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Misra et al.(10) **Pub. No.: US 2008/0184616 A1**(43) **Pub. Date: Aug. 7, 2008**(54) **BIOFUEL PRODUCTION METHODS****Publication Classification**(75) Inventors: **Manoranjan Misra**, Reno, NV (US); **Gautam Priyadarshan**, Reno, NV (US); **Narasimharao Kondamudi**, Reno, NV (US); **Susanta Mohapatra**, Reno, NV (US)(51) **Int. Cl.**
C10L 1/18 (2006.01)(52) **U.S. Cl.** **44/308**

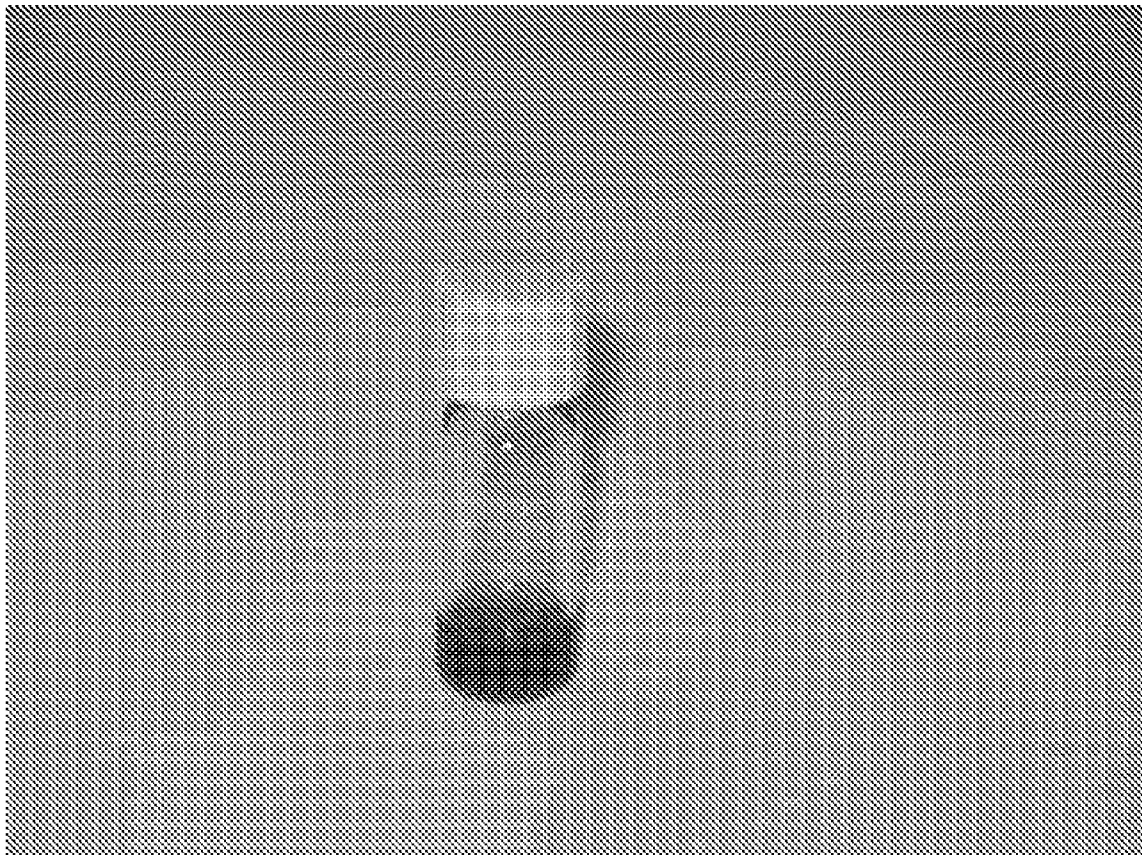
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PORTLAND, OR 97204(73) Assignee: **The Board of Regents of the Nevada System of Higher Education**(21) Appl. No.: **11/971,377**(22) Filed: **Jan. 9, 2008****Related U.S. Application Data**

(60) Provisional application No. 60/884,173, filed on Jan. 9, 2007, provisional application No. 60/970,790, filed on Sep. 7, 2007.

(57) **ABSTRACT**

In some embodiments, the present disclosure provides methods for producing biofuel from a biological material that includes protein and a biofuel feedstock, such as triglycerides. In a specific example, the biological material is hydrolyzed to obtain the biofuel feedstock, such as by treatment with a base. Free fatty acids or triglycerides are then extracted using an organic solvent. The free fatty acids or triglycerides are converted to fatty acid esters, useable as biofuel, by esterification or transesterification, respectively. In a more specific example, the biological material is converted to a biofuel in a one step process by treating the biological material with base and an appropriate alcohol. In some implementations, a disclosed method uses chicken feathers obtained from a chicken processing operation as the biological material.



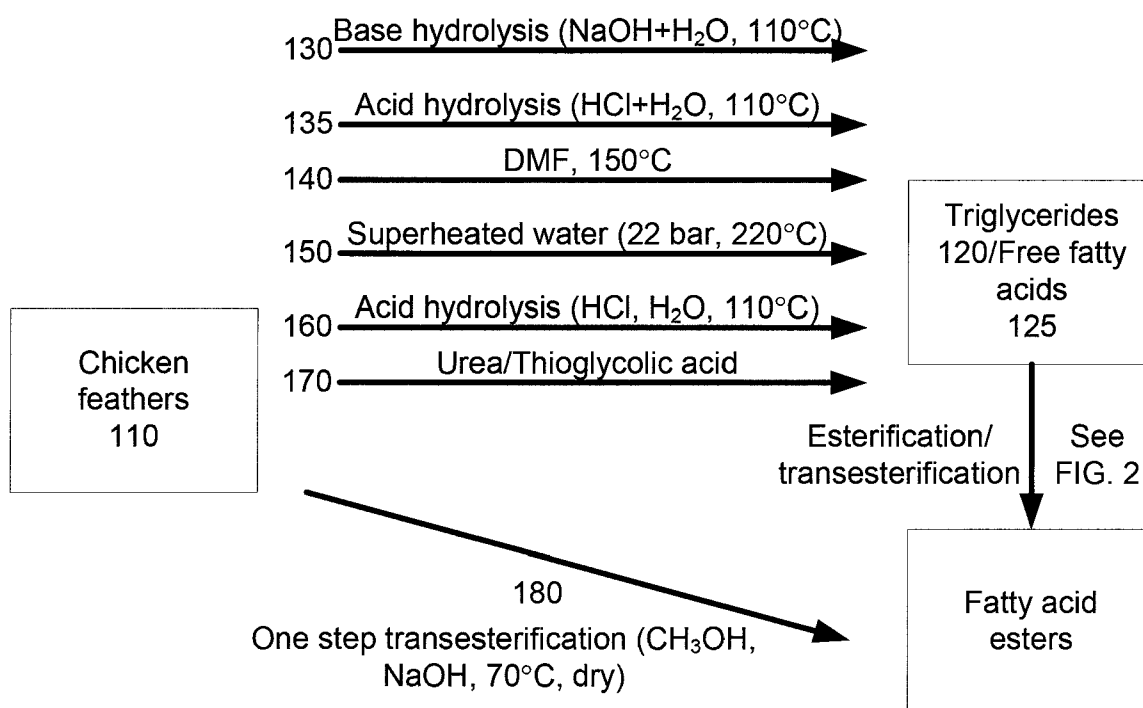


FIG. 1

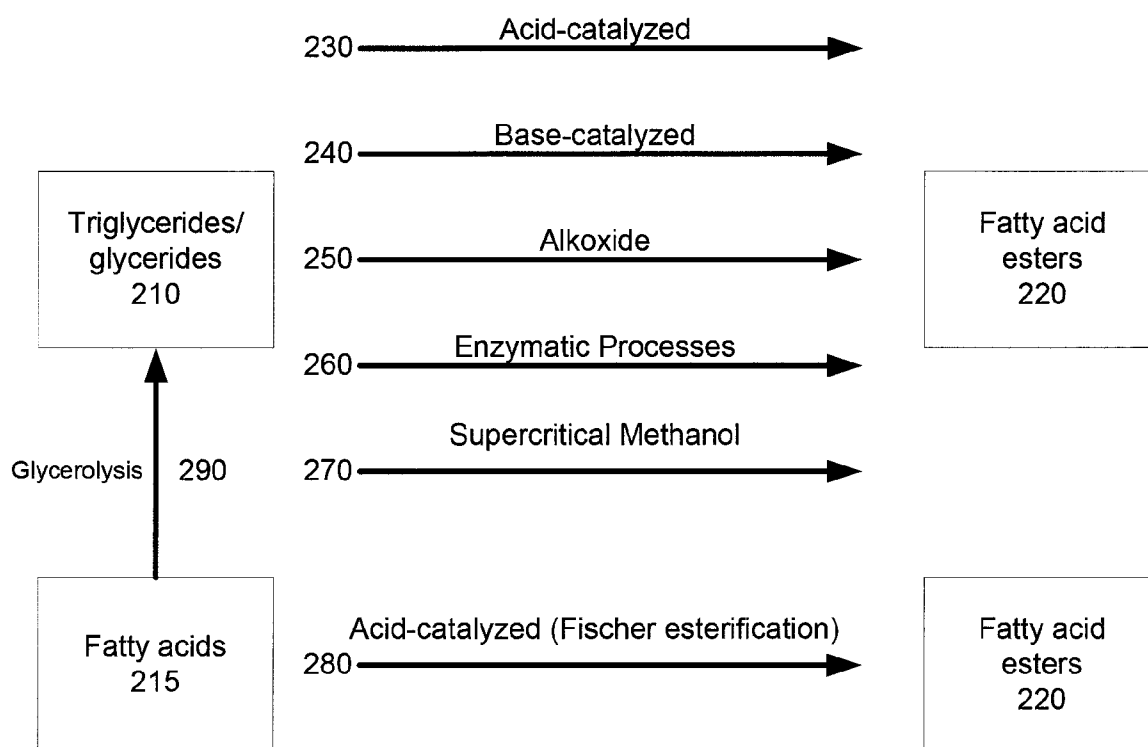
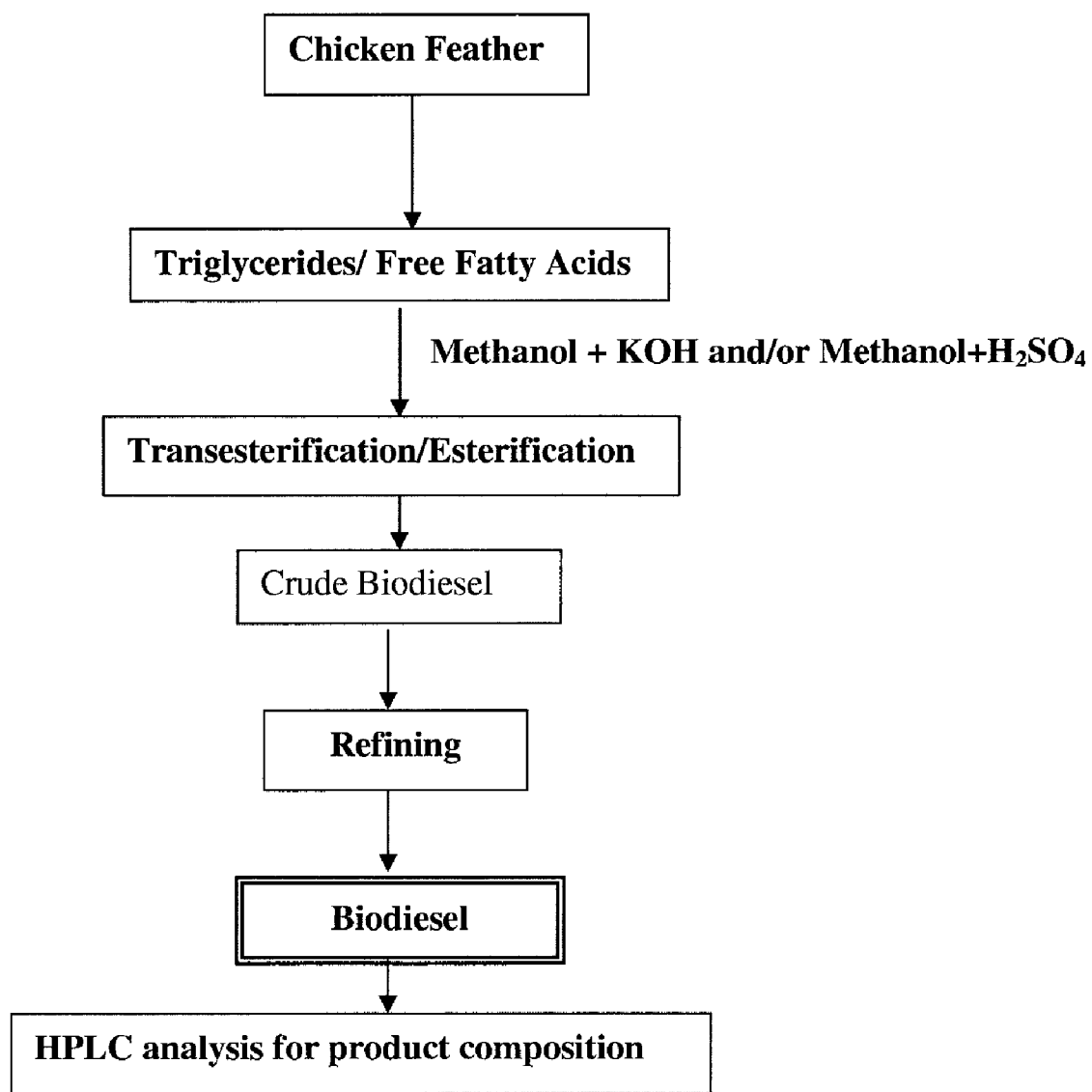


FIG. 2

Biodiesel synthesis from Chicken Feather**FIG. 3**

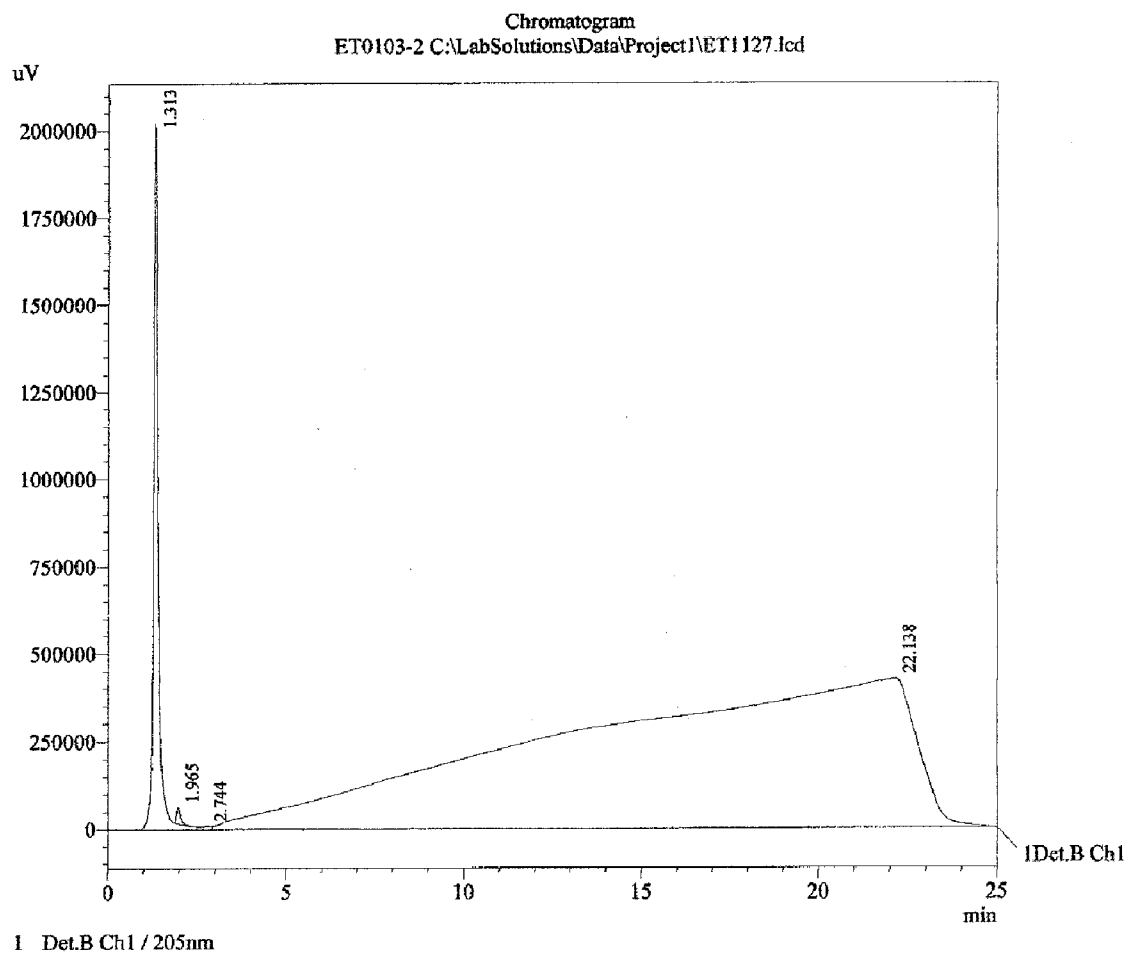


FIG. 4

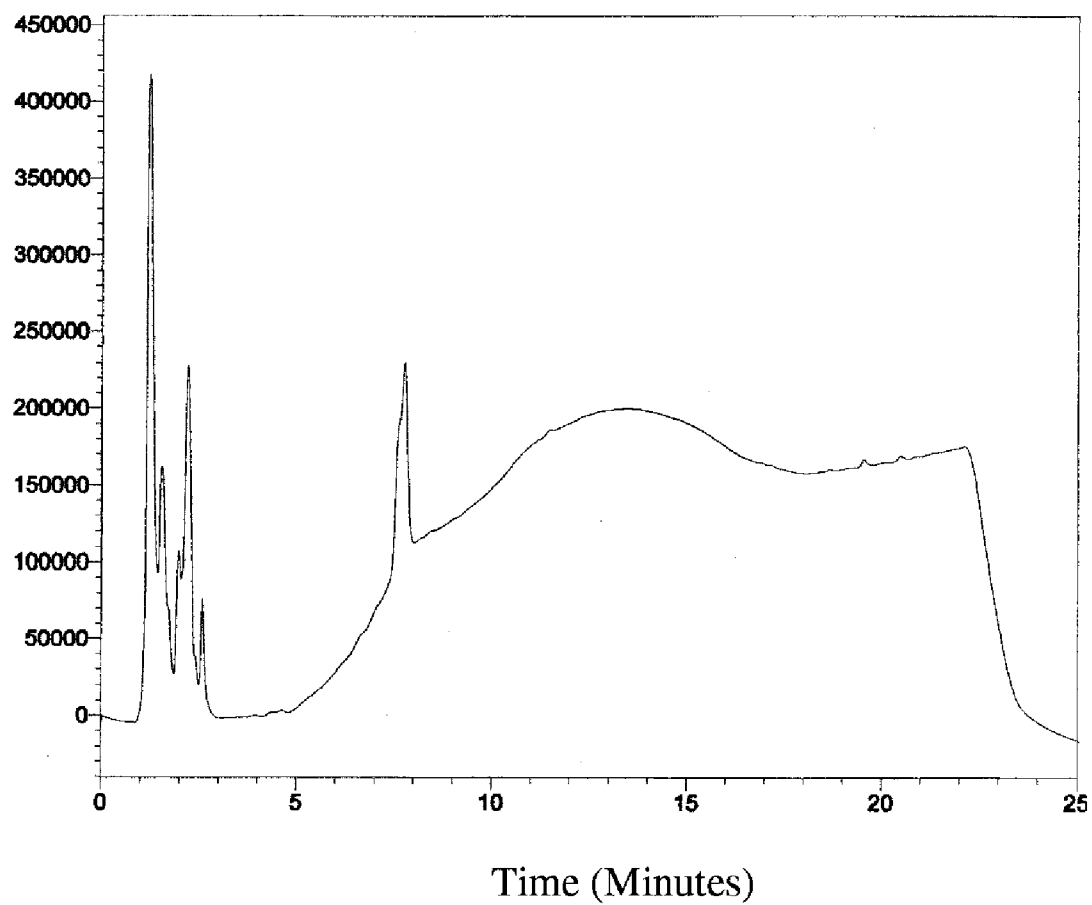


FIG. 5

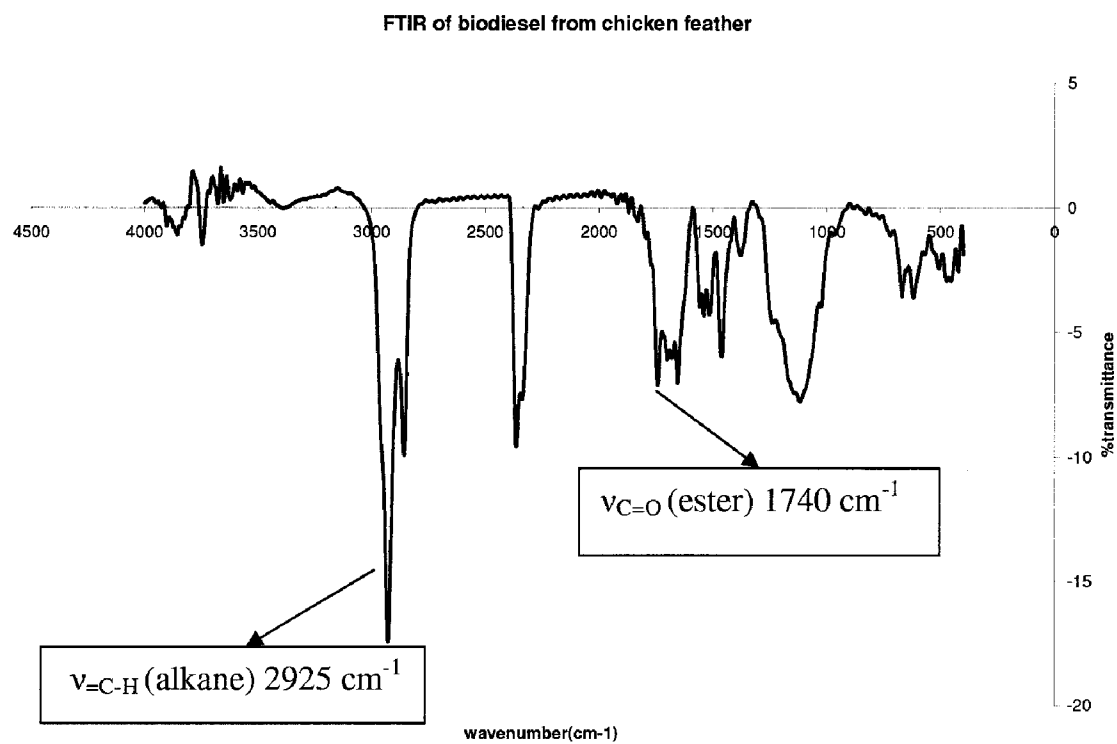


FIG. 6

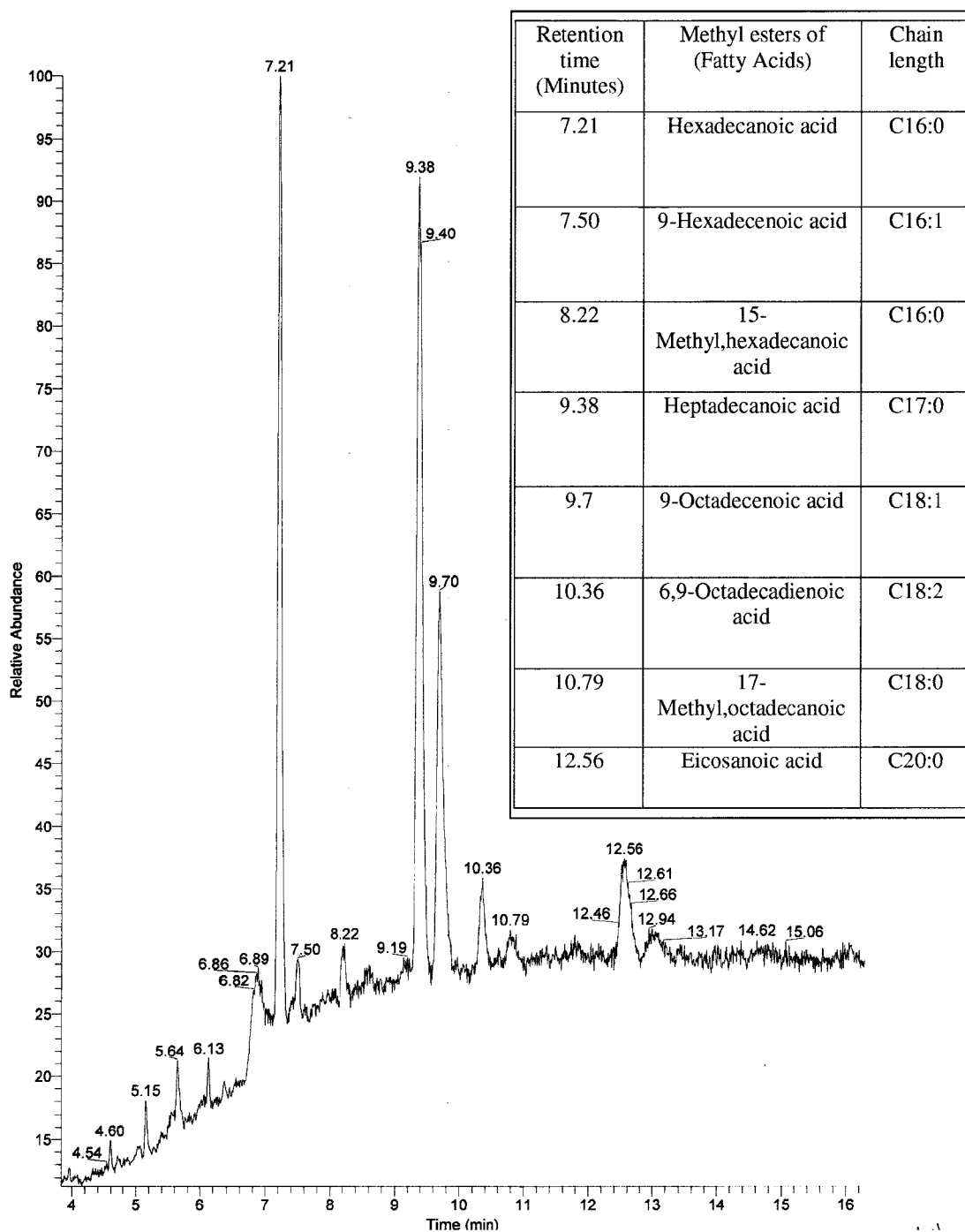


FIG. 7

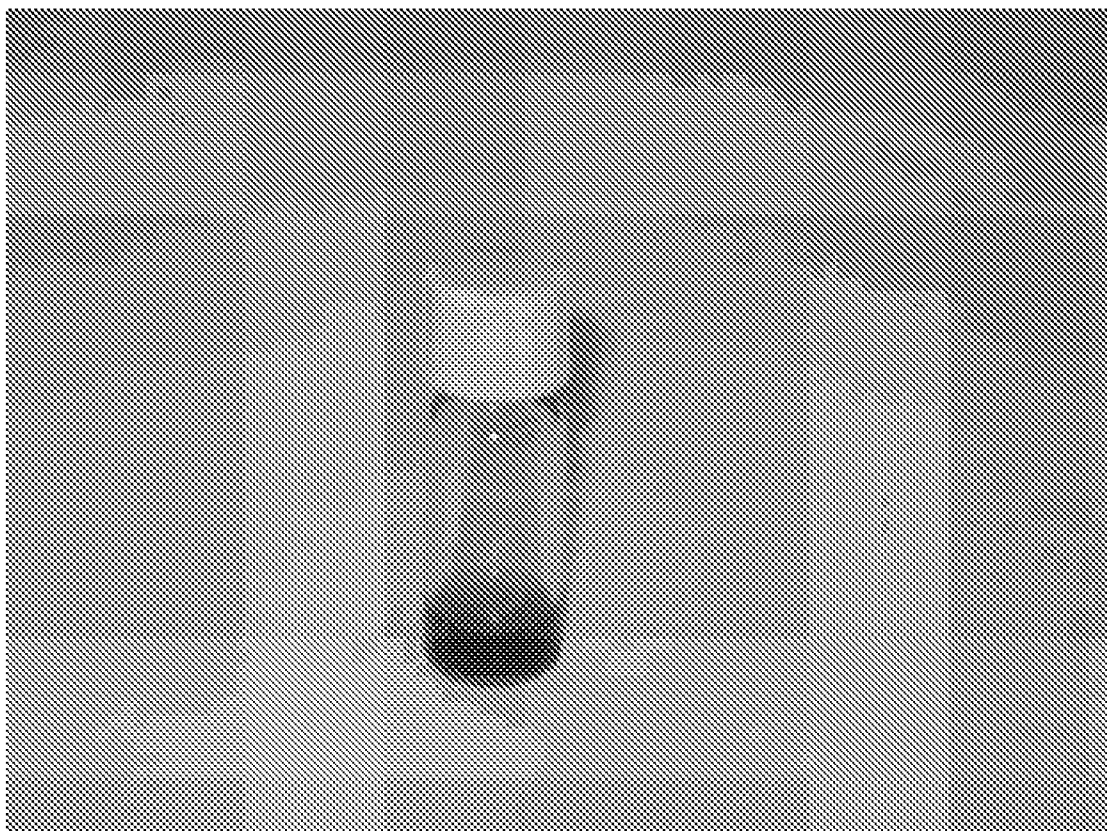


FIG. 8

BIOFUEL PRODUCTION METHODS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of, and incorporates by reference, U.S. Provisional Patent Application No. 60/884,173, filed Jan. 9, 2007, and U.S. Provisional Patent Application No. 60/970,790 filed Sep. 7, 2007.

FIELD

[0002] The present disclosure describes methods of producing fuels from biological materials. In specific examples, the present disclosure provides methods for producing biodiesel from biological sources which include protein and triglycerides, such as chicken feathers.

TECHNICAL BACKGROUND

[0003] The United States produces 2-4 billion pounds of chicken feathers from poultry industries. Science News, "Materials Take Wing", Feb. 23, 2002, Vol. 161. In recent years it has been shown that chicken feathers can be used for many applications, including environmental application and filtration of heavy metals. P. Kar & M. Misra, "Use of keratin Fiber for Separation of Heavy metals from Water", Journal of Chemical Technology & Biotechnology, 79, 1313-1319, 2004; M. Misra & P. Kar, "Avian Keratin Protein Nano-Fiber for Environmental Application," Natural Fibers, Plastics & Composite, 83-89, August 2000. However, much of this material is unused, and can present disposal problems.

[0004] The availability and cost of petroleum based fuels continues to be of concern. A number of efforts are underway to develop fuels from other sources, such as hydrogen-based fuel sources, ethanol, and biological based fuels, such as biodiesel. In particular, various plant and animal oils and fats have been investigated as potential sources of biofuel. However, the energy and resources needed to produce biofuel can make it uneconomical to produce crops specifically for biodiesel production. While waste oil and fats can be used, their supply may be insufficient for mass production of biofuel.

SUMMARY

[0005] The present disclosure provides methods for producing fuels, such as biofuels, from biological materials. In a particular disclosed method, biofuel is produced by hydrolysis of the biological material to liberate triglycerides, free fatty acids, or other substances which can be converted to fatty acid esters useable as biofuels. In a particular implementation, the biological material includes a protein, which is hydrolyzed using an alkaline solution in some examples. The free fatty acids or triglycerides are then esterified or transesterified, respectively, to produce fatty acid esters useable as biofuel. For example, when triglycerides are obtained from the biological material, the triglycerides can be transesterified by treating them with a strongly alkaline solution, although other methods are used in further examples. When free fatty acids are obtained, the free fatty acids may be esterified using an acid catalyzed reaction. In a more particular implementation, triglycerides in the biological source are converted to fatty acid esters in a one step process using basic conditions and an alcohol, or derivative thereof, bearing the appropriate functional group.

[0006] In a specific embodiment, a protein source is hydrolyzed using a base. Free fatty acids or triglycerides are then extracted using an organic solvent. Extracted free fatty acids are then esterified, such as using acid catalyzed esterification and the appropriate alcohol. Extracted triglycerides are then transesterified, such as using a base catalyzed process.

[0007] In a further embodiment, the free fatty acids are converted to glycerides, such as mono-, di-, or tri-glycerides by reaction with glycerol under appropriate conditions. The glycerides are then transesterified to produce fatty acid esters, which may be used as biofuels. In a specific example, the glycerides are transesterified using a base catalyzed reaction.

[0008] The biological source may be any suitable biological material having protein, such as a structural protein, such as keratin, and triglycerides or fatty acids. In various examples the biological source is hair, feathers, skin, hooves, claws, horns, or scales. In a specific example, the protein source is feathers, such as poultry feathers. In some examples, the feathers are obtained from a poultry processing operation.

[0009] In some aspects of the present disclosure, the biological source, or free fatty acids or triglycerides obtained therefrom, is combined with another feedstock, such as a plant oil, such as a vegetable oil, including soybean oil or rapeseed oil, coffee oil, or an animal fat, such as chicken fat. The combined feedstock is then converted to a biofuel, such as using an above-described hydrolysis and/or esterification or transesterification procedure. In further aspects, a biofuel produced from the above-described biological material is combined with a biofuel derived from a different feedstock, such as a plant oil, such as a vegetable oil, including soybean oil or rapeseed oil, oil from coffee, or from an animal fat, such as chicken fat.

[0010] The methods of the present disclosure can provide a number of advantages. For example, the present disclosure can convert chicken feathers, often treated as a waste product, into a high value biofuel product. Accordingly, the supply of biofuel can be increased without the expenditure of energy and other resources in developing a feedstock specifically for use as a biofuel.

[0011] There are additional features and advantages of the subject matter described herein that will become apparent as this specification proceeds.

[0012] In this regard, it is to be understood that this is a brief summary of several aspects of the subject matter described herein. The various features described in this section and below for various embodiments may be used in combination or separately. Any particular embodiment need not provide all features noted above, nor solve any particular set of problems in the prior art noted above.

DESCRIPTION OF THE FIGURES

[0013] Various embodiments are shown and described in connection with the following drawings in which:

[0014] FIG. 1 is a schematic diagram of various methods of extracting a biofuel feedstock, such as free fatty acids or triglycerides, from chicken feathers.

[0015] FIG. 2 is a schematic diagram of various methods of converting triglycerides and free fatty acids to fatty acid esters.

[0016] FIG. 3 is a process diagram of a disclosed method of synthesizing biodiesel from chicken feathers.

[0017] FIG. 4 an HPLC chromatogram of a product produced using the method of FIG. 3.

[0018] FIG. 5 is an HPLC chromatogram of a biodiesel product produced using a method of the present disclosure.

[0019] FIG. 6 is an FTIR spectra of the biodiesel product of FIG. 5.

[0020] FIG. 7 is a GC-MS spectra of the biodiesel product of FIG. 5.

[0021] FIG. 8 is a photograph of a biodiesel sample obtained from chicken feathers using a method of the present disclosure.

DETAILED DESCRIPTION

[0022] Unless otherwise explained, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. In case of conflict, the present specification, including explanations of terms, will control. The singular terms "a," "an," and "the" include plural referents unless context clearly indicates otherwise. Similarly, the word "or" is intended to include "and" unless the context clearly indicates otherwise. The term "comprising" means "including;" hence, "comprising A or B" means including A or B, as well as A and B together.

[0023] Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present disclosure, suitable methods and materials are described herein. The disclosed materials, methods, and examples are illustrative only and not intended to be limiting.

[0024] The present disclosure generally provides methods of producing biofuels from biological materials. Typically, the biological material includes triglycerides or fatty acids and a protein, such as a structural protein. In a specific example, the structural protein is keratin. Suitable biological sources include hair, feathers, skin, hooves, claws, horns, or scales. In a specific example, the protein source is feathers, such as poultry feathers. In some examples, the feathers are obtained from a poultry processing operation. In a more specific example, the biological source is chicken feathers.

[0025] Chicken feathers typically constitute about 18 wt % of the mass of a chicken. The feathers themselves contain about 84 wt % protein, about 12 wt % triglycerides, and about 4 wt % ash, phosphorous and trace metals. The triglycerides in the chicken feathers can be converted to biodiesel using the disclosed methods. Although the following methods specifically describe the use of chicken feathers, similar methods may be used for other, similar, biological sources.

[0026] As shown in FIG. 1, chicken feathers 110 can be converted to triglycerides 120 or fatty acids 125 through a variety of pathways. The chicken feathers 110 can be obtained from a variety of sources, such as poultry processing operations. In some embodiments the feedstock is pretreated to aid the subsequent conversion reactions. For example, chicken feathers may be first crushed or ground, such as by cryogenic grinding or grinding in a burr grinder, conical burr grinder, blade grinder, or hammer mill. The feedstock may also be pretreated by vibration. The chicken feathers may also be subjected to one or more cleaning steps.

[0027] One conversion pathway 130 is base hydrolysis. Base hydrolysis is typically carried out by refluxing a quantity of chicken feathers with a concentrated aqueous solution of base, such as an alkaline earth or alkali metal hydroxide. Other inorganic or organic bases may also be used. In particular examples, the basic solution is a NH_4OH , KOH or NaOH solution, such as a solution having a concentration of

between about 2M and about 8M, such as about 4M. The hydrolysis process is typically carried out from about 1 hour to about 8 hours, such as about 4 hours. The chicken feathers typically dissolve in the basic solution as the reaction proceeds. After the reaction has reached a desired level of completion, the reaction mixture is neutralized, such as by adding an acid, such as an about 1M hydrochloric acid solution to about a 12M hydrochloric acid solution, such as a 6M hydrochloric acid solution. Other mineral acids or organic acids can be used, if desired, for the neutralization.

[0028] The triglycerides in the feathers are typically converted to fatty acids during base hydrolysis. After neutralization, a solid precipitate typically forms. Fatty acids and other components are extracted from the neutralized reaction mixture, typically using one or more organic solvents. Typical solvents include alcohols, such as methanol, ethanol, and isopropanol; hydrocarbons, such as paraffinic hydrocarbons having 4-8 carbons, such as hexane and petroleum ether; chlorinated solvents, such as dichloromethane and chloroform; ethers, such as diethyl ether; aldehydes and ketones, such as methyl ethyl ketone and acetone; fluorinated compounds; and mixtures thereof. In a specific example, a 5% by volume solution of methanol in dichloromethane is used for the extraction.

[0029] In some methods, the solvent is selected to extract selected components of interest. For example, relatively non-polar solvents may be used to extract fatty acids, yet avoid extraction of water and other materials. Fatty acids thus obtained may require fewer processing steps.

[0030] Extraction can occur in a batch or continuous process. Suitable continuous processes include countercurrent extraction processes. In some examples, the reaction mixture is refluxed with solvent for a period of time, such as between about 30 minutes and about 24 hours, such as between about 1 hour and about 8 hours. In a particular example, the mixture is refluxed for about 1 hour.

[0031] After solvent extraction, the solvent may be removed prior to further processing of the fatty acids. Solvent removal may be accomplished by any suitable method, many of which are notoriously well known in the art. For example, the solvent may be distilled from the desired product. In particular implementations, solvent removal occurs under reduced pressure, such as under a full or partial vacuum, in order to reduce the temperature at which the solvent distills, and thus the heat energy needed to volatilize the solvent. In more particular implementations, rotary evaporators or similar devices are used to remove solvent. When mixed solvent systems are used, fractional distillation can be performed and suitable distillation columns incorporated into the solvent removal process or apparatus in order to aid separation of the different solvent components. Fractional distillation can also be used to purify the free fatty acids or to separate the fatty acids from other components. Of course, if mixed recovery of solvents is not of concern, fractional distillation need not be performed.

[0032] Solvent obtained from the above-described solvent removal in process can be recycled into other parts of the system, such as into the solvent extraction process. Appropriate choice of solvents and operating conditions can result in substantial reuse of the solvent, decreasing materials costs and potentially environmentally harmful waste products. In some embodiments, over 85% of the solvent used in the

extraction step is recovered, such as over 95%. The free fatty acids can then be esterified, such as using the processes discussed below.

[0033] Acid hydrolysis **135** can be carried out in a manner similar to base hydrolysis. Typically, the material is refluxed (such as at about 110° C.) in HCl, such as about 6M HCl, for about 4 to about 24 hours. Neutralization may be carried out with a suitable base, such as sodium hydroxide, potassium hydroxide, or other organic or inorganic bases, including alkaline earth or alkali metal oxides or hydroxides. The triglycerides thus obtained can be extracted or purified as described above for the free fatty acids produced during basic hydrolysis.

[0034] Another method **140** of isolating triglycerides from chicken feathers involves refluxing the chicken feathers in N,N,-dimethyl formamide for an extended period of time and then separating the triglycerides using filtration. One procedure for carrying out this process is disclosed in U.S. Pat. No. 3,970,614, incorporated by reference herein.

[0035] A method **150** involves extracting triglycerides from chicken feathers using water at high temperature and pressure. Suitable techniques are described in Yin et al., "Self-organization of Oligopeptides Obtained on Dissolution of Feather Keratins in Superheated Water," *Biomacromolecules*, 8 800-806 (2007), incorporated by reference herein. For example, chicken feathers can be hydrolyzed using superheated or supercritical water.

[0036] In a specific example, the chicken feathers are placed in a suitable pressure vessel, such as a stainless steel vessel, and heated until the pressure cell reaches a temperature of about 220° C. and a pressure of about 22 bar. The feathers are held in this state until a desired degree of hydrolysis has occurred, such as about 2 hours. The triglycerides can be separated from other components, such as proteins and amino acids, using suitable techniques, such as extraction or gravity separation, such as using a hydrocyclone or a separatory funnel. Additional detail regarding procedures for dissolving polymers, including biological polymers such as keratin, using this type of methodology can be found in Rastogi et al., "Dissolution of Hydrogen-Bonded Polymers in Water: A Study of Nylon-4,6," *Macromolecules* 37, 8825-8828 (2004), expressly incorporated by reference herein in its entirety.

[0037] Path **170** illustrates yet another method of obtaining triglycerides from chicken feathers. Chicken feathers are treated with urea and 2-mercaptoethanol, as described in Schrooyen et al., "Partially Carboxymethylated Feather Keratins. 2. Thermal and Mechanical Properties of Films," *J. Agric. Good Chem.* 49, 221-230 (2001), incorporated by reference herein. After solubilization, excess reagents can be removed through suitable means, such as dialysis.

[0038] A one step procedure **180** can be used to extract triglycerides and convert them to fatty acid esters. For example, the chicken feathers may be refluxed with an alcohol bearing the desired functional group, such as methanol, and an esterification reagent or catalyst, such as sodium hydroxide, ammonium hydroxide, or sodium methoxide. Although other esterification reagents or catalysts can be used, methoxide-based transesterification procedures can help reduce the nitrogen and sulfur content of the resulting biofuel.

[0039] The triglycerides **120** can be subjected to further processing steps prior to transesterification. For example, the triglycerides **120** can be washed to remove free fatty acids and

other materials. In some embodiments, the wash is carried out with an alcohol, such as methanol or ethanol, or acetic acid. Multiple washings can increase the amount of free fatty acid removed, thus increasing the pH towards neutral. In some embodiments, the triglycerides **120** are washed until the pH is sufficiently neutral, such as to a pH of at least about 6.7. Particularly when water sensitive materials are used in the subsequent transesterification step, the triglycerides **120** can be dried, such as using molecular sieves or similar materials, such as zeolites, silica gels, or acidic clays, or other drying agents, such as sodium sulfate, calcium chloride, magnesium sulfate, potassium carbonate, and calcium sulfate. If needed or desired, the pH of the triglycerides **120** can be adjusted, such as to a neutral pH, using standard methods, such as addition of an acid or base. The triglycerides **120** can be further purified or fractionated, such as using distillation, as described in U.S. Pat. No. 3,704,132, incorporated by reference herein.

[0040] After solvent removal or any other desired processing steps, the triglycerides **120** are converted to esters, useable as biofuel, in a transesterification process. Any suitable transesterification process may be used in the methods of the present disclosure, many of which are notoriously well known in the art. For example, a number of acid and base catalysts are disclosed in U.S. Pat. No. 5,424,420 and in Schuchardt et al., *J. Braz. Chem. Soc.*, 9(1), 199-210 (1998), each of which is incorporated by reference herein. FIG. 2 illustrates a number of methods for converting triglycerides **210** and fatty acids **215** to fatty acid esters **220**.

[0041] The hydrolysis processes described above, as well as the esterification and transesterification processes described below, can be carried out in the presence of mechanical mixing or ultrasonic treatment. Such treatment can, for example, aid in mixing the fatty acid or triglyceride with the alcohol, catalyst, other reagent or solvent, as triglycerides may be immiscible, or have limited miscibility, in the alcohol. Agitation may be accomplished by a paddle or blade stirrer attached to a motor, such as a motor operating at about 100 rpm to about 1000 rpm, such as about 300 rpm to about 700 rpm or about 400 rpm to about 600 rpm. Stirring may be accomplished by other means, such as using a magnetic stirring device, or other means of agitation used, such as a shaker.

[0042] In further embodiments, ultrasonication, optionally in combination with agitation, is applied during all or a portion of a hydrolysis, esterification, or transesterification process. Suitable ultrasonication devices are available from Hielscher Ultrasonics GmbH of Teltow, Germany and Branson Ultrasonics Corporation of Danbury, Conn. Ultrasonicators of any suitable power can be used, such as those having a frequency of 16-45 kHz, power 100-500 W, 20-400 mW/cm². Ultrasonication power and duration can be selected based on various factors, including the alcohol used for transesterification, the nature of the catalyst, the reaction temperature, and the process conditions of the reaction, such as whether the transesterification occurs as a batch or continuous process. For example, the reaction size or reactant flow rate may influence the power or duration of ultrasonication used.

[0043] Ultrasonication may have other benefits, such as reducing the reaction time and reducing the amount of catalyst or alcohol used in the esterification or transesterification. In some examples, ultrasonication is carried out while the reactants are under pressure, such as a gauge pressure of about 1 bar to about 3 bar.

[0044] The hydrolysis, esterification, and transesterification reactions may be carried out under any suitable conditions. In some methods the reactions are carried out at room temperature or higher, optionally in a pressurized vehicle, such as an autoclave. The use of higher temperatures and pressures may aid in solubilizing the components of the feedstock.

[0045] In typical esterification or transesterification reactions, an alcohol containing the desired substituent group is added to the free fatty acid or triglyceride. Such alcohols can be represented by R—OH, where R is the desired ester group, typically a short chain hydrocarbon, such as a C₁–C₄ hydrocarbon, which may be linear or branched. In more particular examples, the alcohol is methanol or ethanol. Alcohol is typically maintained in a stoichiometric excess, such as at a ratio of alcohol to triglyceride or free fatty acid of between about 3:1 and about 40:1, such as about 6:1 to about 12:1 or between about 9:1 and about 12:1. In a specific example, the ratio of alcohol to triglyceride or free fatty acid is about 9:1. In further examples, the transesterification or esterification mixture includes from about 20% to about 60% alcohol by volume.

[0046] In some embodiments, the transesterification is carried out in the presence of a cosolvent. A cosolvent may, for example, aid in mixing of the alcohol and triglyceride, which can enhance the reaction rate. Suitable cosolvents include pyridine, tetrahydrofuran, hexane, bis-(dimethylsilyl)trifluoroacetamide, and methyl tert-butyl ether.

[0047] With continuing reference to FIG. 2, in at least certain methods, transesterification is accomplished using acid **230** or base **240** catalysis, each of which is further described below. Base catalyzed transesterification **240** is typically better for relatively clean triglyceride sources, such as those which lack substantial amounts of free fatty acids and are relatively water-free. Base catalyzed transesterification is typically faster, more complete, and produces a higher purity product compared with acid catalyzed transesterification. However, acid catalysis **230** can be useful when the starting material is not well suited for the base catalyzed process **240**.

[0048] Transesterification process **230** is catalyzed using a catalytic amount of acid, which may be an organic acid, a mineral acid, or a Lewis acid. Suitable acids include aluminum chloride, benzyl sulfonic acid, boron trifluoride, dichloroacetic acid, hydrochloric acid, iodic acid, methanesulfonic acid, phosphoric acid, nitric acid, acetic acid, citric acid, malic acid, adipic acid, tartaric acid, fumaric acid, p-toluene sulfonic acid, stannic chloride, sulfonic acid, sulfuric acid, and trichloroacetic acid. In at least some examples, the acid or acids used to catalyze the transesterification have an acid dissociation constant (pK_a) of about 2 or less, such as about 1 or less.

[0049] Transesterification process **240** is carried out using a base catalyzed method, such as using organic bases, Lewis bases, or inorganic bases. Suitable base catalysts include alkali metal hydroxides, such as sodium hydroxide and potassium hydroxide, and alkaline earth metal oxides and hydroxides, such as magnesium oxide, calcium hydroxide, calcium oxide, barium hydroxide, and strontium hydroxide.

[0050] Transesterification also may be accomplished using a combination of base **240** and acid **230** catalysis. For example, a portion of the triglycerides may be transesterified using an acid catalyst and then a basic catalyst added to the reaction mixture. The basic catalyst is typically added in an amount sufficient to act as a catalyst for the transesterification

and an additional amount to neutralize the acid catalyst. Salts formed from the acid-base reaction can be removed following the transesterification, such as by washing the fatty acid ester with water. Suitable techniques for such acid/base catalyzed transesterification are described in U.S. Patent Publication US 2006/0094890, incorporated by reference herein.

[0051] A further transesterification method **250** involves treating the triglyceride with an alkoxide of a hydrocarbon alcohol having the desired ester group, such as methoxides or ethoxides. Methoxides are typically prepared from alkali metals, such as sodium and potassium. In particular examples, the transesterification is carried out using sodium methoxide. Alkoxides typically react with water and thus, in some implementations, the transesterification process **250** uses water-free or substantially water-free materials. Molecular sieves or similar materials, such as zeolites, silica gels, or acidic clays, or other drying agents, such as sodium sulfate, calcium chloride, magnesium sulfate, potassium carbonate, and calcium sulfate, may be included in the reaction vessel in order to help remove water from the reaction environment.

[0052] The transesterification reaction is carried out for a time sufficient to allow the reaction to reach a desired level of completion. The reaction time may vary based on the reactants (such as the catalyst and alcohol used) and the reaction conditions, including the temperature of the reaction and the nature of the reaction vessel. Typically, reaction is carried out for a period of about 1 minute to about 72 hours, such as between about 5 minutes and about 2 hours or between about 5 minutes and about 15 minutes. Reaction temperature is typically between about 10° C. and about 200° C., such as between about 25° C. and about 75° C. The reaction temperature may depend on the alcohol used, the reaction time, and other process conditions. For example, acid catalyzed transesterification can take substantially longer than base catalyzed methods, and are typically carried out at higher temperatures.

[0053] When the transesterification is catalyzed, a stoichiometric amount of catalyst is not needed. In particular examples, the amount of catalyst is from about 1 wt % to about 40 wt % based on the amount of triglyceride to be transesterified, such as between about 1 wt % and about 10 wt % or between about 1 wt % and about 2.5 wt %. For non-catalytic transesterifications, the amount of transesterification is typically included in at least a stoichiometric amount, and is added in stoichiometric excess in more particular examples.

[0054] In some implementations, excess catalyst is used to neutralize free fatty acids or other materials in the triglyceride. The presence of free fatty acids is determined, in some embodiments, by measuring the pH of the triglyceride. Acidic pH, such as less than about 6.7, can indicate the presence of free fatty acid. Catalyst, or other base, can be added, when base catalyzed transesterification is used, to neutralize the free fatty acid, such as adding base until the pH of the triglyceride is sufficiently neutral.

[0055] In further examples, other transesterification processes are used in place of or in addition to those discussed above. For example, transesterification can be carried out by enzymatic processes **260**. In addition, transesterification can be carried out using supercritical methanol **270**, such as at about 350° C. and about 35 Mpa. Supercritical methanol transesterification is typically complete in a relatively short time, such as about 4 minutes. Transesterification using supercritical methanol can be advantageous as it does not

typically require acid or base and can thus simplify subsequent purification or processing steps. Suitable techniques for enzymatic processes **260** and supercritical methanol processes **270** are described in Marchetti et al., "Possible Methods for Biodiesel Production," *Renewable and Sustainable Energy Reviews* 11 1300-1311 (2007) and references cited therein, each of which is incorporated by reference herein.

[0056] When free fatty acids **215** are used to produce biofuel, Fischer esterification **280** using an acid catalyst and an appropriate alcohol is typically employed. For example, the free fatty acids **215** may be refluxed in methanol with a catalytic amount of acid, which is typically a mineral acid such as HCl or H₂SO₄, although other acid catalysts may be used. The reaction is allowed to proceed until a desired degree of esterification has been reached, such as between about 5 minutes and about 24 hours, such as about 8 hours. Molecular sieves or similar materials, such as zeolites, silica gels, or acidic clays, or other drying agents, such as sodium sulfate, calcium chloride, magnesium sulfate, potassium carbonate, and calcium sulfate, may be included in the reaction vessel in order to help remove water from the reaction environment and help drive the reaction to completion.

[0057] In some cases, it may be desirable to convert free fatty acids to glycerides, such as mono-, di-, or tri-glycerides before converting the feedstock to fatty acid esters. This can be accomplished using glycerolysis step **290**. Glycerolysis can be performed according to any suitable method. Suitable enzymatic methods are described in Fadiloglu et al., "Reduction of Free Fatty Acid Content of Olive-Pomace Oil by Enzymatic Glycerolysis," *Food Science and Technology International* 9(1) 11-15 (2003) and Damstrup et al., "Process Development of Continuous Glycerolysis in an Immobilized Enzyme-Packed Reactor for Industrial Monoacylglycerol Production," *Journal of Agricultural and Food Chemistry* A-G (Aug. 23, 2007), each of which is incorporated by reference herein. Glycerolysis may also be accomplished by adding glycerol to the free fatty acids and heating the mixture to a relatively high temperature, such as above about 200° C., such as about 250° C. to about 260° C. Addition of a suitable catalyst, such as zinc powder or zinc chloride, can decrease the needed temperature or reaction time. Once the free fatty acids have been converted to glycerides, the glycerides may be transesterified using the techniques shown in FIG. 2 and described above.

[0058] Although adding additional steps to the biofuel production process, glycerolysis of the free fatty acids can provide a number of advantages. For example, base catalyzed, or other non-acidic transesterification processes can be easier to implement on an industrial scale, as they can be less prone to corrode process equipment. In addition, once triglycerides are formed from the free fatty acids, the chicken feather triglycerides can be combined with other feedstocks in a transesterification process. Another potential advantage of transesterification is that yields from transesterification processes, such as base catalyzed transesterification, can be higher than Fisher esterification of free fatty acids.

[0059] After the transesterification or esterification reaction has reached a desired level of completion, the fatty acid ester product is separated from reactants and reaction byproducts in a separation process. In some implementations, the products can be neutralized, such as by an acidic wash when a basic catalyst is used in the transesterification or a basic wash when acid catalyst is used. Washing with water, such as

hot water, can also be used to remove undesired materials, such as acid, from the reaction products.

[0060] Upon standing, such as for about 12, about 24, about 36, about 48, or about 72 hours, or more, one or more layers may form, such as a fatty acid ester layer, a layer which includes soaps, such as glycerin, and a layer that includes other components, such as water, salts, and unreacted alcohol. Various processes may be used to remove the desired layer or layers, such as decantation, draining at the appropriate level, or sequential removal of layers.

[0061] Depending on the processes and materials used in the esterification or transesterification, separation of the layers may be difficult or take longer than desired. Therefore, in some examples, gravity separation devices are used to aid in separating components of the reaction products. The term gravity separator, as used herein, refers to devices which separate materials based on density (specific gravity). Suitable gravity separation devices include separatory funnels, hydrocyclones, and centrifuges. Ultrasonication can also aid in layer separation.

[0062] In further embodiments, the fatty acid ester product is extracted with an organic solvent, which in some embodiments is selected as described above for extraction of triglycerides. In particular examples, the solvent is diethyl ether or hexane. Solvent extraction may take place after other steps, such as neutralization, as described above. Solvent extraction of the fatty acid ester may produce a more pure product.

[0063] Glycerin formed from the transesterification process, and isolated during the separation process, can be further isolated, purified, and put to other beneficial uses. For example, glycerin is used in foods, plastics, lacquers, pharmaceuticals, toothpastes, tobacco, resins, cosmetics, cellulose processing, and explosives.

[0064] After separation, the fatty acid ester can be further purified or treated. For example, the fatty acid ester can be neutralized, particularly if neutralization was not carried out during the separation process. When transesterification is carried out using a base or alkoxide, neutralization is typically carried out by washing the fatty acid ester product with one or more dilute acids, such as an aqueous solution of a dilute acid. Suitable acids include organic, inorganic, and Lewis acids, such as tannic acid, citric acid, salicylic acid, malic acid, maleic acid, acetic acid, salicylic acid, and hydrochloric acid. In a particular example, a neutralization solution is used in an amount of between about 20 vol % to about 40 vol % by volume of the amount of raw triglyceride material used in the transesterification reaction. Acid is added to this neutralization solution, in some embodiments, having a concentration of about 0.1 mM to about a 1 M, such as between about 0.5 mM to about 50 mM.

[0065] Correspondingly, a basic wash can be used to neutralize the product of an acid catalyzed transesterification or esterification. Mineral, organic, or other suitable bases, such as Lewis bases, can be used for the neutralization, such as alkaline and alkaline earth metal hydroxides, such as sodium hydroxide or potassium hydroxide.

[0066] Additional purification steps can be performed on the crude fatty acid ester in order to make it more suitable as a biofuel. For example, the fatty acid ester can be treated with activated carbon or other substances to remove impurities from the product. Additional water washes can be performed on the fatty acid ester, such as to remove residual salts, catalyst, alcohol, or soaps. The fatty acid ester product can also be dried, such as using molecular sieves or similar materials,

such as zeolites, silica gels, or acidic clays, or other drying agents, such as sodium sulfate, calcium chloride, magnesium sulfate, potassium carbonate, and calcium sulfate. The product can also be fractionated to remove impurities or isolate different fuel fractions.

[0067] In particular methods, the biofuel resulting from the disclosed methods conforms to the Avian Biodiesel (ABD-06) standard. According to some aspects of the present disclosure, biofuels produced according to the disclosed methods are mixed with other fuels, including biofuels obtained from other sources. For example, the disclosed fuels may be mixed with biofuels obtained from plant oils, including vegetable oils, such as soybean oil or rapeseed oil, oil from coffee beans, or from animal fats (including chicken fat).

[0068] In yet further embodiments, the feedstock, such as chicken feathers, is mixed with another biofuel feedstock, such as plant oils, such as vegetable oils, including soybean oil or rapeseed oil, coffee beans, or animal fat, and the combined feedstock is converted to biofuel. In some implementations the combined feedstock is treated with alkali and the resulting product transesterified to produce a biofuel. In at least some implementations, the use of such a combined feedstock can enhance biofuel production or increase the quality (or otherwise adjust the properties of) the resulting biofuel.

[0069] In order to enhance the stability or firing properties of the resulting biofuel, various additives can be added to the biofuel produced according to the disclosed methods. For example, antioxidants or other stabilizers can be added to the biofuel. Suitable antioxidants and stabilizers include 2,6-di-tert-butyl-4-methylphenol, BIOSINEOX (available from Antioxidants Aromas and Fine Chemicals (Pty) Ltd. of Richards Bay, South Africa), tocopherols, pyrogallol, propylgalate, tert-Butylhydroquinone, and ETHANOX (available from Albemarle Corporation of Pasadena, Tex.).

EXAMPLES

Example 1

[0070] In the present Example, chicken feathers were crushed in a vibrated mill to produce fine size fibrous materials. The fibrous material was conditioned with NaOH for an extended time at room temperature. The hydrolyzed product was mixed with freshly prepared methoxide (methanol plus NaOH). The mixed product was conditioned for 24 hours. A schematic of the process is shown in FIG. 3.

[0071] Two layers formed after the 24 hour conditioning period. The top fraction was a clear biofuel material corresponding to esterified products. The lower thick layer included glycerin and other substances. The top layer was analyzed using High Pressure Liquid Chromatography (HPLC) to determine the quality of biofuel fraction. The resulting chromatogram, shown in FIG. 4, illustrates that the biodiesel was of good quality.

Example 2

[0072] In this Example, chicken feathers were mixed in a pressurized autoclave in the presence of water and NaOH. The mixed product was heated at 60-70° C. (external temperature 200-300° C.) for 20-30 minutes. After that time, the hydrolyzed and dissolved product was mixed with sodium methoxide (methanol and NaOH) for several hours at 60-70° C. The mixture was then cooled to room temperature. A good

and high quality biofuel (esterified product) was noticed. The presence of biofuel was confirmed by HPLC.

Example 3

[0073] In this Example chicken feathers were mixed with methanol to which sodium hydroxide was added. The mixture was conditioned for several hours. After conditioning, sodium methoxide was added. The resulting mixture was mixed for a long time at 25-60° C. The product was then cooled to room temperature. A clean biofuel layer (esterified product) and glycerin layer were observed. The biofuel layer was analyzed by HPLC, confirming the formation of a high quality biofuel oil.

Example 4

[0074] In this Example, chicken feathers were mixed with alkaline media, consisting of sodium hydroxide and water. The mixture was ultrasonically treated. The hydroxide product was then treated with freshly prepared sodium methoxide for a long time at a temperature of 25-70° C. After cooling, a biofuel layer was obtained. The oil layer was washed several times. The oil was determined to be of high quality.

Example 5

[0075] In this Example, chicken feathers were mixed with ammonium hydroxide. The mixture was allowed to stand for an extended time. The hydrolyzed product was then mixed with freshly prepared ammonium methoxide for an extended period of time. The mixture was then allowed to settle for about 24 hours. Water was added to help settle the layers.

[0076] Three different layers were observed. The upper layer was oil corresponding to esterified products. The middle layer contained water plus oil. The lower layer contained glycerin and other products. HPLC analysis confirmed that the top oil layer consisted of high quality oil.

Example 6

[0077] In this Example, chicken feathers were mixed with water and sodium hydroxide. The mixture was refluxed for 2-24 hours. The hydrolysis product was neutralized with hydrochloric acid. Some of the free sulfur groups in cysteines were converted into hydrogen sulfide, which evolved during the neutralization process. Fatty acids were extracted with ether (dichloromethane, chloroform or a 5% solution of methanol in dichloromethane can also be used for extraction). Three different layers were observed. The upper layer was ether containing fatty acids, the middle layer was polypeptides, and the lower layer was water containing free amino acids. The fatty acids were collected from the top layer (ether) by evaporating the solvent under vacuum. Fatty acids were refluxed with methanol in presence of an acid (e.g. HCl, H₂SO₄, etc.). The quality of the biodiesel produced was measured using HPLC, the results of which are shown in FIG. 5. The product was also analyzed by FTIR, which, as shown in FIG. 6, indicates the presence of the ester group and the hydrocarbon chains. The composition of the methyl esters of fatty acids was analyzed by GC-MS. Retention times and corresponding esters structure are shown in FIG. 7.

Example 7

[0078] In this Example, chicken feathers were hydrolyzed by refluxing with hydrochloric acid for 6 hours. Fatty acids

were extracted using ether (dichloromethane, chloroform or 5% solution of methanol in dichloromethane can also be used for extraction). Three different layers were observed. The upper layer was ether containing fatty acids, the middle layer was polypeptides, and the lower layer was water containing free amino acids and glycerin. Fatty acids were obtained from layer one by evaporating the solvent under vacuum. Fatty acids were then refluxed with methanol in the presence of concentrated sulfuric acid (acid catalyzed esterification) to produce biodiesel.

Example 8

[0079] In this Example, chicken feathers were hydrolyzed by refluxing with methanol and sodium hydroxide for 2-12 hours. Methanol was evaporated and fatty acids were extracted with diethyl ether (dichloromethane, chloroform or 5% solution of methanol in dichloromethane can also be used for extraction). Fatty acids were then refluxed with methanol in the presence of concentrated sulfuric acid (acid catalyzed esterification) to produce biodiesel. A photograph of the biodiesel in methanol obtained from chicken feathers is shown in FIG. 8.

[0080] It is to be understood that the above discussion provides a detailed description of various embodiments. The above descriptions will enable those skilled in the art to make many departures from the particular examples described above to provide apparatuses constructed in accordance with the present disclosure. The embodiments are illustrative, and not intended to limit the scope of the present disclosure. The scope of the present disclosure is rather to be determined by the scope of the claims as issued and equivalents thereto.

What is claimed is:

1. A method of producing biofuel comprising:
obtaining a biological material, the biological material comprising protein and triglycerides;
hydrolyzing the biological material to obtain free amino acids and a biofuel feedstock; and
converting the biofuel feedstock to fatty acid esters.
2. The method of claim 1, wherein the biological material comprises feathers.
3. The method of claim 1, wherein the biological material comprises poultry feathers.
4. The method of claim 1, wherein the biological material comprises chicken feathers.
5. The method of claim 1, wherein the biological material comprises feathers obtained from a poultry processing operation.

6. The method of claim 1, wherein hydrolyzing the biological material comprises treating the biological material with a base.

7. The method of claim 1, further comprising extracting the biofuel feedstock from the hydrolyzed material using an organic solvent.

8. The method of claim 7, wherein the organic solvent comprises at least one of diethyl ether, dichloromethane, and methanol.

9. The method of claim 7, wherein the biofuel feedstock comprises triglycerides and converting the biofuel feedstock to fatty acid esters comprises a base catalyzed transesterification.

10. The method of claim 7, wherein the biofuel feedstock comprises triglycerides and converting the biofuel feedstock to fatty acid esters comprises an acid catalyzed transesterification.

11. The method of claim 7, wherein the biofuel feedstock comprises triglycerides and converting the biofuel feedstock to fatty acid esters comprises treating the triglycerides with a methoxide.

12. The method of claim 1, wherein the biofuel feedstock comprises at least one of free fatty acids and triglycerides.

13. The method of claim 1, wherein the biofuel feedstock comprises free fatty acids and converting the biofuel to fatty acid esters comprises an acid catalyzed esterification.

14. The method of claim 1, wherein the biofuel feedstock comprises free fatty acids, further comprising converting the free fatty acids to glycerides and wherein converting the biofuel feedstock to fatty acid esters comprises transesterifying the glycerides.

15. The method of claim 1, further comprising adding the fatty acid esters to a biofuel derived from another source.

16. The method of claim 1, further comprising adding a stabilizer to the fatty acid esters.

17. The method of claim 16, wherein the stabilizer comprises an antioxidant.

18. A biofuel produced from the fatty acid esters of claim 1.

19. A method of producing biofuel comprising:
obtaining chicken feathers produced from a chicken processing operation;
comminuting the chicken feathers;
hydrolyzing the chicken feathers to obtain triglycerides;
transesterifying the triglycerides to obtain a biofuel; and
extracting the triglycerides or the biofuel with an organic solvent.

20. The method of claim 19, further comprising blending the biofuel with another fuel.

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