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(54) PROCESS FOR CONVERSION OF LOW COST AND HIGH FFA OILS TO BIODIESEL

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(57) ABSTRACT

The present invention describes a process for converting high free fatty acid containing feed stocks (FFA 20-85%) like palm fatty acid distillate (PFAD), restaurant grease, waste cooking oil, Soya deodistillate, acid oil, jatropha curcas oil, mohua oil etc. to biodiesel, which involves esterification of FFA containing oil with lower alcohols like methanol, ethanol, propanol etc. in presence of macro reticular and gel type acidic heterogenous resin as catalyst to bring down acid value in the range of 1-2 mgKOH/g followed by transesterification in presence of homogeneous basic catalyst metal oxides, hydroxides and alkoxides like sodium hydroxide, potassium hydroxide, sodium methoxide, potassium methoxide etc. and separation of biodiesel and glycerine.

PROCESS FOR CONVERSION OF LOW COST AND HIGH FFA OILS TO BIODIESEL

FIELD OF INVENTION

[0001] The present invention relates to a process for conversion of low cost and high free fatty acid (FFA) oils to biodiesel. The present invention particularly relates to a process of converting high FFA containing feed stocks (FFA 20-85%) to biodiesel in the presence of macro reticular and gel type acidic heterogeneous resin followed by transesterification in presence of homogeneous basic catalyst and separation of biodiesel and glycerine.

BACKGROUND OF THE INVENTION

[0002] Vegetable oil or fat is generally obtained by extraction or pressing natural seeds. Vegetable oil usually contains free fatty acids, phospholipids, sterols, water, tocopherols and other impurities. While as Palm fatty acid distillate (PFAD), Soya deodistillate, acid oil, are obtained as byproducts during refining of Palm oil or soya oil. These oils are mainly low cost material containing FFA in the range of 20-85%, while as restaurant grease is the waste oil collecting in grease traps from Kitchens of hotels and restaurants.

[0003] Vegetable seed oils have about 90% of the heat content of petroleum based diesel fuel and a favorable energy output/input ratio and, therefore, have the potential to replace congenital diesel fuel for compression ignition engines.

[0004] The vegetable oils have another advantage as these have high cetane number up to 50. Added advantage of ~10 Cetane number is further obtained when vegetable oils are converted to methyl/ethyl monoesters. Thus these esters, with viscosity, boiling point and heat values in the range of diesel fuel and higher cetane number, have an advantage over the use of vegetable oils, as such. Therefore, these can be used as high cetane number blending components to the diesel fuel.

[0005] The most common catalysts used for transesterification of vegetable oils to produce biodiesel include alkali, acids and enzymes. The alkali includes NaOH, KOH, sodium and potassium alkoxides such as sodium methoxide, potassium methoxide. Generally used acid catalysts are sulfuric acid, phosphoric acid, hydrochloric acid and sulfonic acids. Among the biocatalyst lipase can be used for transesterification. With alkaline catalysts, the free fatty acid and water contents in the oil or fats significantly affect the transesterification by deactivating the catalyst and interfering with the separation of fatty acid esters and glycerol and for acidic catalyst e.g. H_2SO_4 large quantity of alkali is used to neutralize the mineral acids and hence the disposal problems.

[0006] Reference may be made to Patent No. W09115452 where in, they described fatty acid alkyl esters are produced by catalytic transesterification of a vegetable oil using alkaline earth metal calcium, (Ca), or compounds thereof, at normal atmospheric pressure and normal room temperature below 50° C.,

[0007] Reference may be made to CA Patent No. 2,316,141 where in, they described a process comprises forming a single phase solution of said triglyceride in an alcohol selected from methanol and ethanol, the ratio of alcohol to triglyceride being 15:1 to 35:1. The solution further comprises a co-solvent in an amount to effect formation of a single phase and a base catalyst for the esterification reaction. After a period of time, ester is recovered from the solution. Esterification is rapid and proceeds essentially to completion. The esters may be used as biofuel or biodiesel.

[0008] Reference may be made to Patent No. WO 2005/052103A1 where in, they discloses a process for the preparation of biodiesel, whereby oil is subjected to catalytical transesterification, settling, separation, bubble washing and micro filteration under controlled conditions of temperature and turbulence. The process enables production of high quality fuel, termed as biodiesel within a period of as low as 50 hrs.

[0009] Reference may be made to US Patent No. 20060058540 where in, they discloses a process for the preparation of fatty acid esters from fats and oils of biological origin by transesterification with monohydric alcohols in presence of basic catalyst, the catalyst using salts of basic organic compound and carbonic acid e.g. guanidine.

[0010] Reference may be made to U.S. Pat. No. 6,440,057 where in, they described a method for producing fatty acid methyl ester, compounding saturated and unsaturated higher fatty substances from atleast one of vegetable and animal fat with an alkaline solution of potassium dissolved in alcohol to form a mixture. The method also includes emulsifying the mixture to reach a chemical balance state in a reaction section. The method further includes after reacting a chemical balance state, separating residues from the fatty acid methyl ester in a phase separation.

[0011] Reference may be made to Patent No. WO 00/05327/PCT/US99/16669 where in, they described a process producing alkyl esters useful in biofuel and lubricant by transesterifying glyceride or esterifying free fatty acid containing substance in a critical phase medium providing increased reaction rates, decreased loss of catalyst or catalyst activity and improved overall yield of desired product. Reaction temperatures arc typically in the range from about 20 to 200 degrees with reaction pressures in the range of about 150 psig to 400 psig.

[0012] Reference may be made to U.S. Pat. No. 5,424,466 where in, they described an improved process for the production of esters from fatty substances having a natural origin and low molecular weight alcohols, in which the soaps and only compounds entrained in the alkaline phases are recycled by treating them, following acidification and separation, with a fraction of the glycerol phase produced, in the presence of an alkaline catalyst and for forming preferably a triglyceride or a partially substituted glyceride.

[0013] Reference may be made to U.S. Pat. No. 4,303,590 where in, they discloses principle of two step alcoholysis reaction and the product obtained in the first step is separated from the by-product glycerine and then subjected to the second alcoholysis reaction followed by admixing of an appropriate amount of water and phase separation so that the undesirable impurities transfer into the aqueous layer and readily separated from the ester product.

[0014] Reference may be made to U.S. Pat. No. 4,164,506 where in, they discloses a two step process in which esters of fatty acids are produced by esterifying free fatty acids of unrefined fats with a lower alcohol in presence of an acid catalyst e.g H_2SO_4 separating the product mixture into fat layer and the lower alcohol layer and then inter esterification reaction between the resulting refined fats and a lower alcohol with an alkali catalyst.

[0015] Reference may be made to U.S. Pat. No. 5,399,731 where in, they described fatty acid esters of lower monovalent alcohols by transesterification of fatty acid glycerides in the presence of basic catalyst e.g. sodium hydroxide. They claim the addition of alkali for neutralization of excess of FFA to lower the acid value.

[0016] Reference may be made to US Patent application 20060069274 wherein, they described an industrial production process for ethyl ester (biodiesel) through two separate reactions, in two steps: 1) hydrolysis of glyceryl esters from vegetable oils at an approximate temperature of 60° C., at atm pressure splitting the glycerol esters in free fatty acids and glycerol and esterification of free fatty acids with hydrated ethyl alcohol. The reaction occurs in two separate columns each 1.0 meter high and packed with heterogeneous catalyst calcium and magnesium (Cao. Mgo) stones, each 1⁄15 the size of the column diameter. The patent claims of a continuous process for ethyl ester production.

[0017] Reference may be made to U.S. Pat. No. 5,514,820 where in, they claimed a continuous process for the production of lower alkyl esters at temperatures up to 100° C. and under pressure of upto 10 bar by reaction of fatty acid triglyceride containing less than 1% free fatty acid with a lower alcohol in two stages in the presence of homogeneous alkaline catalyst, the glycerol formed being removed after the first stage to enable the process to be carried out with high yields and with lower maintenance.

[0018] Reference may be made to Austria Pat. No. 388743B and U.S. Pat. No. 386222 where in, they described the transesterification take place with a suitable monohydric alcohol in the presence of a basic transesterification catalyst. After removal of glycerol phase which contains the free fatty acids and most of the catalyst, and other impurities in the crude product, final residues of catalyst present in solution are removed from the crude ester phase using an acidic cation exchanger. The fatty acid ester mixture obtained in this way can be employed without further purification both as diesel fuel/heating oil.

[0019] Reference may be made to U.S. Pat. No. 6,399,800 wherein, they claimed a method for producing fatty acid alkyl esters from a feedstock, involving: (a) saponifying the feedstock with an alkali to form a saponified feedstock, (b) removing the water from the saponified feedstock to form a dried saponified feedstock containing no more than about 19% water, (c) esterifying the dried saponifed feedstock with an alcohol in presence of an inorganic acid catalyst to form fatty acid alkyl esters even with water present at levels up to about 3 wt % and (d) recovering the fatty acid alkyl esters.

[0020] Reference may be made to US Patent no. 20050274065 wherein they disclose a process for producing biofuels. The process may be enhanced by one or more of the following: 1) applying microwave or RF energy; (2) passing reactants over a heterogeneous catalyst; claim zeolite or cation exchange resin in H^+ at sufficiently high velocity to achieve high shear conditions; (3) maintaining the reaction at a pressure at or above autogeneous pressure, claim 10-100 psig. Enhanced processes using one or more of these steps can results in higher process rates, higher conversion levels or both.

[0021] Reference may be made to U.S. Pat. No. 6,965,044 wherein, they described a method for converting free fatty acid in acid oil or acid fat into fatty acid methyl esters is disclosed. The process claims to use sulphuric acid as catalyst.

[0022] Reference may be made to U.S. Pat. No. 5,525,126 wherein, they discloses a single step process for producing esters from a feedstock that includes a fat or an oil. The process includes mixing the feedstock with an alcohol, such as methanol and a catalyst comprising of 3:1 by weight mixture of calcium acetate and barium acetate, heating the reaction mixture to 200-250° C. to about 3 hrs and cooling the mixture rapidly. The process is claimed to produce esters from a oil having high free fatty acid content such as 50% by weight to make a mixture of esters to fatty acid in a ratio of about 96:4 by weight.

[0023] Reference may be made to French Pat. No. FR2745296 wherein, they described a process for transesterification of a vegetable or animal oil using a solid heterogeneous catalyst comprising the stage of: (i) mixing a vegetable or animal oil with the required amount of a low alcohol, a fatty alcohol, a petrochemical alcohol, a polyol or a carboxylic acid ester, (ii) maintaining the mixture under a protective atmosphere to avoid possible oxidation of ethylenic groups and to avoid possible oxidation of the glycerol produced; (iii) and maintaining the system at a temperature of >150° C., preferably 150-300° C. in the presence of solid heterogenous catalyst based on Sn, Ge or Pb.

[0024] Reference may be made to US pat. No. 20060014974 wherein, they claimed a process for producing alkyl esters and glycerol of high purity comprising at least one reaction stage in which a charge comprising a vegetable and/or animal oil and an alcohol in the presence of a heterogeneous catalyst, Zinc aluminate, so as to obtain an effluent comprising atleast alkyl esters, glycerol and alcohol, and at lease one separation stage during which a separation stage consists of a membrane separating using at lease one alcohol-permeable membrane.

[0025] Reference may be made to U.S. Pat. No. 6,822,105 wherein, they claimed a process of converting the free fatty acids of the oil source into a mixture of mono-di and triglycerides and subsequently transesterifying the newly formed glycerides as well as the originally present glycerides into fatty acid alkyl esters in presence of dibutyl tin oxide or tetra-butyl titanate at 180° C. and reduced pressure being 760 mm/Hg to 1 mm Hg.

[0026] Reference may be made to U.S. Pat. No. 6,712,987 wherein, they claimed a process comprises forming a single phase solution of said triglyceride in an alcohol methanol/ethanol and mixture the ratio of alcohol to triglyceride being 15:1 to 35:1 in presence of a co solvent (tetrahydrofuran) in an amount to effect formation of single phase and a basic catalyst, NaOH/KOH for the esterification reaction.

[0027] Reference may be made to U.S. Pat. No. 5,908,946 wherein, they described a process for the production of esters from acidic oil and methanol in presence of catalyst Zno, at 170-250° and a pressure of 100 bar and the claims therein.

[0028] Reference may be made to US Pat. No. 20070083056 wherein, they claimed a process for the preparation of hydrocarbon fuels, which comprises contacting fatty acid glycerides with alcohols in the presence of a solid, double metal cyanide catalyst at a temperature in the range of 150 to 200° C. for a period of 2-6 hrs and separating the catalyst from the above said reaction mixture to obtained the desired hydrocarbon fuel.

[0029] Reference may be made to patent WO2007/083213 wherein, they described a process for preparation of biodiesel, which comprises the separation of the triglyceride component from the free fatty acid one, both of which are contained in at least one biolipid, the esterification of said acid component, and the joint trans-esterification of the resulting esterified acid component with said triglyceride component.

The process claims use of >60 moles of methanol for extraction of 0.300 kg of fatty acids in 9.700 kg.triglycerides.

[0030] Reference may be made to a recent publication by S. Chongkhong et. al. in Biomass and Bioenergy Vol. 31, Issue 8, August 2007, page 563-568 entitled "Biodiesel production by esterification of palm fatty acid distillate" wherein Batch esterification of PFAD carried out to study the influence of: including reaction temperature of 70-100° C., molar ratio of methanol to PFAD of 0.4:1-12:1, Catalyst quantity of 0.5-5.5% (Wt. of sulphuric acid/wt. of PFAD and reaction time of 15-240 min).

[0031] In the production of methyl esters of fatty substances from refined oils and dry alcohols, while simple alkaline derivatives, such as sodium, soda or potassium alcoholates, are now used as catalysts, under rather mild conditions (temperature 50 to 80° C. and atmospheric pressure), as indicated in numerous patents or publications, for example in JAOCS 61, 343-348 (1984), a pure product that can be used as a fuel and glycerine within specification can be obtained only after numerous stages and the process may be economically feasible to use the pretreated/refined oils and dry alcohols.

[0032] The major limitation associated with all these processes is that refined oils e.g. soyabean, rape seed etc. are used which are mostly edible having FFA<1%. Another limitation associated with these processes is high temperature 200-250° C. as reported in. U.S. Pat. No.: 5,525,126. Another limitation of reported process is high temperature or pressure e.g. in heterogenous solid catalyst U.S. Pat. No. 5,908,946 or use of critical phase medium reported in WO00/05327/PCT/US99/16669. Another limitation associated with the process is the use of H_2SO_4, which is corrosive and use of large quantity of alkali for neutralization creating disposal problems when such high FFA feedstocks are used as reported in Biomass and Bioenergy Vol. 31, Issue 8, 2007, page 563-568.

[0033] The cost of biodiesel process depends 70-80% on the cost of raw material. In order to achieve an economically feasible process it is desirable to use low cost raw materials e.g PFAD, soya deodistillate, acid oils restaurant grease, or waste cooking oil, Jatropha Curcas oil, mohua oil and animal fat for biodiesel process.

[0034] The novelty of the present invention lies in the esterification of feedstock with high FFA content (20-85%) without any pretreatment for biodiesel in the presence of macroreticular and gel type acidic heterogeneous resin as catalyst which can be used repeatedly (3-4 cycles) and no filteration or washing is required after 1st step of esterification. The esterified oil can be directly taken up for transesterification with base catalyst.

OBJECTIVES OF THE INVENTION

[0035] The main object of the present invention is to provide a process for conversion of low cost and high FFA oils to biodiesel which obviates the drawbacks of the hitherto known prior art as detailed above.

[0036] Another objective of the present invention is to provide a process for converting high FFA containing feed stocks (FFA 20-85%) like palm fatty acid distillate (PFAD), restaurant grease, waste cooking oil, Soya deo distillate, acid oil, jatropha curcas oil, mohua oil etc to biodiesel.

[0037] Yet another objective of the present invention is to provide the heterogenous resin either in a stainless steel basket or used directly with stirring to convert high FFA feedstock without neutralization or pretreatment.

[0038] Still another objective of present invention is to use heterogenous resin repeatedly in the 1st step (4-5 cycles) with lower alcohol.

[0039] Yet another objective of the present invention is use of flexible feedstock without pretreatment or purification.

[0040] Still another objective of present invention is to produce biodiesel at normal temperature and pressure from flexible feed stock having FFA 20-85% meeting the fuel grade quality as specified by ASTM/BIS.

SUMMARY OF INVENTION

[0041] Accordingly, the present invention provides a process for converting high free fatty acid containing feedstocks (FFA 20-85%) into biodiesel which comprises:

[0042] a. providing feed stocks containing 20-85% FFA without pretreatment or purification;

[0043] b. esterifying the feed stocks with lower alcohols in the presence of macroreticular and gel type acidic heterogeneous resin as catalyst;

[0044] c. heating the reactants of step (b) at a temperature in the range of 55-65° C. followed by mechanical stirring for a time period of 8 to 10 hours to obtain esterified oil;

[0045] d. subjecting the esterified oil as obtained from step (c) to transesterification in the presence of homogeneous basic catalyst and methanol;

[0046] e. separating product as obtained from step (d) into upper layer biodiesel and lower layer glycerol followed by recovering of methanol;

[0047] f. washing the biodiesel layer as obtained from step (e) with hot water followed by drying to obtain biodiesel.

[0048] In an embodiment of the invention, the feedstocks containing 20-85% FFA are selected from the group consisting of palm fatty acid distillate (PFAD), restaurant grease, waste cooking oil, Soya deo distillate, acid oil, jatropha curcas oil and mohua oil.

[0049] In another embodiment of the invention, the lower alcohols used for esterification is selected from the group consisting of methanol, ethanol or propanol in the ratio of 3:1 to 35:1 depending upon feedstock.

[0050] In another embodiment of the invention, the acidic heterogeneous resin catalyst is provided either in a jacketed glass reactor with stainless steel basket or used directly with stirring for esterification process without neutralization or pretreatment.

[0051] In another embodiment of the invention, wherein the acidic heterogeneous resin catalyst in a basket is used repeatedly (4-5 cycles).

[0052] In another embodiment of the invention, the acidic heterogeneous resin catalyst used for esterification is selected from the group consisting of Tulsion-42 and Indion-130.

[0053] In another embodiment of the invention, the catalyst Tulsion-42 is used in the range of 5-20% by weight of the feed stocks and Indion-130 is used in the range of 5-25% by weight of the feed stocks.

[0054] In another embodiment of the invention, homogeneous basic catalyst used for transesterification is selected from the group consisting of sodium hydroxide, potassium hydroxide, sodium methoxide and potassium methoxide.

[0055] In another embodiment of the invention, the transesterification is carried out at a temperature in the range of 55-70° C. for a period of 1 to 2 hrs.

[0056] In yet another embodiment of the invention, biodiesel is purified by washing with water or by distillation or adsorbent or combinations thereof.

DETAILED DESCRIPTION OF THE INVENTION

[0057] Weighed quantity of oil (1 mol) and (3-4.5 mol) methanol were taken in the first step in presence of 5-20% of macroreticular and gel type acidic heterogeneous resin catalyst (available commercially) in a stainless steel basket in a jacketed reactor. In case of low cost high free fatty acid oils (FFA>50%) e.g. Palm free acid distillate (PFAD) even 30-35 mol of methanol were taken. The reaction was carried out at a temperature of 60±2° C. After completion of 1st step as monitored by acid value after an interval of **2** hrs, the product with acid value in the range of 1-2 mgKOH/g were transesterified in presence of homogeneous catalyst 0.5-0.75% using 2-3 mol of methanol at a temperature of 55-70° C. for a period of 1 to 2 hrs. After completion of reaction in 1-2 hrs, depending upon feedstock the biodiesel and glycerol layers were separated and the work up resulted in fuel grade biodiesel meeting ASTM/BIS specifications.

[0058] The following examples are given by way of illustration of the working of invention in actual practice and should not be construed to limit the scope of the present invention.

Example-1

[0059] 101.639 gms of Jatropha curcas oil having acid value 40 mgKOH/g, 16.529 gm of methanol were taken in a jacketed glass reactor with SS basket loaded with 5.128 (5%) gms of catalyst Tulsion-42 (available commercially). The reactants were heated to 60° C. with mechanical stirring. The progress of reaction was studied by determining acid value after 2 hrs interval. The acid value after 12 hrs was 3.47 mgKOH/g respectively. The esterified oil was then taken in another jacketed reactor and the oil was transesterified with 0.5% potassium hydroxide in presence of 7.2 g methanol at 65° C. the reaction was complete in one hour. The stirring was stopped and the contents were allowed to settle down, after separating glycerol and upper layer (biodiesel)methanol recovered. The upper layer of biodiesel was washed with hot water (60° C.), lot of emulsion was formed in first two washings due to formation of soaps. The conversion of biodiesel observed was 80% only.

Example-2

[0060] Example 1 was repeated except that 10.02 g (10%) of catalyst Tulsion-42 was taken and acid value is 2.70 mgKOH/g after interval of 8 hrs respectively. The esterified Jatropha curcas oil was taken in second reactor and the transesterification was carried out in presence of 0.75% of potassium hydroxide with 15 g methanol at 60° C. The reaction was complete in one hour, stirring stopped. The glycerol and biodiesel layers were separated, methanol recovered, the biodiesel layer was washed with water, and there was slight emulsion formation water in first two washings in total of four washings. The biodiesel dried and acid value of biodiesel was 0.46 mg KOH/g and the conversion to biodiesel was 98%.

Example-3

[0061] Example 1 was repeated except that 15.37 gms (15%) of catalyst Tulsion-42 was loaded and acid value after 8 hrs is 2.12 mg KOH/g respectively. The esterified Jatropha curcas oil was taken in second reactor and the transesterification was carried out in presence of 0.75% of potassium hydroxide with methanol (21.6 g) at 65° C. .The reaction was completed in one hour, stirring stopped. The glycerol and biodiesel layers were separated, methanol recovered, the biodiesel layer was washed with water, in first two washings there was slight emulsion formation in total of four washings, the biodiesel dried and acid value of biodiesel was 0.45 mg KOH/g and the conversion to biodiesel was observed 99%.

Example-4

[0062] Example 1 was repeated except that catalyst Tulsion-42 was replaced by 10.49 gms (10%) of Indion-130 (available commercially) and acid value after 8 hrs was 10.24 mgKOH/g. The esterified Jatropha curcas oil was taken in second reactor and the transesterification was carried out in presence of 0.75% of potassium hydroxide with (15 g) methanol at 65° C. The reaction was complete in one hour, stirring stopped. The glycerol and biodiesel layers were separated, methanol recovered, the biodiesel layer was washed with water, in first three washings there was emulsion formation in total of six washings. The biodiesel dried and acid value of biodiesel was 1.83 KOH/g and the conversion to biodiesel was 68.9%

Example-5

[0063] Example 4 was repeated and Indion-130 (15%) was loaded and acid value is 5.55 after 8 hrs. The esterified Jatropha curcas oil was taken in second reactor and the transesterification was carried out in presence of 0.75% of potassium hydroxide with (21.6 g) of methanol at 70° C. The reaction was complete in one hour, stirring stopped. The glycerol and biodiesel layers were separated, methanol recovered, the biodiesel layer was washed with water, in first two washings there was emulsion formation in total of four washings. The biodiesel dried and acid value of biodiesel was 0.95 mg KOH/g and the conversion to biodiesel was 79.2%

Example-6

[0064] Example 5 was repeated with 20% Indion-130 and acid value after 8 hrs was 1.99 mgKOH/g. The esterified Jatropha curcas oil was taken in second reactor and the transesterification was carried out in presence of 0.75% of potassium hydroxide (20.9 g) of methanol at 65° C. The reaction was completed in one hour, stirring stopped. The glycerol and biodiesel layers were separated, methanol recovered, the biodiesel layer was washed with water, in first washing there was slight emulsion formation in total of four washings. The biodiesel dried and acid value of biodiesel was 0.52 mg KOH/g and the conversion to biodiesel was 98%.

Example-7

[0065] 100.84 gms of Mohua oil having acid value 44 mg KOH/g, 17.49 gms of methanol were taken in a jacketed glass reactor with SS basket loaded with 15.37 gms (15%) of Tulsion-42. The reactants were heated to 62° C. with mechanical stirring. The acid value after 8 hrs was1.87 mgKOH/g. The esterified oil was then taken in another jacketed reactor and the oil was transesterified with 0.75% potassium hydroxide in presence of 6.94 gms of methanol at 65° C. The reaction was completed in one hour. The stirring was stopped and the contents were allowed to settle down after separating glycerol and biodiesel, methanol was recovered. The upper layer of biodiesel was washed with hot water, in first two washings there was slight emulsion formation in total of four washings, the biodiesel dried and acid value of biodiesel was 0.42 mg KOH/g and the conversion to biodiesel was observed 95%.

Example-8

[0066] Example 7 is repeated except that raw material taken was restaurant Grease having acid value 34 mg KOH/g. The acid value after 8 hrs was 1.92 mgKOH/g. Each esterified oil was then worked up in the same procedure as in example 7. The acid value of biodiesel is 0.39 mgKOH/g and the conversion to biodiesel was observed 97%.

Example-9

[0067] Example 7 is repeated except that raw material taken was soya deodistillate having acid value 38 mg KOH/g. The acid value after 8 hrs was 2.1 mgKOH/g. The esterified oil was then worked up in the same procedure as in example 7. The acid value of biodiesel was 0.47 mg KOH/g and the conversion to biodiesel was observed 94%.

[0068] Example-10

[0069] Examples 7-9 were repeated except that Indion-130 (15%) is used instead of Tulsion-42. The acid value of mohua oil, restaurant grease and soya deodistillate were 44 mg KOH/g, 34 mg KOH/g and 38 mg KOH/g respectively. Each esterified oil was then worked up in the same procedure as in examples 7, the acid value of biodiesel were 0.42 mg KOH/g, 0.39 mg KOH/g and 0.48 mg KOH/g respectively and the conversion to biodiesel was observed 95%, 97% and 94%.

Example-11

[0070] 100.86 gms of palm fatty acid distillate (PFAD) having acid value 177 mg KOH/g, 29.11 gms of methanol and 20.17 gms (20%) of heterogeneous resin Indion-130 catalyst were taken in a jacketed glass reactor in a SS basket. The acid value is lowered to 53.21 mgKOH/g after 8 hrs. The material could neither be neutralized nor transesterified because of such high acid value showing incomplete conversion of PFAD.

Example-12

[0071] Example 11 is repeated except that methanol is 216.49 gms (30 moles). The acid value after removal of methanol is 4.12, 3.34, 3.17, 3.10 mgKOH/g after 2, 4, 6 and 8 hrs respectively.

Example-13

[0072] Example 12 is repeated except that Tulsion-42 (15%) is used instead of Indion-130. The acid value is 2.93 mg KOH/g after 8 hrs.

Example-14

[0073] Example 11 and 12 are repeated and the converted feed/biodiesel is purified by neutralization with NaOH and viscosity of fatty acid methyl ester at 40° C. is 5.82 cSt (centistokes) after drying and washing.

Example-15

[0074] 100.86 gms, of palm fatty acid distillate (PFAD) having acid value 177 mg KOH/g, 216.49 gms of methanol and 20.17 gms (20%) of heterogeneous resin Indion-130 catalyst or 15.78 (15%) of Tulsian-42 were taken in a jacketed glass reactor in a SS basket. The acid value is lowered to 2.93 mgKOH/g after 8 hrs. After the reaction the unreacted methanol is recovered and the product is neutralized with 0.5M NaOH (50 ml). Washing with hot water (65° C.) remove traces of glycerol and drying to remove moisture. The product has viscosity of 5.82 cSt at 40° c.

[0075] Example 15 is repeated and the feed is distilled off to get fuel grade palm fatty acid methyl ester with viscosity 4.47 cSt at 40° C. and acid value 0.42-0.44 mg KOH/g.

THE MAIN ADVANTAGES OF PRESENT INVENTION ARE

[0076] 1) Low cost and high FFA feed stock, Restaurant Grease, Waste Cooking oil, PFAD, Soya distillate, acid oil, Jatropha curcas oil and Mohua oil can be used for biodiesel production.

[0077] 2) Another advantage of the process is using heterogeneous resins in SS basket where no filteration of converted feed stock is required after 1st stage.

[0078] 3) Another important advantage is the repeated use (4-5 cycles) of heterogeneous resin.

[0079] 4) Another advantage is that flexible feedstocks can be used without pretreatment or neutralization.

[0080] 5) The another important advantages is by using such low cost feed stock and repeated use of heterogeneous resin under mild conditions. The process is economically viable.

[0081] 6) Yet another important advantage is the least disposal problems as no washing is required after 1st stage/esterification.

We claim:

1. A process for converting high free fatty acid containing feed stocks (FFA 20-85%) into biodiesel which comprises:

a. providing feed stocks containing 20-85% FFA without pretreatment or purification;
b. esterifying the feed stocks with lower alcohols in the presence of macroreticular and gel type acidic heterogeneous resin as catalyst;
c. heating the reactants of step (b) at a temperature in the range of 55-65° C. followed by mechanical stirring for a period of 8 to 10 hours to obtain esterified oil;
d. subjecting the esterified oil as obtained from step (c) to transesterification in the presence of homogeneous basic catalyst and methanol;
e. separating product as obtained from step (d) into upper layer biodiesel and lower layer glycerol followed by recovering of methanol;
f. washing the biodiesel layer as obtained from step (e) with hot water followed by drying to obtain biodiesel.

2. A process according to claim **1**, wherein the feedstocks containing 20-85% FFA are selected from the group consisting of palm fatty acid distillate (PFAD), restaurant grease, waste cooking oil, Soya deo distillate, acid oil, jatropha curcas oil and mohua oil.

3. A process according to claim **1**, wherein the lower alcohols used is methanol, ethanol or propanol in the ratio of 3:1 to 35:1 depending upon feedstock.

4. A process according to claim **1**, wherein the acidic heterogeneous resin catalyst is provided either in a jacketed glass reactor with stainless steel basket or used directly with stirring for esterification process without neutralization or pretreatment.

5. A process according to claim **1**, wherein the acidic heterogeneous resin catalyst is used repeatedly for 4-5 cycles of the reaction.

6. A process according to claim **1**, wherein the acidic heterogeneous resin catalyst used for esterification is selected from the group consisting of Tulsion-42 and Indion-130.

7. A process according to claim **1**, wherein the catalyst Tulsion-42 is used in the range of 5-20% by weight of the feed stocks and Indion-130 is used in the range of 5-25% by weight of the feed stocks.

8. A process according to claim **1**, wherein homogeneous basic catalyst used for transesterification is selected from the group consisting of sodium hydroxide, potassium hydroxide, sodium methoxide and potassium methoxide.

9. A process according to claim **1**, wherein the transesterification is carried out at a temperature in the range of 55-70° C. for a period of 1 to 2 hrs.

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