, venturi nozzles, tortuous flow path, and other impingement structures. Suitable reactors include those providing high intensity mixing, including high shear. However, depending upon the presence of soaps and phospholipids, care needs to be taken so as not to generate a product that cannot be readily separated by phase separation. The residence time will depend upon the desired degree of conversion of the contained alkanol, the ratio of alkanol to glyceride, reaction temperature, the degree of agitation and the like, and is often in the range of about 0.1 to 20, say, 0.5 to 10, hours.

[0060] The second pretreatment product contains glycerides, fatty esters, base catalyst and glycerin, and it has a reduced concentration of alkanol. The second pretreatment product is passed from second pretreatment reactor 139 via line 141 to
separator 140. Separator 140 may be of any suitable design including a decanter, a phase separation facilitated decanter that contains coalescing sites, and, optionally, a centrifuge. The lower, glycerin-containing phase from separator 140 contains relatively little alkanol, preferably less than about 10 mass percent, and contains base catalyst, and is passed via line 142 to base reactor 134 where catalyst reacts with free fatty acids to form soaps which can then be removed from the glyceride-containing feed.

[0061] As depicted, line 142 is provided with holding tank 142A. Holding tank 142A can serve as a reservoir and enables the rate that glycerin, which contains base, is provided to base reactor 134, to be varied with changes in free fatty acid content of the acid treatment product. It also can permit additional reaction of glycerides with alkanol contained in the glycerin phase to occur prior to introduction into base reactor 134 where catalyst is consumed by conversion of free fatty acids to soaps.

[0062] The upper oil phase is removed from separator 140 via line 144 and is passed to line 146 which also receives the glycerin co-product from transesterification from line 146. The combined streams are passed to third pretreatment reactor 148 via line 146. This stream contains glycerin, alkanol, base catalyst, and usually some water and soaps.

[0063] Third pretreatment reactor 148 is maintained under base transesterification conditions including the presence of base catalyst provided by the glycerin-containing feed and elevated temperatures, often between about 30°C and 220°C, preferably between about 30°C and 80°C to provide a third pretreatment product. Base catalyst in the transesterification component tends to partition to the glycerin phase and often adequate catalyst is provided for the base pretreatment section. In some instances, however, it may be desired to add additional base catalyst to third pretreatment reactor 148 or any preceding base pretreatment reactor. The pressure is typically in the range of between about 90 to 1000 kPa (absolute) although higher and lower pressures can be used. The reactor is typically batch, semi-batch, plug flow or continuous flow tank with some agitation or mixing. The preferred types of vessels are mechanical and sonically agitated reactors, and reactors with static mixing such as reactors containing contact structures such as trays, packing, baffles, orifices, venturi nozzles, tortuous flow path, and other impingement structures. Suitable reactors include those providing high intensity mixing, including high shear. The residence time will depend upon the desired degree of conversion, the ratio of
alkanol to glyceride, reaction temperature, the degree of agitation and the like, and is often in the range of about 0.1 to 20, say, 0.5 to 10, hours.

Typically the transesterification in third pretreatment reactor 148 recovers through transesterification and extraction to the glyceride-containing phase at least about 20, preferably at least about 30, and more preferably at least about 50, mass percent of the alkanol fed to the reactor. Any unreacted alkanol in the oil phase will be carried with the oil phase to the transesterification component of facility 100. Often the total amount of alkanol recovered from the glycerin-coproduct from transesterification using all pretreatment stages is at least about 50, and sometimes at least about 80, mass percent.

The third pretreatment product passes from third pretreatment reactor 148 through line 150 to separator 152. Separator 152 may be of any suitable design including a decanter, a phase separation facilitated decanter that contains coalescing sites, and, optionally, a centrifuge. Separator 152 serves to separate an oil phase containing glycerides, esters and alkanol and some catalyst, from a glycerin-containing phase containing glycerin, reduced concentration of alkanol, and catalyst. The glycerin-containing phase frequently contains less than about 15 mass percent alkanol. The glycerin-containing phase from separator 152 is passed via line 154 to second pretreatment reactor 139.

As shown, the oil phase from separator 152 passes via line 156 to chiller 158. Facility 100 includes chiller 158 to remove high molecular weight glycerides, waxes and esters that are insoluble at the chiller temperature. Chiller 158 is maintained at a temperature sufficient to solidify high molecular weight and other components that lead to an increase in gel point temperature. Typically this temperature is between about 0°C and 20°C. In some instances, cooling will tend to remove monoglycerides and diglycerides. Cooling below the desired temperature and then warming to a temperature to liquefy the mono- and di-glycerides while still maintaining a solid wax, can minimize loss of components that can be converted to biodiesel. The chilled oil phase is then passed via line 160 to centrifuge 162 to remove higher density components including solids and any remaining glycerin phase. The higher density fraction is discharged via line 164. Rather than using a centrifuge, the solids can be filtered from the glyceride-containing stream. Filter aids can be used if desired.
Chiller 158 is optional, and a chiller may also be used elsewhere in facility 100 to remove waxes. The term waxes as used herein is used to describe solids that are observed to drop from solution upon cooling of the oil phase. For instance, a chiller may be used to treat fresh feed in line 102 or can be used to treat biodiesel product from the refining component. It may be advantageous to use the chiller in combination with a separation device such as a filter or centrifuge to more readily remove the waxes.

If desired all or a portion of the composition in line 166 may be withdrawn via line 168 as an intermediate product for storage or sale as a feedstock for transesterification. Line 168 also provides the feed for the transesterification component of facility 100 by introducing the producer composition into line 200.

Transesterification

Line 200 provides glyceride-containing feed to first transesterification reactor 202. Line 200 can also supply additional glyceride-containing feed. Preferably the additional feed is relative free of free fatty acids and phospholipids such as refined oils sourced from rape seed, soybean, cotton seed, safflower seed, castor bean, olive, coconut, palm, corn, canola, fats and oils from animals, including from rendering plants and fish oils.

Alkanol for the transesterification is supplied to first transesterification reactor 202 via line 206. The alkanol is preferably lower alkanol, preferably methanol, ethanol or isopropanol with methanol being the most preferred. The alkanol may be the same or different from the alkanol provided to acid treatment reactor 106 via line 124. Although line 206 is depicted as introducing alkanol into line 200, it is also contemplated that alkanol can be added directly to reactor 202 at one or more points. Generally the total alkanol (line 206 and from the producer composition of line 166) is in excess of that required to cause the sought degree of transesterification in reactor 202. Preferably, the amount of alkanol is from about 101 to 500, more preferably, from about 110 to 250, mass percent of that required for the sought degree of transesterification in reactor 202. In facility 100 three reactors are depicted as being used. One reactor may be used, but since the reaction is equilibrium limited, most often at least two and preferably three reactors are used. Often, where more than one reactor is used, at least about 60, preferably between about 70 and 96, percent of the glycerides in the feed are reacted in first transesterification reactor 202. It is possible to provide all the alkanol required for transesterification to first
transesterification reactor 202, or a portion of the alkanol can be provided to each of the transesterification reactors.

[0071] The base catalyst is shown as being introduced via line 204 to first transesterification reactor 202. The amount of catalyst used is that which provides a desired reaction rate to achieve the sought degree of transesterification in first transesterification reactor 202. Preferably, catalyst is provided to each of the transesterification reactors since base catalyst preferentially partitions to the glycerin phase and is removed with phase separation of the glycerin after each transesterification reactor. The amount of catalyst used will be in excess of that required to react with the amount of free fatty acid contained in the feed oil, which due to the pretreatment, will be relatively little. The base catalyst may be an alkali or alkaline earth metal hydroxide or alkali or alkaline earth metal alkoxide, especially an alkoxide corresponding to the lower alkanol reactant. Preferred alkali metals are sodium and potassium. When the base is added as a hydroxide, it may react with the lower alkanol to form an alkoxide with the generation of water which in turn results in the formation of free fatty acid. Another type of catalyst is an alkali metal or alkaline earth metal glycerate. This catalyst converts to the corresponding alkoxide of the alkanol reactant in the reaction menstruum. Alternatively, the catalyst may be a heterogeneous base catalyst. Catalyst may need to be separately provided to the base pretreatment reactors if the base catalyst, e.g., a heterogeneous or oil soluble catalyst, is not carried with the co-product glycerin in the transesterification component to the base pretreatment reactors. However, homogeneous catalysts that have solubility in glycerin are preferred where the pretreatment component is used since the catalyst serves as at least a portion of the base used therein. The exact form of the catalyst is not critical to the understanding and practice of this invention. For the purposes of the following discussion, homogenous base catalyst is used. Preferably a non-acidic inerting gas such as nitrogen and hydrocarbon gas such as methane is used during base transesterification.

[0072] Often the transesterification is at a temperature between about 30°C and 220°C, preferably between about 30°C and 80°C. The pressure is preferably sufficient to maintain a liquid phase reaction menstruum and typically is in the range of between about 90 to 1000 kPa (absolute) although higher and lower pressures can be used. First transesterification reactor 202 is typically batch, semi-batch, plug flow or continuous flow
tank with some agitation or mixing. Preferably the reactors are mechanical and sonically agitated reactors. Reactors with static mixing such as reactors containing contact structures such as trays, packing, baffles, orifices, venturi nozzles, tortuous flow path, and other impingement structures can be used. Suitable reactors include those providing high intensity mixing, including high shear. As stated above, one of the advantages of the processes of this invention is that the producer compositions do not require an induction period for transesterification to initiate. Accordingly plug flow reactors have enhanced viability. The residence time will depend upon the desired degree of conversion, the ratio of alkanol to glyceride, reaction temperature, the base catalyst concentration, the degree of agitation and the like, and is often in the range of about 0.02 to 20, say, 0.1 to 10, hours.

The partially transesterified effluent from reactor 202 is passed via line 208 to phase separator 210. Phase separator 210 may be of any suitable design including a decanter, a phase separation facilitated decanter that contains coalescing sites, and, optionally, a centrifuge. A glycerin-containing bottoms phase is provided in the separator and is removed via line 212 and is passed to glycerin header 214. As depicted, this stream is used as a portion of the glycerin for the pretreatment component of facility 100. This glycerin phase also contains any soaps made in reactor 202 and a portion of the catalyst. The soaps can be recovered from this stream in acidifying reactor 172 as discussed above. The lighter phase contains alkyl esters and unreacted glycerides and is passed via line 216 to second transesterification reactor 218. A rag layer may form in separator 210. The rag layer may contain unreacted glycerides, alkyl esters, alkanol, soaps, catalyst and glycerin. An advantage of the process set forth in Figure 1 is that withdrawing the rag layer with the glycerin phase does not result in a loss of glycerides, alkyl esters, alkanol, and catalyst since the glycerin phase is passed to the pretreatment component of facility 100.

Reactor 218 may be of any suitable design and may be similar to or different than reactor 202. As shown, additional alkanol is provided via line 206A, and additional catalyst is provided via line 204A. Preferably the transesterification conditions in reactor 218 are sufficient to react at least about 90, more preferably at least about 95, and sometimes at least about 97 to 99.9, mass percent of the glycerides in the feed to the transesterification. The transesterification in reactor 218 is typically operated under conditions within the parameters set forth for reactor 202 although the conditions may be the same or different. The residence time will depend upon the desired degree of
conversion, the ratio of alkanol to glyceride, reaction temperature, the degree of agitation and the like, and is often in the range of about 0.02 to 20, say, 0.1 to 10, hours.

[0075] The effluent from second transesterification reactor 218 is passed via line 220 to phase separator 222 which may be of any suitable design and may be the same as or different from the design of separator 210. A heavier, glycerin-containing phase is withdrawn via line 224 and passed to glycerin header 214. A lighter phase containing crude biodiesel is withdrawn from separator 222 via line 226.

[0076] As depicted, third transesterification reactor 228 is used and the crude biodiesel in line 226 is passed to this reactor. The transesterification conditions in reactor 228 are sufficient to provide essentially complete conversion, at least about 97 or 98 to 99.9, mass percent of the glycerides in the feed converted to alkyl ester. As shown, additional alkanol is provided via line 206B, and additional catalyst is provided via line 204B. The transesterification in reactor 228 is typically operated under conditions within the parameters set forth for reactor 202 although the conditions may be the same or different. The residence time will depend upon the desired degree of conversion. The reactor may be of the type described for reactor 202. The residence time will depend upon the desired degree of conversion, the ratio of alkanol to glyceride, reaction temperature, the degree of agitation and the like, and is often in the range of about 0.02 to 20, say, 0.1 to 10, hours. Advantageously, the transesterification product from third transesterification reactor 228 contains less than about 1, preferably less than about 0.8, and most preferably less than 0.5, mass percent soaps based upon the total mass of alkyl esters and soaps. The lighter phase also contains alkanol. In reactor 228 the reaction proceeds quickly to completion by the addition of additional alkanol and catalyst, and can be conveniently accomplished by a plug flow reactor.

[0077] The overall molar ratio of alkanol to glycerides in the feed to the reactors in the transesterification component, i.e., alkanol provided by lines 206, 206A and 206B, can vary over a wide range. Since transesterification is an equilibrium-limited reaction, the driving force toward the alkyl ester and the conversion of glycerides will be dependent upon the molar ratio of alkanol equivalents to glycerides. Alkanol equivalents are alkanol and alkyl group of the alkyl esters in the feed to the transesterification component. On the basis of transesterifiable substituents in the feed to the transesterification component, the mole ratio of alkanol equivalents to glyceride in the feed to the pretreatment component is
frequently between about 3:1 to 15:1, say 4:1 to 9:1. Advantageously, the pretreatment processes of this invention permit the reuse of alkanol partitioned to the co-product glycerin without intermediate vaporization. Often the amount of total catalyst provided based upon the mass of feed to the first transesterification reactor, i.e., the catalyst provided by lines 204, 204A and 204B, is between about 0.3 and 1 mass percent (calculated on the mass of sodium methoxide).

[0078] The effluent from third transesterification reactor 228 is passed via line 230 to phase separator 232 which may be of any suitable design and may be the same as or different from the design of separator 210. A heavier, glycerin-containing phase is withdrawn via line 234 and passed to glycerin header 214. A lighter phase containing crude biodiesel is withdrawn from separator 232 via line 236. Alternatively, separator 232 can be eliminated provided that in second transesterification reactor 218, the conversion of the glycerides in the feed is at least about 90, preferably 92 to 96 or 98, percent. In some instances, the effluent from reactor 228 may be a single phase containing relatively little glycerin. In some instances it may be advantageous to use a centrifuge to separate the glycerin phase from the oil phase following third transesterification reactor 228.

[0079] Facility 100 contains an optional alkanol replacement reactor 238. The alkanol replacement reactor serves to transesterify the alkyl ester with a different alkanol. For purposes of transesterification in reactors 202, 218 and 228, an alkanol such as methanol provides not only attractive reaction rates but also an effluent that is more easily separated than, say, a reaction effluent where ethanol is the alkanol. In some instances it may be desired to provide a biodiesel that contains fatty esters in which the alkyl group of the fatty ester is branched in order to reduce cloud and gel points. The transesterification between, say, a fatty acid methyl ester, and higher molecular weight alkanol results in methanol, rather than glycerin, being formed, and often is more readily accomplished than the transesterification of glyceride with that higher alkanol. The higher alkanols include those having 2 to 8 or more carbons, and are preferably branched primary and secondary alkanols although tertiary alkanols may find application but generally are less reactive. Examples of higher alkanols include propanol, isopropanol, isobutanol, 2,2-dimethylbutan-1-ol, 2,3-dimethylbutan-1-ol, 2-pentanol, and the like. Other alkanols include benzyl alcohol and 2 ethylhexanol.
Where an alkanol replacement operation is desired, it may be located at various points in the process. For instance, the replacement alkanol may be provided via line 206B to reactor 228, or, as shown, it can follow reactor 228. In either case, alkanol replacement transesterification can take advantage of catalyst contained in the transesterification medium. Alternatively, alkanol replacement may be effected on a biodiesel product by adding catalyst. Thus, it can be located elsewhere in the refining component of facility 100 including, but not limited to, treating biodiesel in line 352.

The amount of higher alkanol provided via line 240 to alkanol replacement reactor 238 can vary over a wide range. Typically the molar ratio of higher alkanol to alkyl ester being fed to reactor 238 is less than 0.5:1, e.g., from about 1:100 to 1:5. Often the alkanol replacement transesterification is at a temperature between about 30°C and 220°C, preferably between about 30°C and 80°C. The pressure is preferably sufficient to maintain a liquid phase reaction menstruum and typically is in the range of between about 90 to 1000 kPa (absolute) although higher and lower pressures can be used. Alkanol replacement reactor 238 can be batch, semi-batch, plug flow or continuous flow tank with some agitation or mixing, e.g., mechanically stirred, ultrasonic, static mixer containing contact surfaces, e.g., trays, packing, baffles, orifices, venturi nozzles, tortuous flow path, or other impingement structures. High intensity mixing reactors, including high shear reactors, may also be used. Preferred reactors are those in which the alkanol being replaced is continuously removed. For instance, a reactive distillation reactor can be used to continuously remove displaced methanol from a transesterification of methyl ester and isopropanol. As depicted, reactor 238 is a reactive distillation unit and lower alkanol is withdrawn via line 330A and passed to the transesterification reactors. Make-up alkanol is provided via line 332.

Where the alkanol replacement reactor is a batch reactor, the vapor fractionation of methanol can continue until completion. Thus, the replacement reaction can be driven to either essentially complete conversion of the higher alkanol or complete conversion of the methyl ester to the higher alkanol ester (depending upon whether the higher alkanol is provided below or at or above the stoichiometric amount required for complete conversion). With continuous reactors, having unreacted methanol and higher alkanol in the alkanol replacement product is likely. For purposes of this discussion, a continuous alkanol replacement reactor is used.
Where the base catalyst has been removed from the fatty acid ester of the lower alkanol, for instance, if the alkanol replacement were to be conducted on a refined or partially refined biodiesel, catalyst is provided. Suitable catalyst includes base catalyst such as is used for transesterification. Since a single liquid phase exists during the alkanol replacement unlike transesterification where a glycerin layer forms, heterogeneous catalysts and homogeneous catalysts having limited solubility in the reaction menstruum can be used. Solid catalysts are preferred to minimize or eliminate post treatment of the alkanol replacement product, but good contact with catalyst is desirable to timely achieve sought conversion. Homogeneous transesterification catalysts such as titanium tetra-isopropoxide are also advantageous as they are readily removed.

The residence time will depend upon the desired degree of conversion, the ratio of higher alkanol to alkyl ester, reaction temperature, the degree of agitation and the like, and is often in the range of about 0.02 to 20, say, 0.1 to 10, hours. Preferably at least about 80, and sometimes at least about 90, mass percent of the higher alkanol is reacted.

Refining

A crude biodiesel is withdrawn from reactor 238 via line 300 and is passed to the refining component of facility 100. The crude biodiesel may be contacted with acid to neutralize any catalyst therein and then refined to remove alkanol, soaps, water and glycerin.

In a preferred process, an acid, preferably an organic acid, is provided via line 302 in an amount sufficient to substantially neutralize residual base catalyst contained in the crude biodiesel. While inorganic acids can be used, organic acids, particularly those less volatile than the alkanol, and acids that do not themselves or any potential reaction product formed in contact with the crude biodiesel, form azeotropes with the alkanol, facilitate processing and minimize the potential of contamination of recovered alkanol. Exemplary acids include acetic acid, oxalic acid, glycolic, lactic, free fatty acid and the like. Citric acid is particularly preferred due not only to its low volatility, but also due to its relatively non-toxic nature, and its beneficial presence as a stabilizer in biodiesel. Generally the amount of catalyst contained in the crude biodiesel is quite small as base catalyst preferentially partitions to the glycerin phase. Accordingly, little acid is required to neutralize sufficient catalyst to enable refining without risk of reversion of alkyl ester.
Often the amount of acid used is at least 0.95 times, sometimes between about 1 and 3 times, that required to neutralize the catalyst.

[0087] Crude biodiesel is passed via line 300 to an alkanol separation unit operation. As shown, a two stage separation unit is used. A single stage separator can be used if desired. The crude biodiesel in line 300 is passed to first alkanol separator stage 304. Separator 304 is of any convenient design including a stripper, evaporator, wiped film evaporator, falling film evaporator, solid sorbent, and the like. Preferably the fractionation is by fast, vapor fractionation. Generally for a fast, vapor separation the residence time is less than about one minute, preferably less than about 30 seconds, and sometimes as little as 5 to 25 seconds. Preferably the vapor fractionation conditions comprise a maximum temperature of less than about 200°C, preferably less than about 150°C, and most preferably, when the lower alkanol is methanol, less than about 120°C. Depending upon the alkanol, the lower boiling fractionation may need to be conducted under subatmospheric pressure to maintain desired overhead and maximum temperatures. Where a falling film stripper is used, it may be a concurrent or countercurrent flow stripper. Concurrent strippers are preferred should there be a risk of undue vaporization of alkanol at the point of entry of the crude biodiesel. An inert gas such as nitrogen may be used to assist in removing the alkanol.

[0088] The fast fractionation may be effected by any suitable vapor fractionation technique including, but not limited to, distillation, stripping, wiped film evaporation, and falling film evaporation. Often the falling film evaporator has a tube length of at least about 1 meter, say, between about 1.5 and 5 meters, and an average tube diameter of between about 2 and 10 centimeters. Usually the vapor fractionation recovers at least about 70, preferably at least about 90, mass percent of the alkanol contained in the crude biodiesel. Any residual alkanol is substantially removed in any subsequent water washing of the crude biodiesel. Advantageously, the amount of alkanol contained in the spent water from the washing may be at a sufficiently low concentration that the water can be disposed without further treatment. However, from a process efficiency standpoint, alkanol can be recovered from the spent wash water for recycle to the transesterification reactors.

[0089] The lower boiling fraction containing the alkanol will contain a portion of any water contained in the crude biodiesel. Since the transesterification is conducted with little water being present, and a portion of the water is removed with the glycerin, the
concentration of water in this fraction can be sufficiently low that it can be recycled to the transesterification reactors. This lower boiling fraction often contains less than about 1, and more preferably less than about 0.5, mass percent water.

[0090] Alkanol is exhausted from first alkanol separator stage via line 306 and may be exhausted from the facility as a by-product, e.g., for burning or other suitable use, or can be recycled. Where no alkanol replacement reaction is used, the alkanol will be the lower alkanol for the transesterification and is recycled to the transesterification section. The bottoms stream from first alkanol separation stage 304 is passed via line 308 to second alkanol separation stage 314 for additional alkanol recovery. The design of second alkanol separation stage 314 may be similar to or different than that of first alkanol separation stage 304 and may be operated under the same or different conditions. Alkanol exits via line 316 and is combined with alkanol from line 306 and is passed to condenser 318. In the process of facility 100, the condensed alkanol will contain both the lower alkanol and the higher alkanol. Condensed alkanol is recycled to line 330 to alkanol replacement reactor 238.

Non-condensed gases exit condenser 318 via line 320. As shown, the alkanol separation operation is maintained under vacuum conditions and these gases are passed to liquid ring vacuum pump 322. The liquid for the liquid ring is provided via line 324 and exits via line 328. As the gases contain some alkanol, the liquid for the liquid ring vacuum pump will remove alkanol from the gases. The liquid may be water, in which case the water may need to be treated to remove alkanol. Alternative liquid streams can be used, including but not limited to glyceride-containing feed, biodiesel, and glycerin. Glyceride-containing feed is preferred as the liquid for the liquid ring vacuum pump since it can be passed to a transesterification reactor and alkanol contained therein used for the transesterification. Gas is removed from liquid ring vacuum pump 322 via line 326.

[0091] The amount of alkanol in the bottoms stream from the second alkanol separation stage contains less than 500 ppm-m, and preferably less than 200 ppm-m, and sometimes between about 5 and 100 ppm-m, alkanol.

[0092] The bottoms stream from the second alkanol separation stage exits via line 334. As shown, the bottoms stream is passed to separator 336 in which a glycerin-containing phase and a biodiesel-containing phase are separated. The presence of alkanol in the crude biodiesel enhances the solubility of glycerin therein. Upon removal of the alkanol, a separate glycerin-containing phase, which also contains soaps, tends to form...
during the alkanol separation operation. The glycerin fraction is removed from separator 336 via line 338 and can be combined with spent glycerin in line 186. The lighter, oil-containing phase is passed via line 340 to a water wash unit operation.

[0093] Line 340 serves as a reactor and mixer where strong acid is supplied. The amount of strong acid provided is sufficient to convert any soaps remaining to free fatty acids. Sufficient strong acid is used such that water used for washing the crude biodiesel is at a suitably low pH. The strong acid is supplied in admixture with a recycle stream in the wash operation as will be explained later. While line 340 serves as an in-line mixer, a separate vessel may be used for the acidification. Where a separate mixer is used, it may be of any convenient design, e.g., a mechanically or sonically agitated vessel, or static mixer containing static mixing devices such as trays, packing, baffles, orifices, venturi nozzles, tortuous flow path, or other impingement structure. In any event, sufficient mixing and residence time should be provided such that essentially all of the soaps are converted to free fatty acids. Often the temperature during the mixing is in the range of about 30°C to 220°C, preferably between about 60°C to 180°C, and for a residence time of between about 0.01 to 4, preferably 0.02 and 1, hours.

[0094] For purposes of discussion only and not in limitation, the water wash operation uses a two stage water wash. Water wash operation may be of any suitable design. Typically, the water wash operates with a recycling water loop, often with the water recycle being at least about 20, say between about 30 and 500, mass percent of the crude biodiesel being fed to the column. Normally washing is operated at a temperature between about 20°C and 120°C, preferably between about 35°C and 90°C. The amount of water provided to each wash vessel is sufficient to effect a sought removal of glycerin. Typically between about 20 and 200, preferably between about 25 and 100, mass parts of wash water are provided to each wash stage (including recycle) per 100 mass parts of crude biodiesel. Usually the free fatty acid is present in an amount less than about 5000, most frequently less than about 2500, parts per million by mass in the biodiesel product, and thus no need exists to remove free fatty acid to provide a biodiesel product meeting current commercial specifications. Preferably between about 1000 and 2500 ppm-m free fatty acid is contained in the biodiesel product to aid in lubricity.

[0095] The vessels used for the water washing may be of any suitable design including a pipe reactor, mechanically or sonically agitated tank, a vessel containing static
mixing devices such as trays, packing, baffles, orifices, venturi nozzles, tortuous flow path, or other impingement structure. Each stage needs to effect a phase separation of the oil phase from the water phase. Such a separation may be inherent in, for instance, a wash column where the water and oil phases are moving countercurrently, or a separate phase separator may be provided. It is understood that other washing operations can be used such as a one vessel washing operation, an acid wash followed by a neutral wash, and the like. As stated above, where significant amount of salts are present, it may be desired to have an alkaline wash followed by a neutral or acidic wash. The washing may be effected in one or more stages and in one or more vessels. A single vessel, such as a wash column can contain a plurality of stages. Where more than one vessel is used, the water, or a portion thereof may pass from one vessel to another. Depending upon the sequencing of the wash stages, the pH of the water may be changed between stages. Alternatively, the water from each stage can be separately handled and passed to the concentration. Typically the water to a wash stage is recycled. Hence, the water purged from the recycle is only a fraction of the water in the total stream being passed to the stage.

[0096] As shown, crude biodiesel is provided via line 340 to first wash stage 342. For purposes of discussion, wash stage 342 comprises an agitated vessel to provide desired contact between the oil and water phases and a decanter to effect separation. Typically, the agitated vessel provides a contact time of about 1 second and 10 minutes, say, 5 to 60 seconds. Crude biodiesel is contacted with acidic water from water loop 368. The washed biodiesel from first wash stage 342 is passed via line 344 to second wash stage 346 having a design similar to or different from that of stage 342. This biodiesel is contacted with water from water loop 364. In each stage the water, after contacting the biodiesel stream being processed, is returned to the respective loops. Acidic water is withdrawn from first wash stage 342 and recycled via line 368. Substantially neutral water is withdrawn from second wash stage 346 and recycled via line 364. Additional water is provided to line 364 via line 376 which will be described later.

[0097] As configured with separate water cycle loops, the pH of the water in second wash stage 346 may be neutral or less acidic than the water in first wash stage 342. Alternatively, either the first wash stage or the second water stage may be alkaline with the other acidic thus enabling the removal of soaps. Make-up water to line 368 is provided by line 366. A purge is taken from line 368 via line 372. The purge balances the amount of
water in the wash loops and is at a suitable rate to maintain desirably low concentrations of impurities such as alkanol and glycerin in the water used for the washing. The purge is usually at a rate of between about 1 and 50, say 5 and 20, mass percent per unit time of the recycle rate in the loop.

[0098] Line 370 provides strong acid to the water recycled via line 368 for combining with crude biodiesel in line 340 or being passed to first wash stage 342. Adequate strong acid aqueous solution is provided that the water in line 368 has a pH sufficiently low to convert the soaps to free fatty acids. The acid may be any suitable acid to achieve the sought pH such as hydrochloric acid, sulfuric acid, sulfonic acid, phosphoric acid, perchloric acid and nitric acid. Sulfuric acid is preferred due to cost and availability and it is a non-oxidizing acid. The amount of strong acid aqueous solution provided is typically in a substantial excess of that required to convert the soaps to free fatty acid and to neutralize any remaining catalyst. The excess of acid is often at least about 5, preferably at least about 10, say between about 10 and 1000 times that required. Consequently the feed to first wash stage 342 provides wash water in line 368 having a pH of up to about 6, preferably between about 4 and 5.

[0099] Returning to line 372, the purge water is passed to evaporator 374 which provides a lower boiling fraction and a higher boiling fraction. Depending upon the materials of construction of evaporator 374, the pH may be adjusted, e.g., by the addition of caustic via line 372A. If salts are reformed, the pH is preferably adjusted to a sufficiently alkaline level that undue foaming or emulsions are not formed in evaporator 374. If the pH for the water washing is such that soaps exist and are removed in the wash water, acidifying the wash water can result in free fatty acids being present. If so, they may form a separate phase in evaporator 374 and can be removed, e.g., by decanting the higher boiling fraction. While an evaporator may be used, it is also possible to use a packed or trayed distillation column with or without reflux. Generally the bottoms temperature of evaporator 374 is less than about 150°C, preferably between about 120°C and 150°C. The distillation may be at any suitable pressure. A membrane separation system may, alternatively or in combination, be used with evaporator 374 to effect the sought concentration of the spent water.

[00100] The lower boiling fraction contains water and some alkanol and is passed via line 376 to water wash loop 364. Fresh water is provided to line 376 by line 380. The
higher boiling fraction, still bottoms, contains glycerin, some alkanol and some water and potentially acid or salts thereof. The higher boiling fraction or a portion thereof is preferably passed via line 382 to line 170 or it can be combined with spent glycerin.

[00101] A washed biodiesel stream is withdrawn from second washing stage 346 via line 348. The washed stream is passed to drier 350 to remove water which exhausts via line 354. Preferably substantially all the alkanol has been removed from the crude biodiesel prior to dying to permit the water vapor to be exhausted without treatment to eliminate volatile organic components. Drier 350 may be of any suitable design such as evaporator, stripper, wiped film evaporator, falling film evaporator, and solid sorbent. Generally the temperature of drying is between about 60°C and 220°C, say, about 70°C and 180°C. The pressure is generally in the range of about 5 to 200 kPa absolute. The dried biodiesel is withdrawn as product via line 352. The biodiesel product contains free fatty acid and preferably has a free fatty acid content of less than about 0.3 mass percent. An inert gas such as nitrogen may be used in facilitating drying.

[00102] The subatmospheric pressure is maintained in drier 350 by the use of liquid ring vacuum pump 356 which is in communication with line 354. Liquid ring vacuum pump 356 uses water as the sealing fluid which provided by line 358 and water exits via line 362. The gases from liquid ring vacuum pump 356 exit via line 360.

[00103] Returning to glycerin header 214, the glycerin-containing streams are passed via line 242 to blending tank 246 such that a relatively uniform glycerin composition can be provided via line 248 to the pretreatment section of facility 100. Blending tank 246 may also provide sufficient residence time for any glycerides in the glycerin to transesterify with alkanol as well as permit any oil entrained in the glycerin phase to separate. As shown, an oil layer that forms in blending tank 246 can intermittently or continuously be withdrawn via line 247 for recycle to first transesterification reactor 202. Alternatively, the oil layer can be withdrawn with the glycerin and passed to the pretreatment section.

[00104] While all glycerin-containing streams from the transesterification and refining components of facility 100 have been show to be directed to glycerin header 214, it is within the purview of the process to use fewer streams. Moreover, any of the glycerin-containing streams may be used elsewhere prior to being passed to blending tank 246, and the blended stream or a portion thereof in line 248 may be used elsewhere and either returned to glycerin header 214 or passed to pretreatment component of facility 100.
[00105] One such use may be to pretreat a feed provided by line 200 to dehydrate the feed. If the feed contains free fatty acids or phospholipids, its introduction into the pretreatment component rather than via line 200, may be preferred. In such a pretreatment, a portion of the alkanol contained in the glycerin phase as well as some of the base catalyst, will be partitioned to the oil phase.

[00106] With respect to Figure 2, biodiesel manufacturing facility 400 uses a suitable raw material feed provided via line 402. The feed may be one or more suitable oils or fats derived from bio sources, especially vegetable oils and animal fats. As shown, the raw material feed in line 402 is passed to pretreatment unit 406 which may effect one or more unit operations to enhance the feed as a transesterification feedstock such as drying, free fatty acid removal, filtration to remove particulates, and the like. Line 404 shows a discharge of rejected material from such unit operations.

[00107] A glyceride-containing feed is passed from pretreatment unit 406 via line 408 to reactor 410 for transesterification. The transesterification is a catalyzed reaction with a lower alkanol, preferably methanol, ethanol or isopropanol. Higher alkanols can be used. Methanol is the most preferred alkanol not only due to its availability but also because of its ease of recovery by vapor fractionation. For purposes of the following discussion, methanol will be the alkanol. The catalysis may be acid or base catalysis. Acid catalysts include heterogeneous and homogeneous acids including, but not limited to, sulfuric acid, hydrochloric acid, sulfonic acid, toluene sulfonic acid, phosphoric acid, perchloric acid, and nitric acid as well as acidic ion exchange resins. For representative processes, see U.S. Patent No. 6,822,105; U.S. Patent Application Publication No. 2005/0204612; and Canakci, et al., Transactions of ASAE, 42, 5, pp. 1203-10 (1999), herein incorporated in their entireties by reference.

[00108] As shown, methanol is supplied via line 412 to methanol header 414. Line 416 supplies methanol to reactor 410. Although line 416 is depicted as introducing methanol into line 408, it is also contemplated that methanol can be added directly to reactor 410. Generally methanol is supplied only in a slight excess above that required to achieve the sought degree of transesterification in reactor 410. The base catalyst is shown as being introduced via line 418 to reactor 410.

[00109] The transesterification in reactor 410 is often at a temperature between about 30°C and 220°C, preferably between about 30°C and 80°C. The pressure is typically
in the range of between about 90 to 500 kPa (absolute) although higher and lower pressures can be used. The reactor is typically batch, semi-batch, plug flow or continuous flow tank with some agitation or mixing, e.g., mechanically stirred, ultrasonic, static mixer, e.g., a packed bed, baffles, orifices, venturi nozzles, tortuous flow path, or other impingement structure. The residence time will depend upon the desired degree of conversion, the ratio of methanol to glyceride, reaction temperature, the degree of agitation and the like, and is often in the range of about 0.1 to 20, say, 0.5 to 10, hours.

[00110] The partially transesterified effluent for reactor 410 is passed via line 420 to phase separator 422. Phase separator 422 may be of any suitable design and provides a glycerin-containing bottoms stream passed via line 424. The material in line 424 can be subjected to suitable unit operations to recover components thereof. This stream also contains any soaps made in reactor 410 and a portion of the catalyst. The lighter phase contains alkyl esters and unreacted glycerides and is passed via line 426 to second transesterification reactor 428.

[00111] Reactor 428 may be of any suitable design and may be similar to or different than reactor 410. As shown, additional methanol is provided via line 430 from methanol header 414 and additional catalyst is provided via line 432.

[00112] The effluent from reactor 428 is passed via line 434 to phase separator 436 which may be of any suitable design and may be the same as or different from the design of separator 422. A heavier, glycerin-containing phase is withdrawn via line 438. This stream contains some catalyst and methanol. A lighter phase containing crude biodiesel is withdrawn from separator 436 via line 440. The lighter phase also contains catalyst and methanol.

[00113] The crude is then passed without catalyst neutralization to methanol separator 442. Methanol separator 442 effects a fast, vapor fractionation of the lower alkanol from the crude biodiesel and may be of any convenient design including a stripper, wiped film evaporator, falling film evaporator, and the like. Where subatmospheric pressure is used, it is preferred to use a liquid ring vacuum pump.

[00114] As stated above, a falling film evaporator is the preferred apparatus for effecting the vapor fractionation. The tubes of the falling film evaporator may be circular in cross section or any other convenient cross-sectional shape, and the tubes may have a
constant cross-sectional configuration over their length or may be tapered or otherwise change in cross-sectional configuration.

[00115] The lower boiling fraction containing the lower alkanol will contain a portion of any water contained in the crude biodiesel. Since the transesterification is conducted with little water being present, and a portion of the water is removed with the glycerin, the concentration of water in this fraction can be sufficiently low that it can be recycled to the transesterification reactors. This lower boiling fraction often contains less than about 0.1, and more preferably less than about 0.05, mass percent water. The methanol-containing fraction is removed from methanol separator 442 via line 444 and may be exhausted from the facility as a waste stream, e.g., for burning or other suitable disposal, or can be added to the methanol header 414.

[00116] The methanol separation preferably lowers the lower alkanol content of the bottoms stream to less than about 10, more preferably less than about 2, milligrams of lower alkanol per kilogram of alkyl ester in the bottoms stream. The bottoms stream from methanol separator 442 is contacted with an aqueous acid solution to neutralize the catalyst.

[00117] The bottoms stream is passed via line 446 to mixer 448. Into mixer 448 is passed a strong acid aqueous solution via line 452. Mixer 448 may be an in-line mixer or a separate vessel. Mixer 448 should provide sufficient mixing and residence time that essentially all of the soaps are converted to free fatty acids. Often the temperature during the mixing is in the range of about 80°C to 220°C, and for a residence time of between about 0.01 to 4, preferably 0.02 and 1, hours.

[00118] A strong acid aqueous solution introduced via line 452 has a pH sufficient to convert the soaps to free fatty acids. Often the pH is less than about 6, sometimes between 3 and 5. The acid may be any suitable acid to achieve the sought pH such as hydrochloric acid, sulfuric acid, sulfonic acid, phosphoric acid, perchloric acid and nitric acid. Sulfuric acid is preferred due to cost and availability. The amount of strong acid aqueous solution provided is typically in a substantial excess of that required to convert the soaps to free fatty acid and to neutralize any remaining catalyst. The excess of acid is often at least about 5, preferably at least about 10, say between about 10 and 1000 times that required.

[00119] The effluent from mixer 448 is passed via line 460 to phase separator 462. Phase separator 462 may be of any suitable design. A lower aqueous phase is withdrawn
via line 464 for distillation. If desired, a portion of this aqueous phase can be recycled via line 452 to mixer 448. Make-up acid is provided via line 450 to line 452. Alternatively, make-up acid can be added to line 472, described below and no recycle 452 need be employed.

The lighter phase which contains crude biodiesel and free fatty acid is withdrawn via line 466 and is passed to water wash column 468. Fresh water enters column 468 via line 470 and serves to remove glycerin from the crude biodiesel. Normally the column is operated at a temperature between about 20°C and 80°C, preferably between about 35°C and 75°C. In a preferred embodiment, the spent water from wash column 468 is passed via line 472 to mixer 448 or combined with the aqueous solution in line 452.

Water wash column 468 may be of any suitable design. Typically, the water wash column operates with a recycling water loop, often with the recycle being at least about 20, say between about 50 and 500, mass percent of the crude biodiesel being fed to the column. A purge is taken from the loop via line 472. The purge balances the amount of water (aqueous phase) being provided via line 470. The purge is usually at a rate of between about 1 and 50, say 5 and 20, mass percent per unit time of the recycle rate in the loop. Alternately the feed from 460 can be washed with water at a pH of about 8 to 11, preferably 8 to 10.5, to remove glycerin and salts. The water layer is fed as above and the biodiesel-containing layer is fed to the second stage water contacting under acidic conditions.

With reference to Figure 3, a two stage water wash column 468 is depicted having a first stage 468A and a second stage 468B. As shown, crude biodiesel is provided via line 466 to first stage 468A and is cocurrently contacted with water from water loop 469A. The washed biodiesel from first stage 468A is passed via line 466A to second stage 468B where it is cocurrently contacted with water from water loop 469B. In each stage the water, after contacting the biodiesel stream being processed, is returned to the respective loops. The water being provided via line 470 is directed to loop 469B for the second stage. A portion of the stream in loop 469B is passed via line 469C to loop 469A for the first stage of the water wash column. The purge is taken from loop 469A via line 472.

Returning to Figure 2, a washed biodiesel stream is withdrawn from washing column 468 via line 474 and is passed to drier 476 to remove water and residual methanol which exhaust via line 478. Drier 476 may be of any suitable design such as
stripper, wiped film evaporator, falling film evaporator, and solid sorbent. Generally the temperature of drying is between about 80°C and 220°C, say, about 100°C and 180°C. The dried biodiesel is withdrawn as product via line 480.

[00124] Returning to line 464, the aqueous phase from separator 462 is passed to evaporator 482 which provides a lower boiling fraction and a higher boiling fraction. While an evaporator may be used, it is also possible to use a packed or trayed distillation column with or without reflux. Generally the bottoms temperature of evaporator 482 is less than about 150°C, preferably between about 120°C and 150°C. The distillation may be at any suitable pressure. A membrane separation system may, alternatively or in combination, be used with evaporator 482 to effect the sought concentration of the spent water.

[00125] By way of example, a biodiesel production facility in which spent water stream from the water washing of crude biodiesel is sewered, has a biochemical oxygen demand of 0.020 kilograms of oxygen per liter of biodiesel product for waste water streams. The same plant, but using the process of this invention, has a biochemical demand of less than 0.0004 kilograms of oxygen per liter of biodiesel product for waste water streams.

[00126] As shown, the glycerin-containing layer from line 424 is fractionated to recover glycerin, which can be sold or used as a by-product, and recover methanol, which can be recycled to the reaction system. In further detail, but not in limitation of the broad aspects of the invention, the glycerin-containing layer from line 424 and the higher boiling fraction from line 484 of evaporator 482 are passed to stripping column 485 which provides a methanol and water-containing overhead and a glycerin bottoms stream which generally contains less than about 5 mass percent methanol. The glycerin bottoms stream is discharged via line 486 and the overhead is passed via line 488 to dehydration column 490.

[00127] As shown, dehydrating column 490 provides a water-containing bottoms stream for discharge via line 492. A lower boiling stream is recovered via line 494. Condensed methanol is passed via line 496 to line 408 for recycle to the reaction system. A gaseous fraction is discharged via line 498.
IT IS CLAIMED:

1. A process for removing impurities from crude biodiesel stream comprising: (a) washing the crude biodiesel stream, which stream contains alkyl esters of fatty acids, lower alkanol in an amount less than about 5000 parts per million by mass, and glycerin, with water for a time sufficient to remove at least a portion of the glycerin therein to provide an alkyl ester stream having reduced concentration of glycerin and to provide a spent water stream; (b) concentrating the spent water stream to provide (i) an aqueous fraction comprising water, said fraction containing less than about 5 mass percent of the total glycerin in the spent water stream, and (ii) an aqueous, glycerin-containing fraction containing at least about 10 mass percent glycerin; and (c) recycling at least a portion of the aqueous fraction to step (a) as a portion of the water.

2. The process of claim 1 wherein the lower alkanol is at least one of methanol, ethanol and isopropanol.

3. The process of claim 2 wherein the lower alkanol is methanol.

4. The process of claim 1 wherein the concentrating is achieved by a membrane separation.

5. The process of claim 1 wherein the concentrating is achieved by distillation.

6. The process of claim 5 wherein the distilling is effected by flash distillation.

7. The process of claim 1 wherein the concentration of lower alkanol in the crude biodiesel is less than about 200 ppm-m.
8. The process of claim 7 wherein the concentration of lower alkanol in the crude biodiesel is less than about 10 milligrams per kilogram.

9. The process of claim 1 wherein soaps are contained in the crude biodiesel stream and at least a portion of the washing with water occurs in the presence of soaps to provide an alkyl ester stream having a reduced concentration of soaps.

10. The process of claim 9 wherein at least two wash stages are used and the pH of the wash water is greater than 8 in at least one wash stage.

11. In a process for making biodiesel comprising:
   a. contacting a glyceride-containing feed and lower alkanol under transesterification conditions, wherein the molar ratio of lower alkanol to glyceride is at least about 3:1 to provide a crude biodiesel containing alkyl esters of fatty acids, glycerin, and lower alkanol, said contacting being for a time sufficient to convert at least about 90 mass percent of the glycerides in the glyceride-containing feed;
   b. separating by phase separation said crude biodiesel to provide a heavier glycerin-containing layer and a lighter alkyl ester-containing layer, wherein a portion of the glycerin is contained in each of the heavier and lighter layer;
   c. subjecting the lighter layer to vapor fractionation conditions to provide a lower boiling fraction containing lower alkanol and a higher boiling fraction containing alkyl ester and glycerin; and
   d. washing the higher boiling fraction containing alkyl ester with water to provide a biodiesel having a decreased concentration of glycerin and a spent water stream,

the improvement comprising conducting step (c) to provide a higher boiling fraction containing less than about 2000 parts per million by mass of lower alkanol; in step (d) concentrating the spent water stream to provide an aqueous fraction and an aqueous, glycerin-containing fraction and providing at least a portion of the aqueous fraction as a portion of the water for step (d).
12. The process of claim 11 wherein the lower alkanol is at least one of methanol, ethanol and isopropanol.

13. The process of claim 12 wherein the lower alkanol is methanol.

14. The process of claim 12 wherein the glycerin-containing fraction contains at least about 10 mass percent glycerin.

15. The process of claim 14 wherein the lower alkanol concentration of the higher boiling fraction containing alkyl ester is less than about 10 milligrams per kilogram of alkyl ester.

16. The process of claim 14 wherein the higher boiling fraction containing alkyl ester of step (c) is provided at a pH stream of less than about 6 for step (d).

17. The process of claim 14 wherein the concentrating is achieved by distillation.

18. The process of claim 17 wherein the washing is effected in at least two countercurrent stages.

19. The process of claim 18 wherein between about 20 and 200 mass parts of wash water (including recycle) are used per 100 mass parts of crude biodiesel.

20. An apparatus for conducting the process of claim 11.