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CA 2526074 C 2010/11/30

(11)(21) 2 526 074

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(86) Date de dépôt PCT/PCT Filing Date: 2004/05/03
(87) Date publication PCT/PCT Publication Date: 2004/12/02
(45) Date de délivrance/Issue Date: 2010/11/30
(85) Entrée phase nationale/National Entry: 2005/11/16
(86) N° demande PCT/PCT Application No.: US 2004/013851
(87) N° publication PCT/PCT Publication No.: 2004/103934
(30) Priorité/Priority: 2003/05/16 (US60/471,272)

(51) Cl.Int./Int.Cl. *C07C 67/08* (2006.01),
C11C 3/04 (2006.01)

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(54) Titre : PROCEDE DE FABRICATION D'ESTERS D'ALKYLE PAR PRESSION
(54) Title: METHOD OF MAKING ALKYL ESTERS USING PRESSURE

(57) Abrégé/Abstract:
A method for making alkyl esters, or methylester specifically, such as biodiesel, from an oil source is described. The method involves simultaneously reacting the free fatty acids and glycerides of the oil source with methanol, under pressure up to 500 psia, into fatty acid alkyl esters. The conversion is catalyzed by an acid at temperatures between about 80°C to about 200°C.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
2 December 2004 (02.12.2004)

PCT

(10) International Publication Number
WO 2004/103934 A3

(51) International Patent Classification[7]: C11C 1/00, 3/00

(21) International Application Number:
PCT/US2004/013851

(22) International Filing Date: 3 May 2004 (03.05.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/471,272 16 May 2003 (16.05.2003) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

(88) Date of publication of the international search report:
16 March 2006

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/103934 A3

(54) Title: METHOD OF MAKING ALKYL ESTERS USING PRESSURE

(57) Abstract: A method for making alkyl esters, or methylester specifically, such as biodiesel, from an oil source is described. The method involves simultaneously reacting the free fatty acids and glycerides of the oil source with methanol, under pressure up to 500 psia, into fatty acid alkyl esters. The conversion is catalyzed by an acid at temperatures between about 80°C to about 200°C.

Attorney Docket No. 15009WO01

METHOD OF MAKING ALKYL ESTERS USING PRESSURE

BACKGROUND OF THE INVENTION

[0003] Alkylesters, or methylester specifically, such as biodiesel, are a clean-burning replacement for conventional petroleum-based diesel. Biodiesel may be made from natural, renewable sources such as new or used vegetable oils and animal fats. Biodiesel is fatty acid alkyl esters (typically being C_{16} to C_{18}) and can generally be burned in combustion-ignition engines as a direct replacement for petroleum-based diesel. Aside from providing the benefit that biodiesel may be generated from renewable sources, biodiesel also provides the added benefit of decreased emissions from its combustion as compared to the combustion of petroleum-based diesel.

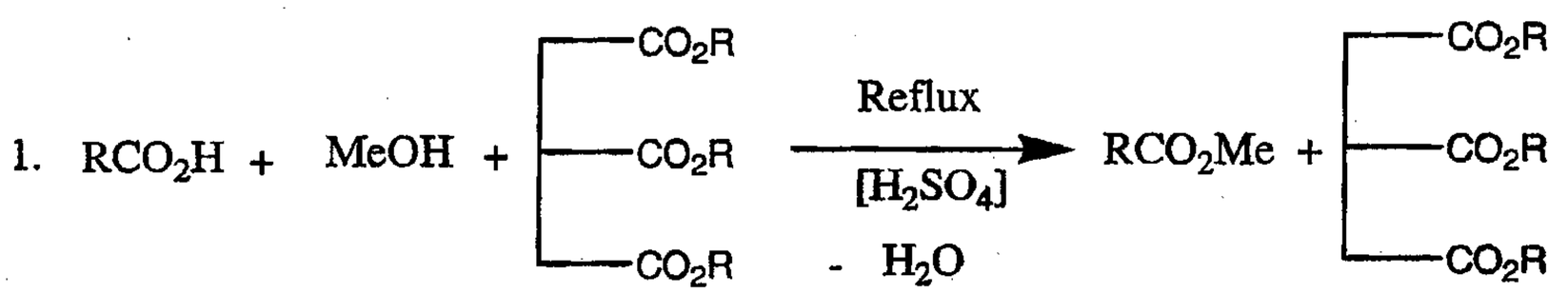
[0004] Alkylesters, in particular biodiesel, may be derived from the oils of the soybean or the rapeseed. The crude vegetable oil from these sources may be filtered, refined and subjected to several processing steps before the oil may be usable as biodiesel. Additionally, biodiesel may be derived from varying grades of vegetable oils. Such grades include virgin oil, yellow grease, used oils from food processing, or by-products from the edible oil refining process such as soap stock. Each of these sources has varying amounts of free fatty acids and/or glycerides -- i.e., mono-, di-, or tri-glycerides -- that may be processed into biodiesel.

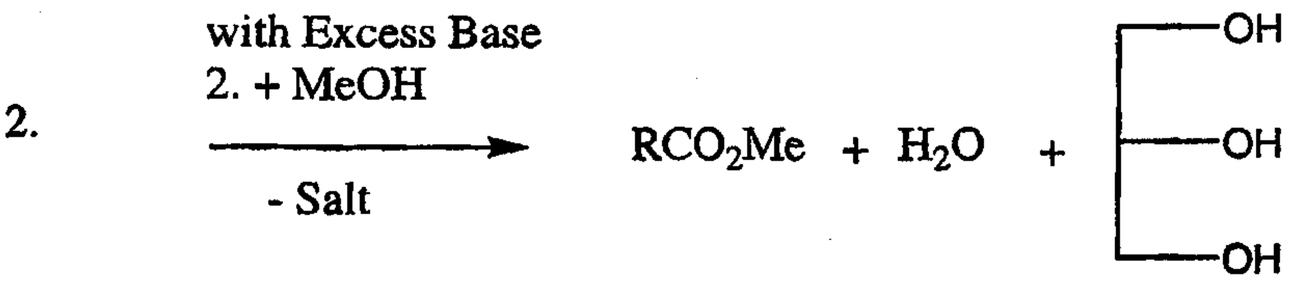
[0005] Of these sources of vegetable oil, soap stock is generally considered the most cost effective source. Soap stock is derived from the crude oil extracted from the soybean or rapeseed. The crude oil of these seeds may be separated into two components: refined oil (which may then be further processed and converted into edible oil) and soap stock. The soap stock may then be acidulated with sulfuric acid

to provide a composition having about 70% free fatty acids that may be further processed into biodiesel.

[0006] One contemplated method of processing the free fatty acids from these various grades of vegetable oils is the direct transesterification of the free fatty acids in the presence of alkali to produce the fatty acid alkyl esters for use as biodiesel. Such an approach, however, causes the free fatty acids to precipitate as soap, creating an additional recovery step in the contemplated method.

[0007] To avoid the precipitation problem, a two-step method for processing the free fatty acids has been proposed. This method can be found in EP 07 708 813 and WO 02/28811, and generally consists of the steps of (1) acid catalyzed esterification of free fatty acids with methanol in the presence of sulfuric acid, and (2) neutralization of the acid catalyst followed by conventional base catalyzed transesterification. These steps can be described by the following reaction scheme.





where each R may be the same or different and an aliphatic chain typically found in vegetable or animal oil sources, typically C_8 to C_{22}.

[0008] Even though transesterifications are both acid and base catalyzed, neutralization of the acid catalyst is necessary because acid catalyzed transesterifications typically exhibit slower kinetics than base catalyzed transesterifications, under comparable conditions. The disadvantages of two-step methods as disclosed in EP 07 08 813 and WO 02/28811 are the additional salt waste

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from neutralization, long cycle times, and a cumbersome recovery scheme of residual free fatty acids.

BRIEF SUMMARY OF THE INVENTION

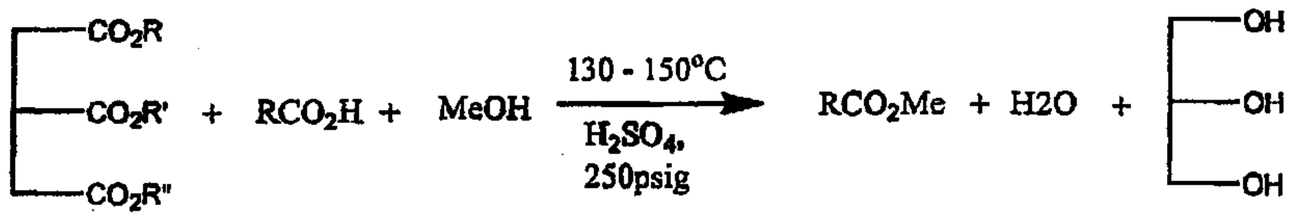
[0009] It is therefore an object of the present invention to provide a method of processing free fatty acids from a vegetable or animal oil source into alky esters in which the salt and aqueous waste is reduced or eliminated.

[0010] It is a further object of the present invention to provide a method of processing free fatty acids from a vegetable or animal oil source into alkyl esters in which the cycle times are reduced.

[0011] It is a further object of the present invention to provide a method of processing free fatty acids from a vegetable or animal oil source into alkyl esters in which the recovery scheme of residual free fatty acids is conveniently performed or the need for such recovery is eliminated.

[0012] It is a further object of the invention to provide a method capable of performing esterification and transesterification simultaneously in one step.

[0013] These and other advantages are accomplished by subjecting the vegetable or animal oil source to a single step method constituting a direct transformation of the free fatty acid and glycerides of the vegetable or animal oil source with methanol. The single step process does not involve a neutralization step thus simplifying the process. The single step method is generally described below.



where each R may be the same or different and may be H or an aliphatic chain typically found in vegetable or animal oil sources, typically C_8 to C_{22}.

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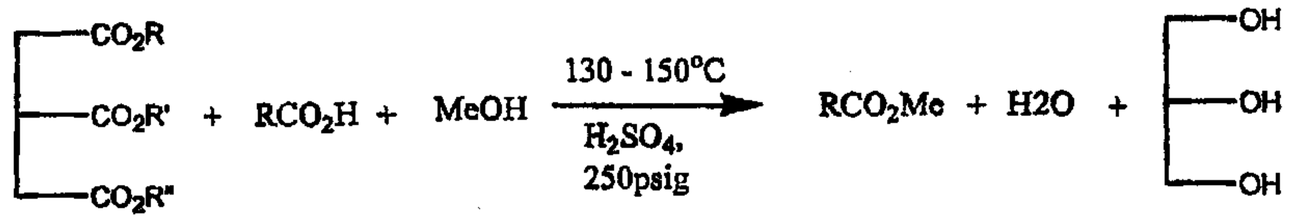
DETAILED DESCRIPTION OF THE INVENTION

[0014] As noted above, the method of the present invention of processing a vegetable oil source can be represented by the following reaction scheme.



[0015] where each R may be the same or different and may be H or an aliphatic chain typically found in vegetable or animal oil sources, typically C_8 to C_{22}. The reaction scheme may be undertaken at temperatures from about 80°C to about 200°C, preferably within the range of about 120°C to about 180°C, and most preferably within the range of about 150°C to about 170°C. The pressure under which the reaction scheme is run is about 25 psia to about 500 psia, preferably in the range of about 100 psia to about 300 psia.

[0016] Suitable vegetable oil sources for the present invention include, but are not limited to soy bean and rapeseed oil, and is preferably soap stock derived from rapeseed oil. Depending on the vegetable oil source utilized, the vegetable oil source preferably comprises between about 60 wt % to about 90 wt % of the total mixture to be reacted. Preferably, the vegetable oil source comprises between about 65 wt % to about 80 wt % of the total reaction mixture. Methanol is preferably utilized in the reaction mixture in an amount between about 10.0 wt % to about 40.0 wt %, more preferably, between about 20 wt% to about 35 wt% of the total reaction mixture. The catalyst concentration ranges may be from about 0.0 to about 1.0 wt%, preferably within the range of about 0.1 to about 0.5 wt% of the total reaction mixture. Preferably, the catalyst is an acid. More preferably, the catalyst is an inorganic mineral acid, such as, but not limited to, sulfuric acid.

[0017] Described differently, the methanol is preferably utilized in an amount in excess of that needed for reaction. The methanol may range from about 1.0 molar equivalent to about 5 molar equivalents, compared to the total moles of fatty acids and/or glycerides containing in the vegetable oil source. Preferably, the methanol is within the range of about 1.5 molar equivalents to about 3.0 molar equivalents.

preferably comprises between about 60 wt % to about 90 wt % of the total mixture to be reacted. Preferably, the vegetable oil source comprises between about 65 wt % to about 80 wt % of the total reaction mixture. Methanol is preferably utilized in the reaction mixture in an amount between about 10.0 wt % to about 40.0 wt %, more preferably, between about 20 wt% to about 35 wt% of the total reaction mixture. The catalyst concentration ranges may be from about 0.0 to about 1.0 wt%, preferably within the range of about 0.1 to about 0.5 wt% of the total reaction mixture. Preferably, the catalyst is an acid. More preferably, the catalyst is an inorganic mineral acid, such as, but not limited to, sulfuric acid.

[0025] Described differently, the methanol is preferably utilized in an amount in excess of that needed for reaction. The methanol may range from about 1.0 molar equivalent to about 5 molar equivalents, compared to the total moles of fatty acids and/or glycerides containing in the vegetable oil source. Preferably, the methanol is within the range of about 1.5 molar equivalents to about 3.0 molar equivalents. Additionally, the amount of catalyst may be described in terms of the amount of vegetable oil source as ranging from about 0.0 to about 2.0% compared to the weight of the vegetable oil source, or more preferably, between 0.1 to 1.0%.

[0026] Preferably, the reaction mixture has a starting acid value, at time 0, between 26 – 240, more preferably 53 – 214, and most preferrably 107 - 187. . The ending acid value, after the reaction has proceeded substantially to completion, is preferably less than about 10.0, more preferably less than 6.0, and most preferably less than 2.5.

[0027] In some embodiments of the present technology, the by-products of reaction, such as water and glycerin, are removed. The by-products may be removed either continuously or by interrupting the reaction. In one embodiment, the step of removing dissolved water from the reaction product comprises vacuum drying the reaction product. Preferably, the reaction is quenched as quickly as possible by removing the heat source and cooling the reactor using the internal cooling coil and an external ice-water bath. Make-up catalyst (0.25 g) and methanol (5 g) are preferably added as necessary to the remaining phase, which is then poured back into a vessel to continue the reaction.

[0028] The present technology is characterized by substantial efficiency. Preferred embodiments of the present technology produce greater than 70.0 grams of biodiesel per 100 grams of starting reaction mixture. More preferably, the efficiency is greater

than 80.0%, and most preferably, greater than 90.0%. Some embodiments of the present invention have exhibited greater than 95.0% efficiency.

[0029] Additionally, the present technology is characterized by fast reaction times. Preferably, the reaction will proceed to greater than 80.0% completion within 5.0 hours. More preferably, the reaction will proceed to greater than 80.0% completion within 2.5 hours. Some embodiments of the present invention can produce greater than 80.0 grams of biodiesel per 100 grams of vegetable oil source within 1.0 hours.

[0030] The above reaction scheme provides a method of making alky esters that provides the advantages of fast reaction times, moderate temperature and pressure requirements, and reduced overall cycle times. To demonstrate the effectiveness of the above reaction scheme of the present invention, acidulated soap stock samples were subjected to the reaction scheme and the acid value of the reaction products was determined as a function of time. The decreasing acid value demonstrated that the reaction scheme provides a satisfactory method of processing the free fatty acids of the acidulated soap stock into fatty acid alkyl esters for use, for example, as biodiesel. Further, to demonstrate that the products of the above reaction scheme compared favorably to a known biodiesel reference (obtained from the Stepan Company of Northfield, Illinois), ^{1}H-NMR of both the products of the various examples of the present invention were compared to the ^{1}H-NMR of the biodiesel reference. The comparison demonstrates that the products of the above reaction scheme provide products comparable to the biodiesel reference.

[0031] **Example 1**

[0032] Example 1 sets forth systems in which the reaction scheme proceeded and where by-products were not removed. The acid values of the systems were measured as a function of time at two different temperatures (130°C and 150°C) to measure the extent of reaction. Even without the removal of the by-products, the reaction scheme of the present invention is demonstrated to provide an effective method of making biodiesel from various sources of vegetable oil.

[0033] Pressure reactions were generally carried out in a 300 ml 316 ss Parr™ autoclave with glass liner. The autoclave was equipped with a turbine agitator, thermocouple

Time (min.)	Run 1 -- 130°C	Run 2 -- 150°C
0	112.2	112.2
5		13.27
10		11.33
15	47.19	9.43
30	20.16	10.54
60	11.14	9.3
90	7.76	
120	11.15	10.4
180	9.43	9.35

[0028] The products of Run 1 were further analyzed to confirm the transesterification of the glycerides in the acidulated soap stock. The analysis confirmed that the glycerides are transesterified simultaneously with the conversion of free fatty acids into fatty acid alkyl esters. The following table sets forth the ratio of the glyceride ^{1}H-NMR signal and the overall integration versus time. Though the exact concentration of glycerides cannot be ascertained in this manner, it does show the relative decrease in concentration over time.

[0029] TABLE 2 -- Glyceride ^{1}H-NMR integral as % of total integration for Run 1.

Time (min.)	Run 1 -- 130°C
0	2.02
15	1.68
30	1.52
60	1.09
120	0.09

Comparison of ^{1}H-NMR for acidulated soap stock, known biodiesel reference, and Run 1 at 15 and 120 minutes showed that glycerides were reduced and methyl esters were increased.

[0030] Comparative Example

[0031] The comparative example was an acidulated soap stock subjected to the reaction scheme but under ambient pressure. The comparative example resulted in a complete conversion of the free fatty acids into fatty acid alkyl esters but the glycerides were not transesterified demonstrating the need for pressure above ambient.

[0032] 90 g of acidulated soap stock together with 70 g of methanol and 0.5 g of sulfuric acid (98%) were charged into a 300 ml 3-neck round bottom flask. The flask was equipped with a mechanical stirrer, thermocouple and a reflux condenser atop a Soxhlett extractor filled with anhydrous calcium chloride. The mixture was heated by means of a heating mantle to reflux temperature (68 - 70°C). Methanol was continuously recycled through the calcium chloride bed to remove water. After 6 hrs of reflux the mixture was washed with a 10% sodium bicarbonate solution followed by twice washing with 5wt% (with regard to ester) water. The organic layer was dried under vacuum on a Rota-Evaporate at ~ 60°C. A significant emulsification took place during washing, which eventually could only be dealt with by stripping the water in vacuo.

[0033] The comparative example of the esterification with methanol in the presence of sulfuric acid as the catalyst at ambient pressure lead to complete esterification of the free fatty acid after 6 Hrs (AV 0.5). However, with 1.25% (by ^{1}H-NMR determined as above) glycerides remaining, the advantage of using increased pressure becomes clear.

[0034] Example 2

[0035] Example 2 sets forth systems in which the reaction scheme proceeded and where by-products (i.e., water and glycerin) were removed. The final measured acid values of the systems demonstrated that removal of the by-products facilitates the reaction scheme.

was equipped with a mechanical stirrer, thermocouple and a reflux condenser atop a Soxhlett extractor filled with anhydrous calcium chloride. The mixture was heated by means of a heating mantle to reflux temperature (68 - 70°C). Methanol was continuously recycled through the calcium chloride bed to remove water. After 6 hrs of reflux the mixture was washed with a 10% sodium bicarbonate solution followed by twice washing with 5wt% (with regard to ester) water. The organic layer was dried under vacuum on a Rota-Evaporate™ at ~ 60°C. A significant emulsification took place during washing, which eventually could only be dealt with by stripping the water in vacuo.

[0042] The comparative example of the esterification with methanol in the presence of sulfuric acid as the catalyst at ambient pressure lead to complete esterification of the free fatty acid after 6 Hrs (AV 0.5). However, with 1.25% (by ^{1}H-NMR determined as above) glycerides remaining, the advantage of using increased pressure becomes clear.

[0043] Example 2

[0044] Example 2 sets forth systems in which the reaction scheme proceeded and where by-products (i.e., water and glycerin) were removed. The final measured acid values of the systems demonstrated that removal of the by-products facilitates the reaction scheme.

[0045] These runs were charged as outlined in Example 1. The removal of water and glycerin during pressure reactions could not be done from the reactor itself. Instead, the reaction was quenched as quickly as possible by removing the heart source and cooling the reactor using the internal cooling coil and an external ice-water bath. After cooling to 30°C or less the reactor was opened and the content was weighed and transferred to a 250 ml separatory funnel. After settling the water/glycerin layer was removed. Make-up catalyst (0.25 g) and methanol (5 g) were added as necessary to the remaining phase, which was then weighed and poured back into the Parr reactor, to continue the reaction.

[0046] Run 3 was carried out at 150°C for a total time of 2.6 hours. Run 3 resulted in a final acid value of 2.5 demonstrating the improved results over Runs 1 and 2 where

[0040] Run 5 was run at 180°C and demonstrated that the higher temperature of 180°C did improve the reaction time over Runs 1 and 2.

[0041] For Run 5, the reactor was charged according to procedure 1, with 100.0 g soap stock, 35.0 g methanol and 0.25 g sulfuric acid. The autoclave was heated to 180°C within 45 minutes and held at this temperature for 30 minutes, before being quenched. The content was transferred to a separatory funnel and 14.29 g of bottom phase were removed. The remaining amount was brought back to the autoclave and heating at 180°C continued for 60 minutes. The reaction was cooled again and a total of 10.83 g was removed after separation. The remaining phase was washed twice with 25 g of water, and finally dried under vacuum at 60°C. The resulting acid value was 6.3.

[0042] The following table summarizes the conditions and results for Runs 3, 4, and 5.

[0043] Table 3: Reaction summary for Runs 3, 4, and 5.

	Temp (°C)	Total Time [hrs]	Soap Stock [g]	Methanol [g]	98% Sulfuric Acid [g]	Final AV [meq/g]	Glycerin Phase [g]	Yield (based on g soap stock) [g]
Run 3	150	2.6	100.0	35.0	0.25	2.5	23.73	89.2
Run 4	150	4.5	100.1	35.0	0.125	0.8	n.d.	92.5
Run 5	180	1.5	100.0	35.0	0.25	6.3	25.12	90.6

(n.d. = not determined)

[0044] ^{1}H-NMR results for Runs 6 and 7 did not reveal any side reactions taking place under the conditions of the reaction scheme, indicating that the reaction scheme of the present invention may be the subject of a continuous process. Additionally, ^{1}H-NMR for Run 7confirmed that the higher reaction temperature of Run 7 does not have a negative effect as far as decomposition is concerned.

[0045] While particular elements, embodiments and applications of the present invention have been shown and described, it will be understood that the invention is not limited thereto since modifications may be made by those skilled in the art, particularly in light of the foregoing teachings. Therefore, it is understood that the

embodiments described above are merely for illustrative purposes and are not intended to limit the spirit and scope of the invention, which is defined by the following claims as interpreted according to the principles of patent law, including the doctrine of equivalents.

THE EMBODIMENTS OF THE INVENTION FOR WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method of making biodiesel comprising the following steps:

(a) forming a reaction mixture having an acid value of between 53 and 240 comprising:

(i) a vegetable oil source in an amount between about 60 wt% to about 90 wt% of the total weight of the reaction mixture, wherein the vegetable oil source comprises free fatty acids and glycerides;

(ii) methanol in an amount between about 1.0 molar equivalents to about 5.0 molar equivalents compared to the total moles of free fatty acids and glycerides;

(iii) a catalytic acid in an amount between 0.1 wt% to 2 wt% compared to the weight of the vegetable oil source;

(b) heating the reaction mixture to a temperature of between about 80°C to about 200°C;

(c) maintaining a pressure of about 25 psia to about 500 psia for the heated reaction mixture;

(d) reacting the methanol and the free fatty acids and glycerides for a sufficient reaction time to produce a reaction product comprising fatty acid alkyl esters; and

(e) recovering the fatty acid alkyl esters.

2. The method of claim 1, wherein the pressure is maintained at between about 100 psia to about 300 psia.

3. The method of claim 1, wherein the reaction mixture is heated to a temperature of between about 120°C to about 180 °C.

4. The method of claim 3, wherein the reaction mixture is heated to a temperature of between about 150°C to about 170°C.

5. The method of claim 1, wherein the catalytic acid is present in an amount between 0.1 wt% to 0.25 wt% compared to the weight of the vegetable oil source.

6. The method of claim 1, wherein the methanol comprises between about 1.5 molar equivalents to about 3.0 molar equivalents compared to the total moles of free fatty acids and glycerides.

7. The method of claim 1, further comprising a step of removing by-products of reaction during processing.

8. The method of claim 1, wherein the reaction mixture reacts substantially to completion.

9. The method of claim 1, wherein greater than about 85.0 grams of biodiesel per 100 grams of vegetable oil source are produced.

10. The method of claim 1, wherein the reaction mixture has a starting acid value between 107 and 187.

11. The method of claim 1, wherein the reaction product has an acid value less than about 10.0.

12. The method of claim 11, wherein the reaction product has an acid value of less than about 2.5.

13. The method of claim 1, further comprising the step of removing dissolved water from the reaction product and then subjecting it to further reaction.

14. The method of claim 13, wherein the step of removing dissolved water comprises vacuum drying the reaction product.

15. The method of claim 1, wherein the reaction time is less than about 5 hours to proceed to greater than about 80.0% completion.

16. The method of claim 15, comprising a total reaction time of less than about 2.5 hours to proceed to greater than 80.0% completion.

17. A method of making biodiesel comprising the following steps:

(a) forming a reaction mixture having an acid value of between 53 and 240 comprising:

(i) a vegetable oil source in an amount between about 60 wt% to about 90 wt% of the total weight of the reaction mixture, wherein the vegetable oil source comprises free fatty acids and glycerides;

(ii) methanol in an amount between about 1.5 molar equivalents to about 3.0 molar equivalents compared to the total moles of glycerides and free fatty acids;

(iii) a catalytic acid in an amount between 0.1 wt% to 2 wt% compared to the weight of the vegetable oil source;

(b) heating the mixture to between about 150°C to about 170°C;

(c) maintaining a pressure of about 25 psia to about 500 psia for the heated mixture;

(d) reacting the methanol with the free fatty acids and glycerides for a sufficient reaction time to produce a reaction product comprising fatty acid alkyl esters; and

(e) recovering the fatty acid alkyl esters.

18. The method of claim 17, further comprising a step of removing by-products of reaction during processing.

19. The method of claim 17, wherein the pressure is maintained at between about 100 psia to about 300 psia.

20. The method of claim 17, wherein the reaction mixture has a starting acid value between 107 and 187.

21. The method of claim 17, wherein the reaction product has an acid value less than about 10.0.

22. The method of claim 17, wherein the reaction product has an acid value less than about 2.5.

23. The method of claim 17, wherein the reaction time is less than about 5 hours to proceed to greater than about 80.0% completion.

24. The method of claim 17, wherein the vegetable oil source is acidulated soap stock.

25. A method of making alkyl esters comprising the following steps:

(a) forming a reaction mixture having an acid value of between 53 and 240 comprising:

(i) a vegetable oil source in an amount between about 60 wt% to about 90 wt% of the total weight of the reaction mixture, wherein the vegetable oil source comprises free fatty acids and glycerides;

(ii) methanol in an amount between about 10 wt% to about 40 wt% of the total weight of a reaction mixture;

(iii) a catalytic acid in an amount between 0.05 wt% to 2 wt% compared to the weight of the vegetable oil source;

(b) heating the reaction mixture to a temperature of between about 120°C to about 180°C;

(c) maintaining a pressure of about 25 psia to about 500 psia for the heated reaction mixture;

(d) reacting the methanol and the free fatty acids and glycerides to produce a reaction product comprising fatty acid alkyl esters; and

(e) recovering the fatty acid alkyl esters.

26. The method of claim 25, wherein the pressure is maintained at between about 100 psia to about 300 psia.

27. The method of claim 26, wherein the reaction mixture is heated to a temperature of between about 150°C to about 170°C.

28. The method of claim 25, further comprising a step of removing by-products of reaction during processing.

29. The method of claim 25, wherein greater than about 85.0 grams of alkyl esters per 100 grams of vegetable oil source are produced.

30. The method of claim 25, wherein the reaction product has an acid value less than about 10.0.

31. The method of claim 25, wherein the reaction product has an acid value less than about 2.5.

32. The method of claim 25, further comprising a step of removing dissolved water from the reaction product and then subjecting it to further reaction.

33. The method of claim 25, wherein the reaction time is less than about 5 hours to proceed to greater than about 80.0% completion.