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ABSTRACT

A method for production of alkyl esters from a mixture of glycerides and free fatty acids, originating primarily from grease trap waste, is provided.

The mixture is first solvated in a low boiling point alcohol and then the pH of the solution is adjusted to about 2 by addition of an acid to effect acid-catalysed alkyl esterification. The acidic solution is then treated with a concentrated alkoxide solution to raise the pH of the solution to about pH12 to effect base-catalysed transesterification of glycerides contained in the mixture. The resulting solution is then treated with an acid to decrease the pH of the solution to about 2 to effect acid-catalysed esterification of residual saponified by-products.

The alcohol solvent is removed by distillation and the resulting alkyl esters are separated from any remaining residues.

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The following Statement is a full description of this invention including the best method of performing it known to us:

METHOD FOR PRODUCTION OF ALKYL ESTERS

"METHOD FOR PRODUCTION OF ALKYL ESTERS "

The present invention relates to a method for production of alkyl esters from mixtures of glycerides and free fatty acids, in particular mixtures of glycerides and free fatty acids from grease trap waste, tallows, animal fats and other high fatty acid content lipids. In addition to these lipids it has been found to be very effective in efficiently producing alkyl esters from lower fatty acid, higher glyceride content lipids.

Alkyl esters of fatty acids found in natural lipids, commonly known as biodiesel, are becoming increasingly recognised as viable fuel alternatives for diesel engines. They are known to reduce the output of particulate, hydrocarbon pollutants and improve the lubrication of diesel engines. Biodiesel may also be successfully used as a lubricant, a hydraulic fluid and as a multi-purpose solvent.

Furthermore, biodiesel is attractive from a commercial and environmental viewpoint because the raw materials may be sourced from renewable oilseed feedstocks, used vegetable oils, palm oil, coconut oil, soapstock materials as a lipid-rich byproduct of vegetable oil refining, tallows, animal fats, or from grease trap waste which would normally be disposed of in land fill.

The widespread adoption of biodiesel as an alternative to petroleum-based diesel fuel is hampered by inefficient methods for the production of biodiesel. Known methods for the production of biodiesel are limited by incomplete esterification of all fatty acids in the starting material, lengthy purification methods such as water washing, relatively long reaction times, contamination and separation difficulties associated with co-production of glycerol, and saponification of the starting material under certain reaction conditions.

The Boocock method for formation of methyl esters from vegetable oils has sought to accelerate reaction times for a two-step acid then base-catalysed methanolysis of vegetable oils by forming a single phase reaction mixture using a cosolvent such as tetrahydrofuran (THF) or methyltetrabutylether (MTBE). Boocock reports that a 99% recovery of methyl ester is achieved with this method. Glycerol is a byproduct and the resultant alkyl ester normally requires extensive purification including water washing of the alkyl ester.

The Haas *et al* method for synthesis of fatty acid methyl esters from soapstock involves another two-step process wherein the soapstock is first saponified and then esterified in an acidic alcohol solution. Haas *et al* reports that a 60% recovery of fatty acid methyl ester is achieved with this method. The method is characterised, however, by high consumption of the reagents.

The present invention attempts to overcome at least in part some of the aforementioned disadvantages.

In accordance with a first aspect of the present invention there is provided a method for production of alkyl esters from a mixture of glycerides and free fatty acids, comprising:

a) addition of an acid to an alcoholic solution of the mixture to decrease the pH of the solution to about 2 to effect acid-catalysed alkyl esterification;

b) treatment of the solution from step a) with a concentrated alkoxide solution to raise the pH of the solution to about 12 to effect base-catalysed transesterification of glycerides contained in the mixture;

c) treatment of the solution from step b) with an acid to decrease the pH of the solution to about 2 to effect acid-catalysed esterification of residual saponified by-products from step b);

d) distillation of the solution from step c) to remove alcohol; and

e) separation of resulting alkyl esters.

The present invention describes a method for reacting a mixture of free fatty acids and glycerides, commonly found in grease trap waste, tallows, animal fats, palm oil, coconut oil, and other naturally occurring lipids, including waste or fresh unused vegetable oils and tallows with short-chain alcohols such as methanol, ethanol, propanol, or butanol to produce corresponding alkyl esters.

It will be understood that grease trap waste encompasses a highly variable mixture of organic fats, greases and vegetable oils, comprising a high free fatty acid and mono-, di-, and triglyceride content, contaminated by detergents, soaps, inorganic and particulate matter. Throughout this specification the term total free fatty acid content (FFA) will be taken to mean the total content of free fatty acids and mono-, di-, and triglycerides comprised in grease trap waste, tallows, animal fats, and other naturally occurring lipids, and available for alkyl esterification. Typically, the grease trap waste is between 80 to 100% total free fatty acid content.

The alcohol includes low-boiling point alcohols, preferably methanol, ethanol, propanol, and butanol in their single-chain and isomerised forms. However, it is envisaged that longer-chain alcohols can be utilised in a similar fashion in accordance with the present invention.

A mixture of free fatty acids and glycerides, in the form of grease trap waste, tallows, animal fats, and other naturally occurring lipids, is mixed and agitated in the alcohol to form a miscible single-phase alcoholic solution of the mixture.

Depending on the composition of the mixture, occasionally an immiscible suspension of lipids may form in the alcohol. In this case, the suspension is continually agitated to prevent separation of the lipid and alcohol into two distinct phases. For the purposes of the invention, the agitated suspension is to be regarded and treated as an alcoholic solution of the mixture of lipids and glycerides.

Neither type of mixture is dependent on, or requires a co-solvent in the process. However, use of such co-solvents will not impair the reaction or its final alkyl ester product. Co-solvent usage may marginally increase the reaction rate but the reaction is quite rapid and goes to completion in the absence of co-solvent.

Preferably, the mixture of free fatty acids and glycerides is dissolved in a similar volume of alcohol to afford about 50% v/v alcoholic solution of the mixture. In this way, the alcohol is in molar excess of the total free fatty acid content, preferably in a range of 1:10 to 1:25.

The reaction proceeds satisfactorily with a lesser proportion of alcohol to lipids, however the reaction proceeds optimally at about 50% v/v.

Certain mixtures of free fatty acids and glycerides, such as tallow and vegetable oils, may not form a single-phase alcoholic solution. However, vigorous stirring of the two-phase homogeneous solution throughout the reaction procedure effects similar results with regard to alkyl ester production. Grease trap waste grease has been shown to readily dissolve in alcohol.

The alcoholic solution of the mixture is first treated with an acid catalyst to effect acid-catalysed alkyl esterification, then treated with a base catalyst to effect base-catalysed transesterification of glycerides contained in the mixture. The resulting reaction mixture is finally treated with an acid catalyst to effect acid-catalysed alkyl esterification of residual saponified by-products resulting from the previous treatment steps.

Preferably, the acid-catalysed esterification and base-catalysed transesterification steps are performed under reflux conditions, although said steps may also be performed at ambient temperatures, albeit with longer reaction times.

The method of the present invention is preferably performed at ambient atmospheric pressure. However, it is envisaged that said method can be successfully performed under higher pressures with use of a pressure vessel, or under autoclave conditions.

Acid catalysts include, but are not limited to, concentrated strong inorganic acids such as sulphuric acid, hydrochloric acid, phosphoric acid, and perchloric acid. Preferably, the ratio of added acid-catalyst to total fatty acid content is about 1:20 in the first acid-catalysed alkyl esterification reaction step, and about 1:5 in the second acid-catalysed esterification reaction step.

Base catalysts include, but are not limited to, alcoholic solutions of sodium hydroxide and/or potassium hydroxide, or sodium or potassium dissolved in the short-chain alcohol of choice. Preferably, a 10% w/w alkali metal alkoxide solution is used as the base catalyst, such that the ratio of added base-catalyst to total fatty acid content is about 1:5.

The alcohol is removed from the resulting reaction mixture by distillation, with or without vacuum assistance, leaving a two-phase heterogeneous mixture of alkyl esters and a solid phase. The alkyl esters are separated from the solid phase by decantation, and further purified by filtration or separated by filtration alone.

Once the alcohol has been removed from the reaction mixture by distillation, or the alkyl ester has been separated from the solid phase by decantation, the alkyl ester can be treated with a weak base to effectively neutralise residual acid remaining in the alky ester phase. It is envisaged that the pH of the alkyl ester phase will be neutralised to about pH 6-7.

The neturalisation step is achieved by addition of small amounts of sodium bicarbonate to the alkyl ester phase. It is envisaged that other well known means for neutralising pH such as elution of the liquid phase through an ion exchange resin, can be successfully employed to effect neutralisation of residual acid within the alkyl ester phase.

Residual water can then be removed by conventional means such as passing the alkyl ester phase over a hygrosopic dessicant or by heating the alkyl ester sufficiently to remove steam at atmospheric pressures or under vacuum.

Depending on the final intended use of the alkyl ester, a small amount of entrained water may be acceptable and its removal may not be necessary.

Surprisingly, the inventors have found that the alkyl esters produced by the method of the present invention remain uncontaminated by glycerol byproducts from the acid-catalysed esterification and base-catalysed transesterification reactions. An exception was found from the treatment of fresh unused vegetable oil whereby a small quantity of good quality glycerol was readily separated. The amount of glycerol byproduct was at less than 8% of the starting oil and noticeably less than the amount generated by other esterification methods. No noticeable glycerol production occurred when treating other lipids such as palm oil, coconut oil, animal tallow or grease trap waste.

The present invention will now be illustrated according to the following example.

Example

A single phase 1:1 v/v methanolic solution of grease trap waste (800 ml) in methanol (800 ml) was prepared. A GC/MS analysis of the grease trap waste indicated that the major components of the grease trap waste were octadecanoic acid and *n*-hexadecanoic acid. The pH of the methanolic solution of grease trap waste was 4, reflecting a high fatty acid content.

Concentrated sulphuric acid (98%) (8.5 g) was added with stirring to the methanolic solution resulting in a solution pH of between 1 and 2. The methanolic solution was refluxed for 30 minutes.

A sodium methoxide solution of 10% w/w NaOH in methanol (160 ml) was then added dropwise to the stirred refluxing methanolic solution resulting in a final pH of 12.

Concentrated sulphuric acid (98%) (21 ml) was added dropwise to the stirred refluxing methanolic solution resulting in a final pH of 2.

Excess methanol was removed by distillation. The resulting methyl esters (825 ml) were separated from a semi solid basal residue (64.5 g) by decantation, and finally filtered to remove fine sediment. It was estimated that there was a better than 91% conversion of waste trap grease to methyl esters.

A similar amount of grease trap waste was treated according to the present invention as described in the abovementioned Example wherein ethanol, rather than methanol, was used as the solvent. It was found that a similar degree of conversion of the grease trap waste to corresponding ethyl esters was achieved.

Furthermore, similar experiments using a potassium alkoxide solution rather than a sodium hydroxide solution produced similar results as those exemplified in the abovementioned Example.

Although the residual sediment formed from the reaction mixture using ethanol and potassium hydroxide was less crustiform than the sediment described in the Example, it was readily separated from the ethyl esters by filtration.

On testing, the crustiform residue was found to comprise mostly sodium sulphate with minor entrained methyl ester that totalled 9% by weight of the starting grease trap waste. The conversion of grease trap waste to methyl ester therefore exceeded 91%. The entire processing time to final product alkyl ester is less than 1 hour.

It is a rapid and efficient process and method that can be made even faster by increasing reaction kinetics by many well known methods including increased heat, pressure and agitation.

The final product alkyl ester does not require water washing thereby eliminating a major processing step common to other methods that is both time consuming and polluting. Glycerol byproduction is eliminated in most lipid feedstocks tested. The method and process permits design of commercial plants that should be low in capital cost, small in size, with high production rates and be portable as truck mounted, trailer-coupled units, or as a static plant.

Modifications and variations as would be apparent to a skilled addressee are deemed to be within the scope of the present invention. The process and method allows the alkylesterification of various stated lipids.

CLAIMS

1. A method for production of alkyl esters from a mixture of glycerides and free fatty acids, comprising:

a) addition of an acid to an alcoholic solution of the mixture to decrease the pH of the solution to about 2 to effect acid-catalysed alkyl esterification;

b) treatment of the solution step a) with a concentrated alkoxide solution to raise the pH of the solution to about 12 to effect base-catalysed transesterification of glycerides contained in the mixture;

c) treatment of the solution from step b) with an acid to decrease the pH of the solution to about 2 to effect acid-catalysed esterification of residual saponified by-products from step b);

d) distillation of the solution from step c) to remove alcohol; and

e) separation of resulting alkyl esters.

2. The method according to claim 1, wherein the alcoholic solution of the mixture is formed by dissolving the mixture of glycerides and free fatty acids in a similar volume of alcohol to afford about 50% v/v alcoholic solution of the mixture.

3. The method according to claim 2, wherein the alcohol has a low-boiling point.

4. The method according to claim 3, wherein the alcohol is selected from a group comprising methanol, ethanol, propanol, and butanol, including *n*-propyl alcohol, *n*-butyl alcohol, isopropyl alcohol, isobutyl alcohol, *sec*-butyl alcohol, *t*-butyl alcohol.

5. The method according to any one of the preceding claims, wherein step a) is performed under reflux conditions.

6. The method according to any one of the preceding claims, wherein step b) is performed under reflux conditions.

7. The method according to any one of the preceding claims, wherein the acid is a strong inorganic acid including but not limited to sulphuric acid, hydrochloric acid, phosphoric acid, perchloric acid and mixtures thereof.

8. The method according to any one of the preceding claims, wherein the concentrated alkoxide solution comprises sodium and/or potassium hydroxide dissolved in the alcohol used in step a), or sodium or potassium dissolved in the alcohol used in step a).

9. The method according to claim 8, wherein the concentrated alkoxide solution comprises a 10% w/w alkali metal alkoxide solution.

10. The method according to any one of the preceding claims, wherein any residual acid remaining in the solution resulting from step d) or the alkyl ester resulting from step e) is neutralised to about pH 6 - 7 by treating the solution or the alkyl ester with a weak base.

DATED THIS 31ST DAY OF MAY 2002.

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