

**METHODS FOR MAKING DIESEL FUEL USING CATALYST-FREE
TRANSESTERIFICATION OF VEGETABLE OILS**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of, and priority to, U.S. Provisional Patent Application Serial No. 63/607,280 filed on December 7, 2023 and U.S. Provisional Patent Application Serial No. 63/563,614 filed on March 11, 2024. The entire contents of the foregoing applications are incorporated by reference herein.

BACKGROUND

[0002] Diesel fuel, derived from the diminishing reservoirs of non-renewable petroleum, is a major source of global warming gases upon its combustion. Crude petroleum, sourced from these depleting reserves, is composed of an extensive mixture of hydrocarbon molecules. Through the process of fractional distillation, various products like gasoline, aviation fuel, diesel fuel, and tar are obtained. Notably, each of these end products is typically constituted by a complex mixture of hundreds of distinct hydrocarbons. Gasoline is the first distillate of petroleum and is composed of hydrocarbons typically ranging from C₄-C₁₂. Aviation fuel is the middle distillation product between gasoline and diesel, with significant overlap in the boiling point ranges of gasoline and almost complete overlap in the boiling points for diesel fuel. Aviation fuel is typically a mixture of hydrocarbons ranging from C₈-C₁₆. Diesel fuel has the highest boiling point with mixtures ranging from C₈-C₂₃. Tar is the residue of the petroleum distillation process.

[0003] Biodiesel includes the fatty acid alkyl esters (FAAEs), such as fatty acid methyl esters (FAMES), derived from the transesterification of triglycerides, such as vegetable oils or animal fats. These fatty acid methyl esters can be used in classic diesel engines, without the need for any modifications. Biodiesel is a net zero or near net zero carbon emission fuel since the carbon produced from combustion originated from carbon absorbed from the air by plants. Furthermore,

waste cooking oil can serve as a feedstock chemical for biodiesel production, thus, eliminating reliance on fresh vegetable oils (e.g., soybean, canola, coconut, sesame, etc.), while significantly decreasing biodiesel production costs. At present, the use of virgin vegetable oils places biodiesel at a cost of 1.5 times that of petroleum-based diesel. It also alleviates the burden on restaurants and commercial fast-food chains to dispose of enormous quantities of cooking oil waste. Biodiesel, as compared to conventional diesel, is also low in nitrogen and sulfur content. These compounds lead to the production of highly polluting compounds, such as nitrogen oxides and sulfur oxides, respectively. Additionally, unlike fossil fuel derived diesel, biodiesel contains no aromatics, whose compounds are responsible for increasing the soot/smoke production of diesel.

[0004] Conventional biodiesel production methods utilizing vegetable oils come with significant drawbacks, which include unwanted soap production, low yields and/or difficulty in purification. Currently, homogenous base catalysts have received the most attention for biodiesel production due to their availability and low price. Common base catalysts utilize hydroxide in the form of sodium hydroxide (NaOH) or potassium hydroxide (KOH) for the transesterification of vegetable oils in methanol (MeOH). The role of hydroxyl group ($-OH$) is to deprotonate the mildly acidic proton of MeOH, forming $[^-OMe]$ ions for the transesterification reaction. Both NaOH and KOH show excellent catalytic activity towards biodiesel production but come with the major drawback of producing water. This reduces biodiesel yield and adds complications for purification of the desired biodiesel from the alkali-metal fatty acid carboxylates side products, known as soap. Sodium methoxide (NaOMe) and potassium methoxide (KOMe) have also been utilized for biodiesel production since they are a direct source of $[^-OMe]$ ions. However, these reagents also add complications to the separation of biodiesel from the byproducts and decrease the appeal of this method. Mostly notable, FAMES containing double bonds are not suitable for diesel engines

since the alkenes react with hydroxyl radicals present during combustion. These radicals polymerize diesel fuel during burning and result in premature aging of the engine. Thus, a catalyst-free approach to the transesterification of vegetable oils thereby converting them into high-value biodiesel FAMES is desired.

SUMMARY

[0005] The present disclosure overcomes the limitations of the currently known methods for biodiesel production from vegetable oils. This was achieved by developing a reaction that does not rely on a hydroxide base, is solvent free, and does not require any extreme conditions. Currently, a widely adopted practice is to use sodium hydroxide (NaOH) or potassium hydroxide (KOH) in the presence of methanol (MeOH) to produce biodiesel from vegetable oils using a metal catalyst. This method has several highly undesirable effects. The hydroxide base used to deprotonate MeOH to form methoxide [O^-Me] for the transesterification process also reacts with the ester group of the biodiesel fatty acid methyl esters (FAMES) to form the sodium salt of the fatty acid carboxylates, known as soap. This undesirable product results in soapy biodiesel, and thus lower biodiesel yields that require additional purification steps to obtain a product usable in unmodified diesel engines.

[0006] The presently disclosed methods may be used to produce biodiesel FAMES from commercial waste oils and/or virgin cooking oils. The method includes reacting sodium borohydride (NaBH_4) with methanol (MeOH). NaBH_4 is a source of hydride and reacts with MeOH to produce [O^-Me] ions for transesterification of vegetable oils to form FAMES. The reaction of NaBH_4 with MeOH may be performed either in a neat environment or in a solvent, e.g., toluene, and produces sodium tetramethoxyborate [$\text{NaB}(\text{OMe})_4$]. Hydrogen gas is also produced as a byproduct of the reaction and can be used to hydrogenate the fatty acid chains of the

newly formed biodiesel. In some embodiments, NaB(OMe)_4 can also be produced using trimethoxyborate $[\text{B(OMe)}_3]$ and NaOMe in methanol to produce FAMES.

[0007] As noted above, FAMES containing double bonds are not suitable for diesel engines given that the alkenes react with hydroxyl radicals present during combustion thereby causing these radicals to polymerize diesel fuel during burning and result in premature aging of the engine. This problem is completely avoided if the FAME's alkyl chain is fully reduced. Thus, the presently disclosed method focuses on the transesterification aspect of biodiesel production from vegetable oils using a transesterification reagent, NaB(OMe)_4 , synthesized from either reacting NaBH_4 with MeOH or by combining B(OMe)_3 with NaOMe in MeOH .

[0008] The presently disclosed method also avoids the use of hydroxide bases, thereby averting the production of soapy diesel and eliminating the necessity for water removal from the reaction mixture. Furthermore, the byproduct glycerol-borate compounds form a solid that stays at the bottom of a reaction vessel, facilitating an easy isolation of the biodiesel by simple decantation. The resulting methyl esters of vegetable oils can be used as a renewable, carbon neutral alternative to petroleum-based diesel for use in any diesel engine with no modifications. Transesterification reactions were successful when using waste cooking oil from a major fast-food chain, as well as with commercial soybean oil, sesame oil, olive oil, and animal fat. An average yield of about 85% at 80 °C was achieved with approximately a one-hour reaction time. Characterization through ^1H and ^{11}B NMR showed the efficacy of the process and quality of the obtained biodiesel. The presently disclosed methods were extended to the synthesis of other FAAEs, such as those including ethyl, propyl and butyl groups. This was achieved by adding used cooking oil to *in situ* generated sodium tetraethoxyborate $[\text{NaB(OEt)}_4]$, sodium tetrapropoxyborate NaB(OPr)_4 and

sodium tetrabutoxyborate $\text{NaB}(\text{OBu})_4$, which were formed by reaction of NaBH_4 with ethanol (EtOH), propanol (PrOH) and butanol (BuOH), respectively.

[0009] Issues associated with unwanted soap production, low yields and/or difficulty in purification are eliminated by using a reaction between NaBH_4 and MeOH to form $\text{NaB}(\text{OMe})_4$, a previously unexplored molecular species capable of delivering $[\text{OMe}]$ for the transesterification of vegetable oils. The presently disclosed methods were successful at producing biodiesel from used cooking oil, a commercially realistic feedstock chemical that both alleviates the environmental burden of waste cooking oil and is a cheap starting material. Both aspects are vital components for making biodiesel prices competitive to those of classic fossil fuel diesel.

[0010] The presently disclosed methods also allow biodiesel to be easily synthesized and isolated at temperatures as low as 40°C in about one hour. The resulting byproduct glycerol-boron compounds do not form an emulsion with the product biodiesel, but rather form an easily separable solid, e.g., at the bottom of a reaction vessel, thus, the biodiesel can be easily decanted.

^{11}B NMR was used to confirm that the supernatant was free of any detectable levels of boron contamination. Extra purification steps may be performed, such as centrifugation, to remove any solids that were transferred with the FAMES during the decanting process in addition to rinsing the product with hexanes to extract the biodiesel and remove excess MeOH from the reaction. The yield for all oils has been demonstrated to be about 85%, being performed on a small scale using about 4 mmol of vegetable oil.

[0011] According to one embodiment of the present disclosure, a method of transesterification of triglycerides is disclosed. The method includes combining tetraalkoxyborate with a triglyceride composition to form a reaction mixture. The method may include heating the reaction mixture above 40°C to form fatty acid alkyl esters.

[0012] According to another embodiment of the present disclosure, a method of making a diesel fuel is disclosed. The method includes combining tetraalkoxyborate with a triglyceride composition to form a reaction mixture, where the triglyceride composition includes one of a vegetable oil or an animal fat. The method also includes heating the reaction mixture above 40 °C to form the diesel fuel may include fatty acid alkyl esters.

[0013] Implementations of any of the above embodiments may include one or more of the following features. According to one aspect of the above embodiments, tetraalkoxyborate may be one of tetramethoxyborate, tetraethoxyborate, tetrapropoxyborate, or tetrabutoxyborate. The fatty acid alkyl esters may be one of fatty acid methyl esters, fatty acid ethyl esters, fatty acid methyl esters, fatty acid propyl esters, and fatty acid butyl esters. Heating may occur from about 1 hour to about 24 hours. The methods may also include making the tetraalkoxyborate in a reaction vessel and adding the triglyceride composition to the reaction vessel. Making the tetraalkoxyborate may include combining borohydride with an alcohol. The alcohol and the tetraalkoxyborate may include the same alkoxy group, which may be one of a methoxy group, an ethoxy group, an epoxy group, and a butoxy group. Making the tetraalkoxyborate may include combining trialkoxyborane with an alkoxide salt. The trialkoxyborane, the alkoxide salt, and the tetraalkoxyborate may include the same alkoxy group, which may be one of a methoxy group, an ethoxy group, an epoxy group, and a butoxy group. The methods may further include hydrogenating fatty acid alkyl esters. Hydrogenation may be performed using hydrogen collected during making of the tetraalkoxyborate. The tetraalkoxyborate may be one of tetramethoxyborate, tetraethoxyborate, tetrapropoxyborate, or tetrabutoxyborate.

BRIEF DESCRIPTION OF DRAWINGS

[0014] Various embodiments of the present disclosure are described below with reference to the following figures:

[0015] FIG. 1A is an ^1H NMR spectrum of biodiesel produced by reacting coconut oil with NaOMe at 80 °C according to an embodiment of the present disclosure;

[0016] FIG. 1B is an ^1H NMR spectrum of the resulting glycerol byproduct solid contaminated with residual FAMES according to an embodiment of the present disclosure;

[0017] FIG. 2 is a ^{11}B NMR spectrum showing the presence of the tetrahedrally coordinated boron of $\text{NaB}(\text{OMe})_4$;

[0018] FIG. 3 is an ^1H NMR spectrum of pure coconut oil with the protons of the glycerol backbone labeled;

[0019] FIG. 4 is an ^1H NMR spectrum of the decanted product/toluene layer of the reaction mixture according to an embodiment of the present disclosure and the inset is a ^{11}B NMR spectrum of the same sample;

[0020] FIG. 5 is an ^1H NMR spectrum of pure biodiesel (FAMES) from coconut oil at 80 °C in 1 hour using a (^-OMe :fatty acid) molar ratio of 2:1 according to an embodiment of the present disclosure and the inset is a ^{11}B NMR spectrum of the same sample showing no glycerol-boron byproducts;

[0021] FIG. 6 is a ^{11}B NMR spectrum obtained from the solid byproduct in methanol- d_4 according to an embodiment of the present disclosure;

[0022] FIG. 7 shows ^1H NMR spectra of a product of a reaction between $\text{NaB}(\text{OMe})_4$ and coconut oil in toluene showing lack of FAMES production at 25 °C for 1 hour and 24 hours reactions according to an embodiment of the present disclosure;

[0023] FIG. 8 shows ^1H NMR spectra of FAMES synthesized from soybean oil (25 °C) or coconut oil (40, 60 and 80 °C) showing the effects of temperature on transesterification of either soybean oil (25 °C) or coconut oil (40, 60 and 80 °C) over the course of a 1-hour reaction period according to embodiments of the present disclosure;

[0024] FIG. 9 is an ^1H NMR spectrum of biodiesel synthesized from used cooking oil according to an embodiment of the present disclosure and the inset is a ^{11}B NMR spectrum of the same that is free of boron byproduct contaminants;

[0025] FIG. 10 is a ^{11}B NMR spectrum of the starting reaction mixture produced by combining $\text{B}(\text{OMe})_3$ and NaOMe in MeOH according to an embodiment of the present disclosure and the inset zooms in on signals present;

[0026] FIG. 11A is an ^1H NMR spectrum of the product FAMES from reacting coconut oil with $\text{NaB}(\text{OMe})_4$ produced from combining $\text{B}(\text{OMe})_3$ and NaOMe in MeOH according to an embodiment of the present disclosure;

[0027] FIG. 11B is a ^{11}B NMR spectrum of the solid by-product left behind after decanting off the FAMES according to an embodiment of the present disclosure;

[0028] FIG. 12 shows ^{11}B NMR spectra with integration of the product mixture for reactions between NaBH_4 and EtOH (top), PrOH (middle) and BuOH (bottom) according to embodiments of the present disclosure;

[0029] FIG. 13A is an ^1H NMR spectrum of FAMES produced from cooking oil according to an embodiment of the present disclosure;

[0030] FIG. 13B is an ^1H NMR spectrum of ethyl fatty esters produced using a method according to an embodiment of the present disclosure;

[0031] FIG. 13C is an ^1H NMR spectrum of propyl fatty ester produced using a method according to an embodiment of the present disclosure;

[0032] FIG. 13D is an ^1H NMR spectrum of butyl fatty ester produced using a method according to an embodiment of the present disclosure; and

[0033] FIG. 14 shows a flow chart of a method for making fatty acid alkyl esters from triglycerides according to an embodiment of present disclosure.

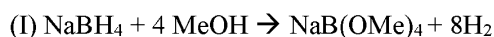
DETAILED DESCRIPTION

[0034] The present disclosure provides a method for making fatty acid alkyl esters (FAAEs), such as fatty acid methyl esters (FAMEs), which may be used as biodiesel. The method includes transesterification of triglycerides, which are the main constituents of vegetable oils or animal fats. Transesterification includes adding a transesterification agent with the oil to form FAMEs or any other desired FAAEs.

[0035] FIG. 14 shows a method 10 for making FAAEs suitable for use as biodiesel. The method 10 includes making a transesterification agent at step 12. The transesterification agent may be a salt of tetraalkoxyborate, such as sodium tetramethoxyborate $[\text{NaB}(\text{OMe})_4]$, sodium tetraethoxyborate $[\text{NaB}(\text{OEt})_4]$, sodium tetrapropoxyborate $[\text{NaB}(\text{OPr})_4]$, and sodium tetrabutoxyborate $[\text{NaB}(\text{OBu})_4]$. Any suitable salt of the compositions described in this disclosure may be used and sodium is used herein as an exemplary cation.

[0036] The choice of the alkoxy group corresponds to the fatty ester that is produced by the transesterification reaction. Sodium tetraalkoxyborate may be prepared by adding sodium borohydride (NaBH_4) to an alcohol, which may include but is not limited to, methanol (MeOH), ethanol (EtOH), propanol (PrOH), and butanol (BuOH). An exemplary reaction for producing

NaB(OMe)₄ is shown in equation I below, where sodium borohydride is combined with an alcohol to form tetraalkoxyborate.



[0037] The alkoxy group of the alcohol and the tetraalkoxyborate may be the same and may be one of methoxy group, ethoxy group, epoxy group, or a butoxy group. The resulting product from either of the reactions of equation (I) is an alkoxyborate/alcohol (e.g., NaB(OMe)₄/MeOH) slurry, which acts as a source of methoxide anion for the formation of FAMES from vegetable oils. During the reaction, the hydrides of NaBH₄ react with the acidic protons of MeOH to form [O⁻Me] and hydrogen gas. The reaction may continue for about 30 minutes or more, or until hydrogen gas generation is stopped. At step 14, the hydrogen gas can be collected and stored for later use. In embodiments, hydrogen can be used for the hydrogenation of the fatty acid chains. The reaction of equation (I) may be performed at room temperature, in any suitable vessel equipped with gas outlets for collection of hydrogen gas and may be aided via stirring.

[0038] In embodiments, the resultant slurry may be dried to remove traces of alcohol. Drying may be performed using any suitable technique, such a vacuum oven, which may be operated at about 80 °C, 20 torr.

[0039] In further embodiments, sodium tetraalkoxyborate salt, such as NaB(OMe)₄, may be also prepared using a reaction shown in equation II below, wherein trialkoxyborane is combined with an alkoxide salt to form tetraalkoxyborate.



[0040] The reaction of equation (II) may be carried out in an alcohol, e.g., methanol, having the same alkoxy group as trialkoxyborane, alkoxide, and tetraalkoxyborate, which may be one of

methoxy group, ethoxy group, epoxy group, or a butoxy group. The resulting solution may be stirred and then combined with a triglyceride composition, as described below.

[0041] At step 16, the transesterification agent is combined with the triglyceride composition, e.g., vegetable oil and/or animal fat. Suitable vegetable oils may be used (e.g., collected from fryers) or unused and include soybean oil, canola oil, coconut oil, sesame oil, nut oils, olive oil, seed oils, and combinations thereof. The oil may be added to the vessel including the transesterification agent at a molar ratio of the transesterification agent to oil of approximately 2:1 or more. Oil may be added with or without a solvent, such as toluene.

[0042] At step 18, the reaction vessel may be heated above 40 °C, which in embodiments may be from about 40 °C to about 80 °C. Heating may be done for from about 1 hour to about 24 hours. In further embodiments, the reaction may continue from about 1 hour to about 3 hours. The reaction mixture may be agitated via stirring or any other suitable mechanism.

[0043] At step 20, the resulting product of FAAEs are isolated. Once reaction is complete, the FAAEs form a liquid and a solid byproduct settling to the bottom of the reaction vessel. The liquid may be separated using any suitable means, such as decanting, filtration, centrifugation, and the like. In further embodiments, a solvent, such as hexane, may be used to extract remnants of the liquid FAAEs from the solid byproduct by rinsing the reaction vessel with the solvent. The solvent may then be removed from the liquid product via evaporation by heating the product to the boiling point of the solvent, which may be about 80 °C.

[0044] At optional step 22, hydrogenation may be performed using hydrogen generated during production of tetraalkoxyborate and/or from any other suitable source. The extracted FAAEs may be hydrogenated in a reaction vessel to which hydrogen is introduced in the presence of a catalyst, which may be a bifunctional catalyst containing both acidic and metallic sites. The hydrogenation

reaction may take place under temperatures of around 300°C and pressure of around 5 MPa. The hydrogen reacts with the double bonds present in the fatty acid chains of the FAAEs. This reaction saturates the double bonds via the addition of hydrogen atoms, converting the unsaturated FAAEs into their saturated counterparts. In addition, during hydrogenation, the catalyst also promotes hydrocracking, which involves breaking down the long fatty acid chains into smaller molecules with lengths similar to those found in conventional diesel fuel. The final product may be further processed to remove impurities and obtain high-quality biodiesel.

[0045] The following Examples illustrate embodiments of the present disclosure. These Examples are intended to be illustrative only and are not intended to limit the scope of the present disclosure. Also, parts and percentages are by weight unless otherwise indicated. As used herein, “room temperature” or “ambient temperature” refers to a temperature from about 20 °C to about 25 °C.

EXAMPLES

EXAMPLE 1

[0046] This example describes the synthesis of FAMEs using sodium methoxide.

[0047] For (–Ome:fatty acid) 1:1 (mol/mol), a 50 mL round-bottom flask was equipped with a stir bar and melted coconut oil (2.75 g, 4.0 mmol, 12 mmol equivalent of fatty acid) was added to MeOH (2.5 mL). To this mixture, NaOMe (0.65 g, 12 mmol) was then added. The flask was fitted with a septum and venting needle and the reaction mixture was heated to about 80 °C for about one hour. The resulting white slurry was decanted into a conical centrifuge tube, the reaction flask was rinsed twice with hexanes (2×5 mL) and the decant was added to the centrifuge tube and then centrifuged. The supernatant liquid was decanted into a 100-mL round-bottom flask and the hexanes were evaporated at about 80 °C under vacuum (approximately 20 Torr). The residue was an oily solid and was dissolved in Chloroform-d (CDCl₃) for ¹H NMR analysis.

[0048] NMR was performed using a Bruker 500 MHz spectrometer at 300 K with a composite pulse sequence. Signals were recorded at 160 and 500 MHz for ^{11}B and ^1H , respectively. ^{11}B and ^1H NMR chemical shifts were measured relative to the external standards $\text{BF}_3\cdot\text{Oet}_2$ ($\delta = 0$ ppm) and TMS ($\delta = 0$ ppm), respectively.

[0049] For reactions taking place at 80 °C with an (^-Ome :fatty acid chain) ratio of 1:1, the reaction mixture after one hour resulted in a white slurry. This slurry was rinsed with hexanes to extract the biodiesel and was decanted into a centrifuge tube. Even after multiple centrifuge attempts, the residual solid byproduct of the decant could not be separated from the hexanes/biodiesel product. The decant was added to a round-bottom flask, despite small amounts of solid being present, and the hexanes were evaporated off at 80 °C under a house vacuum. There was no obvious collection of biodiesel left in the flask. There were crystals of byproduct in the flask and the presence of the FAMES were nothing more than grease on the flask walls. Chloroform- d was added to the flask to dissolve the greasy substance, which was confirmed to be biodiesel though ^1H NMR as shown in FIG. 1A. The solid glyceroxide containing byproduct was dissolved in methanol- d_4 and analyzed using ^1H NMR as shown in FIG. 1B.

[0050] Additional experiments were performed using a (^-Ome :fatty acid) ratio of 2:1 at 25 and 80 °C. For both temperatures, NaOMe powder was added to a round-bottom flask containing only oil and was stirred vigorously. Both reaction mixtures quickly thickened up into a brown paste that immobilized the stir-bars. These reaction mixtures were not analyzed further.

[0051] For (^-Ome :fatty acid) 2:1 (mol/mol), a 50-mL round-bottom flask was equipped with a stir bar and melted coconut oil (2.75 g, 4.0 mmol, 12 mmol equivalent fatty acid) was added to MeOH (2.5 mL). To this mixture, NaOMe (1.30 g, 24 mmol) was then added. The flask was fitted with a septum and venting needle and the reaction mixture was brought to 80 °C. Within minutes, the

mixture thickened up into a brown paste that immobilized the stir-bars. No liquid was visibly present, and the mixture was discarded. An identical experiment was carried out at 25 °C and the results were the same as those obtained at 80 °C. These reaction mixtures were not analyzed further.

EXAMPLE 2

[0052] This example describes synthesis of NaB(OMe)₄ for use in synthesizing FAMES from vegetable oils.

[0053] [−OMe] was introduced in the form of NaB(OMe)₄ as a means of producing FAMES from vegetable oils. Synthesis of NaB(OMe)₄ was accomplished by combining NaBH₄ (0.228 g, 6.0 mmol) with MeOH (2.5 mL) in a 50-mL round-bottom flask equipped with a stir bar. The flask was fitted with a septum and venting needle and allowed to proceed at room temperature, with stirring, for about 30 minutes, or until hydrogen gas was no longer observed originating from the NaB(OMe)₄/MeOH slurry. For this reaction, the hydrides of NaBH₄ reacted with the acidic protons of MeOH to form [−OMe] and hydrogen gas. The hydrogen can be stored and used for the hydrogenation of the FAMES fatty acid chains, making them a completely practical substitute for classic diesel. 1 mole of NaBH₄ reacts with 4 moles of MeOH to produce NaB(OMe)₄ as the exclusive product. In a separate container, liquid coconut oil (2.15 g, 3.0 mmol) was dissolved in toluene (5 mL). This solution was then added to the NaB(OMe)₄/MeOH slurry, heated to 80 °C and allowed to react for two hours, with stirring. The liquid was then decanted into a separate container without further purification and analyzed by ¹H and ¹¹B NMR.

[0054] To generate FAMES from vegetable oils, [−OMe] is used. In Example 1, this was obtained from NaOMe. However, this resulted in liquid FAMES that were difficult to separate from the solid byproduct compounds, even with filtration and centrifugation.

[0055] Biodiesel from vegetable oil transesterification was achieved through a reaction between NaBH_4 and MeOH as demonstrated by equation (I) above.

[0056] Upon the addition of NaBH_4 to MeOH , hydrogen gas is evolved from the solution as the hydrides of NaBH_4 react with the acidic protons of MeOH . A sufficient amount of MeOH was used to allow the resulting viscous mixture to freely stir using a magnetic stirrer. After the hydrogen generation stops, approximately 30 min after the start of the reaction, the resulting thick slurry of NaB(OMe)_4 in MeOH acts as the source of methoxide anion for the formation of FAMES from vegetable oils.

[0057] Initially, the transesterification reactions were carried out in toluene using solid NaB(OMe)_4 . The NaB(OMe)_4 was prepared as described in Example 2 and a vacuum oven (80 °C, 20 torr) was employed to remove excess MeOH , leaving pure NaB(OMe)_4 for the initial set of experiments. Transesterification was carried out by adding coconut oil (2.15 g oil, 3 mmol oil; 9 mmol fatty acids) in toluene (5 mL) to the solid NaB(OMe)_4 . The reaction was performed at 80 °C, with vigorous stirring, using NaB(OMe)_4 produced from NaBH_4 (0.228 g NaBH_4 , 6 mmol NaBH_4 ; 24 mmol ^-OMe).

[0058] All four hydrides of NaBH_4 react with MeOH , resulting in the formation of ^-OMe , which combines with boron to form NaB(OMe)_4 exclusively, as shown by ^{11}B NMR depicted in FIG. 2. NaB(OMe)_4 is the source of ^-OMe for the formation of FAMES from vegetable oils. The reaction goes to completion since there is no NaBH_4 quintet at about -42 ppm. The quintet associated with NaBH_4 is shown in FIG. 10.

EXAMPLE 3

[0059] This example describes the effects of (NaBH₄:Fatty Acid) ratio on the FAME synthesis of Example 2.

[0060] A variety of reaction conditions were explored to understand the reaction between NaB(OMe)₄ and triacylglycerides. First to be investigated was the ratio of NaBH₄ to vegetable oils. Since the ⁻OMe of NaB(OMe)₄ reacts with the ester groups of the coconut oil to form FAMEs, reactions were performed with regards to ⁻OMe and fatty acid chains as opposed to NaB(OMe)₄ or NaBH₄ and coconut oil. Consequently, each molecule of NaB(OMe)₄ contains four molar equivalents of ⁻OMe, capable of forming FAMEs from the vegetable oils. In addition, since each triacylglyceride contains three molar equivalents of ester groups, the molar ratios of 1:1, 3:2 and 2:1 (⁻OMe:Fatty acid alkyl ester) were explored. The corresponding (NaBH₄:coconut oil) were 3:4, 1:1 and 3:2, respectively. Reactions were carried out using coconut oil, neat, at 80 °C with stirring for one hour.

[0061] Reactions that used a (⁻OMe:fatty acids) ratio of 1:1 (mol/mol) produced a homogenous emulsion and made it difficult to isolate the biodiesel using the isolation protocols developed in the lab. This is likely due to the formation of surfactants produced from the vegetable oil when ⁻OMe is not present in excess amounts. These surfactants could be monolaurin and/or glycerol dilaurate. Surfactants promote emulsification of the FAMEs and the byproduct, making separation a difficult endeavor.

[0062] When an excess of [⁻OMe] was used in either a 3:2 or 2:1 (⁻OMe:fatty acids) ratio, an easier separation of biodiesel from the byproduct could be achieved. The FAMEs could be decanted off from the byproduct, making this a highly desirable method for producing biodiesel. Hexanes are used to increase the yield by extracting the FAMEs from the byproduct and residual

MeOH. Evaporation of the solvent hexanes gave essentially pure FAMES with a methyl peak at about 3.6 ppm and no discernible peaks attributable to the starting triglyceride or MeOH in the ^1H NMR spectrum as shown in FIG. 5. Since a 2:1 (^-OMe :fatty acids) molar ratio afforded an optimal yield of FAMES, values near this (^-OMe :fatty acid) molar ratio were used to screen different vegetable oils as well as to investigate the effect of temperature on the production of biodiesel.

[0063] The absence of glycerol peaks in the ^1H NMR spectrum of biodiesel product is a good qualitative tool for determining the progression of the reaction. As a more quantitative measure for determining reaction completion using ^1H NMR, integration of the methyl ester peak of FAMES was compared with that of the terminal $-\text{CH}_3$ group of the fatty acid side chain of FAMES. Since both the methyl group and the terminal carbon have three protons, the two integrals must have the same value to indicate purity of FAMES as shown in FIG. 5. Essentially pure methyl laurate was obtained as the major product of the reaction shown in FIG. 5. This molecule is shown along with its ^1H NMR. ^{11}B NMR spectrum of the same sample showed the produced FAMES was pure, with no glycerol or boron byproducts present after centrifugation.

[0064] The initial reaction mixture of coconut oil and $\text{NaB}(\text{OMe})_4$ exists as an emulsion and is homogeneous. As the reaction proceeds, the FAMES layer separates from the denser, semi-solid gel-like byproduct. The byproduct is composed of excess starting $\text{NaB}(\text{OMe})_4$ (3.01 ppm) in addition to three other glycerol borates as shown in FIG. 6. The starting $\text{NaB}(\text{OMe})_4$ has four methoxides bonded to a B-atom. As the methoxide reacts with the triacylglycerides of coconut oil, glyceroxide was formed and remains in its deprotonated state due to the presence of excess ^-OMe ions. The newly formed negatively charged oxygen atoms of glyceroxide form new boron-oxygen bonds, resulting in glyceroxide borate byproducts.

[0065] On the basis reported chemical shift values for several five- and six-membered mono- and bis-chelated polyols of boric acid ($[\text{B}(\text{OH})_2\text{L}]^-$ and $[\text{BL}_2]^-$), the peak at about 10.47 ppm could be attributed to the five-membered bis(glycerol)borate shown in FIG. 6, whose signal typically ranges from about 9.8 to about 14.0 ppm. The peak at about 6.83 and about 1.68 ppm in the ^{11}B NMR spectrum cannot be assigned unambiguously and could be multiple cyclic borate species.

[0066] The dense byproduct accumulates on the bottom of the flask, allowing the newly formed FAMES to be isolated by simple decantation. An additional bonus of this reaction is the glyceroxide byproducts and product FAMES do not form emulsions and allow easy separation. The initially isolated FAMES layer has a slightly hazy appearance but can be made clear by centrifugation followed by decanting of the top layer. The haziness is attributed to a small amount of suspended glycerol-boron byproduct. This was confirmed by taking the ^{11}B NMR spectrum of the small amount of solid that accumulates at the bottom of the centrifuge tube. The collected ^{11}B spectrum was identical to that of the bulk byproduct.

[0067] The effects of the ratio of NaBH_4 to vegetable oil on the production of biodiesel were studied. Since the $[\text{OMe}]$ equivalents available from $\text{NaB}(\text{OMe})_4$ are the active components of the reaction, various ratios of $[\text{OMe}]$ equivalents to the fatty acid chains of the vegetable oils were evaluated. When 1 mol equivalent NaBH_4 reacts with excess MeOH, 4.0 mol equivalents of $[\text{OMe}]$ are produced due to the formation of $\text{NaB}(\text{OMe})_4$. On the other hand, 1 mol equivalent of vegetable oils contains 3 mol equivalents of fatty acids that can be used to produce FAMES biodiesel. Each molar ratio explored had the same quantity of NaBH_4 added to varying amounts of coconut oil. Thus, for reactions with molar ratios of ($[\text{OMe}]$:fatty acid) equal to 1:1, 3:2, and 2:1 (mol/mol), NaBH_4 (0.228 g NaBH_4 , 6.0 mmol NaBH_4 ; 24 mmol $[\text{OMe}]$) were added to MeOH (2.5 mL) in a 50-mL round-bottom flask equipped with a stir bar. The flask was then fitted with a

septum and a needle for venting evolved hydrogen gas, while allowing a minimal amount of air into the reaction mixture. The mixture was stirred at room temperature for about 30 minutes or until hydrogen bubbling visibly stopped and the septum and needle were removed.

[0068] For 1:1, 3:2, and 2:1 reactions, the following amounts of coconut oil and fatty acid equivalents were added to the flask, respectively: 5.51 g oil (8.0 mmol oil; 24 mmol of fatty acids); 3.65 g oil (5.3 mmol oil; 16 mmol of fatty acids); 2.18 g oil (3.2 mmol oil; 10 mmol of fatty acids). The needle and septum were returned to the flask and the mixture was allowed to react at 80 °C with strong stirring for one hour.

[0069] For the 1:1 reaction, a viscous emulsion was observed, and no biodiesel layer could be discerned. Hexanes (10 mL) were added to this mixture to extract the biodiesel, but the emulsion remained, and no phase separation was visible. No further action was taken with this reaction mixture.

[0070] For the 3:2 reaction mixture, there was a clear separation of the FAMES and byproduct at the end of the one hour reaction period. The FAMES were decanted away from the solid byproduct, which stuck to the bottom of the round-bottom flask. The flask was then rinsed twice with hexanes and added to the decant before centrifugation to remove any solids that were transferred. The liquid layer was added to a round-bottom flask and the hexanes were evaporated off at 80 °C under vacuum (20 Torr). The resulting product was a clear, colorless liquid and was collected for ^1H and ^{11}B NMR analysis.

EXAMPLE 4

[0071] This example describes the effects of temperature on the FAMES synthesis of Example 2.

[0072] Investigations into the effect of various reaction temperatures were performed using a 2:1 (–OMe:fatty acid) molar ratio. Reactions performed at 40 °C and 60 °C were run neat, where liquid coconut oil was added directly to the NaB(OMe)₄/MeOH slurry. At 25 °C, soybean oil was used since it is a liquid at room temperature as opposed to coconut oil. A reaction temperature of 80 °C was excluded since most of the results discussed above were obtained at 80 °C.

[0073] Transesterification using coconut oil was explored due to the relatively simple chemical nature of this vegetable oil. ¹H NMR of the starting coconut oil with proton assignments for the glycerol backbone is shown in FIG. 3. All signals to the right of 3 ppm are associated with protons of the fatty acid chain, which for all practical purposes, is assumed to be entirely lauric acid and is labeled as “R”. The small signal to the left of the leftmost “H” originates from the small amount of unsaturation in coconut oil.

[0074] Coconut oil contains a much higher saturated fat content than other commonly consumed vegetable oils and is primarily composed of lauric (12:0), myristic (14:0) and palmitic (16:0) acids, which represent about 32 to about 51%, about 17 to about 21% and about 6.9 to about 14%, respectively. With an understanding of the ¹H NMR of the starting oil, the reaction progress towards FAMES can be monitored.

[0075] After a one hour reaction between NaB(OMe)₄ and coconut oil in toluene, the top layer of the mixture was decanted and collected for ¹H and ¹¹B NMR analysis (FIG. 4). The ¹H NMR spectrum showed complete conversion of coconut oil to biodiesel as evidenced by the disappearance of ¹H signals of glycerol and the emergence of the methyl peak of product FAMES. The small ¹H singlet, which is occasionally two overlapping singlets, at about 3.3 ppm is due to residual methanol (*vide infra*). ¹¹B NMR, as shown in FIG. 4, showed the absence of any boron

impurities in the toluene/biodiesel layer. The small boron signal of the inset arises from the borosilicate glass of the NMR tube.

[0076] Using a (^-OMe :fatty acid) ratio of 2:1 (mol/mol), the effect of various temperatures (25 °C, 40 °C, 60 °C, and 80 °C) was investigated on the synthesis of FAMES. To a 50-mL round-bottom flask equipped with a stir bar, NaBH_4 (0.228 g NaBH_4 , 6 mmol NaBH_4 ; 24 mmol of ^-OMe) was added to MeOH (2.5 mL). The flasks were then fitted with a septum, complete with a needle for venting the evolved hydrogen and allowed to react, with stirring at 25 °C for about 30 minutes, or until bubbling noticeably stopped. To the resulting $\text{NaB(OMe)}_4/\text{MeOH}$ slurry, liquid coconut oil (2.18 g oil, 3.2 mmol oil; 10 mmol fatty acids) was added. The septum and venting needle were placed back on the flask and the mixture was brought to 80 °C, with stirring, for one hour. The resulting liquid layer was decanted into a Falcon tube, the reaction mixture was rinsed with hexanes (2 mL) to extract residual biodiesel and the rinse was added to the decant. This solution was then centrifuged to remove small amounts of solid byproduct transferred with the decant. The resulting liquid layer was added to a round-bottom flask and the hexanes were evaporated off at 80 °C under vacuum (20 Torr). The residue was collected for ^1H and ^{11}B NMR analysis.

[0077] ^1H NMR showed that the reaction at 25 °C barely produced any FAMES. This is apparent by the presence of glyceride proton signals at about 4.2 ppm and the lack of a methyl ester peak for FAMES at about 3.6 ppm as shown in FIG. 7. Even after 24 hours, the signals associated with glycerol are still prominent, indicating large amounts of starting soybean oil. The singlet at about 3.4 ppm is due to methanol which is present because the product was not extracted using hexanes. If the reaction is allowed to stir for 24 hours, far more biodiesel is produced, but there were still unreacted glyceride signals that indicate the presence of unreacted soybean oil in the FAMES. The spectra of the 24 hour reaction also contained far less MeOH left over from the starting

NaB(OMe)₄/MeOH slurry as shown in FIG. 7. This is likely due to the MeOH evaporating off over the long reaction period.

[0078] Reactions carried out at 40 °C and 60 °C for one hour gave complete conversion of coconut oil to FAMES as shown in FIG. 8 just like the reactions carried out at 80 °C. The singlet at about 3.46 ppm in the 25 °C, 40 °C, and 60 °C spectra was due to left over MeOH since the final product was simply decanted from the reaction mixture and not extracted with hexanes. At 80 °C, the product was extracted with hexanes to confirm the MeOH peak would be fully removed from the ¹H spectrum. A distinguishing feature of reactions run at 80 °C as opposed to 40 °C and 60 °C is the complete disappearance of the glycerol hydrogens in the ¹H NMR spectra for the former. While they are not apparent in FIG. 8, zooming in on the region around about 4.20 ppm exposes small glycerol signals just emerging above the background noise on the original spectra. Its presence is so small that the integration of the methyl and terminal fatty acid protons are not affected, for which integration shows 100% reaction completion despite its signal being slightly detectable. No magnification of the ¹H NMR for reactions run at 80 °C were able to expose signals associated with glycerol. To completely eliminate the presence of any detectable glycerol in the product diesel, experiments were performed investigating used cooking oil as a feedstock chemical at 80 °C and with a ratio of (–OMe:fatty acid) 2:1.

EXAMPLE 5

[0079] This example describes synthesizing FAMES from used cooking oil.

[0080] To a 50-mL round-bottom flask equipped with a stir bar, NaBH₄ (0.228 g NaBH₄, 6 mmol NaBH₄; 24 mmol of –OMe) was added to MeOH (2.5 mL). The flask was fitted with a septum and needle for venting evolved hydrogen and allowed to react at room temperature with stirring for

about 30 minutes, or until bubbling subsided. Cooking oil (3.23 g oil, 3.5 mmol oil; 10 mmol fatty acids) was then added and the mixture was refitted with the septum and needle. The reaction mixture was brought to 80 °C and allowed to react with strong stirring for one hour. The liquid was decanted away from the solid byproduct and the flask was rinsed twice with hexanes (2×2 mL) and combined with the decant before being centrifuged to remove any additional small amounts of solid byproduct. The hexanes were then evaporated off at 80 °C under vacuum (20 Torr). The product FAMES were a yellow orange, slightly viscous liquid and were collected for ^1H and ^{11}B NMR analysis.

EXAMPLE 6

[0081] This example describes synthesizing FAMES using NaB(OMe)_4 synthesized from a reaction between B(OMe)_3 and NaOMe in MeOH .

[0082] To a 50 mL round-bottom flask equipped with a stir bar, MeOH (3 mL) was added followed by the addition of B(OMe)_3 (0.67 mL, 6 mmol). To this solution, NaOMe (0.324 g, 6 mmol) was added and stirred briefly to dissolve all the solid. To this solution, melted coconut oil (3.23 g, 3.5 mmol oil, 10 mmol fatty acids) was added. The flask was equipped with a septum and venting needle and allowed to react with stirring at 80 °C for one hour. After one hour, the product was removed from the heat and allowed to cool slightly so the product FAMES could easily be decanted from the solid byproduct. The liquid was decanted away from the solid byproduct and the flask was rinsed twice with hexanes (2×2 mL) and combined with the decant before being centrifuged to remove any additional small amounts of solid byproduct. The hexanes were then evaporated off at 80 °C under vacuum (20 Torr). The product FAMES were a clear and colorless, slightly viscous liquid and were collected for ^1H and ^{11}B NMR.

[0083] The above experiment showed that NaB(OMe)_4 is an effective source of ^-OMe that allows for the simple synthesis and isolation of FAMES without producing water or the need for heterogeneous catalysts. The Examples thus far have synthesized NaB(OMe)_4 from a reaction between NaBH_4 and MeOH . However, this salt can also be synthesized using the highly inexpensive chemicals B(OMe)_3 and NaOMe , as demonstrated in equation (II) above.

[0084] This alternative chemical route for the production of NaB(OMe)_4 that uses abundant and cheap reagents makes this biodiesel production process truly industrially feasible. The presently disclosed method was successful at producing pure FAMES under the same conditions explored using NaBH_4 and MeOH .

[0085] The process involved the addition of B(OMe)_3 and NaOMe to MeOH to form a NaB(OMe)_4 containing mixture. ^{11}B NMR showed the mixture is not pure NaB(OMe)_4 but rather a combination of four different boron products, possibly resulting from impurities in the commercially purchased NaOMe as shown in FIG. 10. The signal at about 3.3 ppm corresponds to NaB(OMe)_4 , as was seen from the production of this molecule using NaBH_4 and MeOH . The presence of additional boron species did not affect the production of FAMES from coconut oil, as shown in FIG. 11A. The solid byproduct left behind after decanting the FAMES was chemically identical to that produced from transesterification reactions using NaB(OMe)_4 produced from NaBH_4 and MeOH , as shown in FIG. 11B.

[0086] Further experimentation revealed that reactions could be run under neat, solvent free conditions. It was also discovered that excess MeOH , used to make NaB(OMe)_4 , need not be evaporated before introducing coconut oil. However, it is highly imperative that hydrogen gas evolution is completed before adding coconut oil to the reaction flask. This will indicate that all the NaBH_4 had reacted with the MeOH and that no hydride would be present to reduce the ester

group of the coconut oil. For these reactions, MeOH was added directly to NaBH₄ to get a NaB(OMe)₄/MeOH slurry. Coconut oil was then added directly to this slurry. This experimental protocol permitted investigation of the following variables: 1) the effects of (⁻OMe:fatty acid) ratio; 2) reaction temperature; 3) type of vegetable oil that could be used for the formation of FAMES. Hexanes were used to extract the biodiesel from the crude reaction mixture in essentially quantitative yield and to eliminate MeOH from the final product.

EXAMPLE 7

[0087] This example describes synthesis of fatty acid ethyl esters.

[0088] To further investigate the versatility of using NaBH₄ in the presence of an alcohol for the synthesis of FAAEs from used cooking oil, the synthesis of ethyl esters was tested. This was performed by adding NaBH₄ to ethanol (EtOH) and allowing the solutions to react until no additional hydrogen was visibly produced. The reaction of NaBH₄ with EtOH proceeded at room temperature, but at a slower pace than the reaction of NaBH₄ with MeOH. Just as was observed with the reaction of NaBH₄ and MeOH, the product of the reaction of NaBH₄ with EtOH is NaB(OEt)₄. However, unlike with NaBH₄ and MeOH, the NaBH₄ did not fully react with EtOH as illustrated by quintets at -42 ppm in ¹¹B NMR of FIG. 12. This is despite allowing the reaction to proceed until no hydrogen evolution could be observed in the presence of excess alcohol.

[0089] The reaction was performed using a 50-mL round-bottom flask equipped with a stir bar. NaBH₄ (0.228 g NaBH₄, 6 mmol NaBH₄; 24 mmol of ⁻OEt) was added to EtOH (2.5 mL). The flask was fitted with a septum and needle for venting the evolved hydrogen and allowed to react at room temperature with stirring for about 10 minutes, during which light bubbling was observed. The reaction was then brought to 80 °C and was allowed to react for an additional one hour, after

which no bubbling was observed. Not all NaBH_4 reacted. A sample of this mixture was collected for ^{11}B NMR. To this foggy reaction mixture, used cooking oil (3.23 g oil, 3.5 mmol oil; 10 mmol fatty acids) was added and the septum with needle was returned to the flask. The mixture was then brought to 80 °C and allowed to react for two hours with strong stirring. The mixture at the end of the two-hour reaction period was a clear, yellow-orange putty like substance. The ethyl fatty acid was extracted using hexanes (4×10 mL) and centrifuged. The liquid layer was decanted into a round-bottom flask and the hexanes were evaporated off at 80 °C under vacuum (20 Torr). A sample of the product and the residual byproduct were collected for ^1H and ^{11}B NMR analysis, which is described in Example 9.

EXAMPLE 8

[0090] This example describes synthesis of fatty acid propyl esters.

[0091] To further investigate the versatility of using NaBH_4 in the presence of an alcohol for the synthesis of FAAEs from used cooking oil, the synthesis of propyl esters was also tested. This was performed by adding NaBH_4 to propanol (PrOH) and allowing the solutions to react until no additional hydrogen was visibly produced. Reactions between NaBH_4 and PrOH did not proceed at an appreciable pace at room temperature so were heated at 80 °C until no more hydrogen evolution was observed. Just as was seen with the reaction of NaBH_4 and MeOH , the product of the reaction of NaBH_4 with PrOH is $\text{NaB}(\text{OPr})_4$. However, unlike with NaBH_4 and MeOH , the NaBH_4 does not fully react with PrOH as illustrated by quintets at -42 ppm in ^{11}B NMR of FIG. 12. This is despite allowing the reaction to proceed until no hydrogen evolution could be observed in the presence of excess alcohol.

[0092] The reaction was performed using a 50-mL round-bottom flask equipped with a stir bar. NaBH₄ (0.228 g NaBH₄, 6 mmol NaBH₄; 24 mmol ⁻OPr) was added to PrOH (2.5 mL). The flask was fitted with a septum and needle for venting the evolved hydrogen and allowed to react at room temperature with stirring for about 10 minutes, during which no bubbling was observed. The mixture was brought to 80 °C and allowed to react for about one hour with strong stirring after which no further bubbling was observed. Not all the NaBH₄ dissolved, and an aliquot of the viscous, hazy mixture was collected for ¹¹B NMR analysis. To the reaction flask, used cooking oil (3.23 g oil, 3.5 mmol oil; 10 mmol fatty acids) was added and the septum with needle was returned to the flask. The mixture was then brought to 80 °C and allowed to react for two hours with strong stirring. The unpurified mixture was a thick, clear yellow-orange substance. Hexanes (4×10 mL) were used to extract the propyl fatty acid alkyl ester and added to a centrifuge tube. The mixture was then centrifuged and the clear, hexanes layer was added to a round-bottom flask. The hexanes were evaporated off at 80 °C under vacuum (20 Torr), and the residue was collected for ¹H and ¹¹B NMR analysis. The solid byproduct was also collected for ¹H and ¹¹B NMR analysis which is described in Example 9.

EXAMPLE 9

[0093] This example describes synthesis of fatty acid butyl esters.

[0094] To further investigate the versatility of using NaBH₄ in the presence of an alcohol for the synthesis of FAAEs from used cooking oil, the synthesis of butyl esters was additionally tested. This was performed by adding NaBH₄ to butanol (BuOH) and allowing the solutions to react until no additional hydrogen was visibly produced. Reactions between NaBH₄ and BuOH did not proceed at an appreciable pace at room temperature so were heated at 80 °C until no more hydrogen

evolution was observed. Just as was seen with the reaction of NaBH_4 and MeOH , the product of the reaction of NaBH_4 with BuOH is $\text{NaB}(\text{OBu})_4$. However, unlike with NaBH_4 and MeOH , the NaBH_4 does not fully react with BuOH as illustrated by quintets at -42 ppm in ^{11}B NMR of FIG. 12. This is despite allowing the reaction to proceed until no hydrogen evolution could be observed in the presence of excess alcohol. The order of reactivity for NaBH_4 with alcohols described in Examples 7, 8, and the present Example follows the trend $\text{MeOH} > \text{EtOH} > \text{PrOH} > \text{BuOH}$.

[0095] The reaction was performed using a 50-mL round-bottom flask equipped with a stir bar. NaBH_4 (0.228 g NaBH_4 , 6 mmol NaBH_4 ; 24 mmol ^-OBu) was added to BuOH (5.0 mL). The flask was fitted with a septum and needle for venting the evolved hydrogen and allowed to react at room temperature with stirring for about 10 minutes, during which no bubbling was observed. The reaction mixture was brought to 80°C and allowed to react for about 20 minutes with strong stirring after which an additional BuOH (5 mL) was added. The mixture was brought back to 80°C and allowed to react for about three hours with strong stirring after which no further bubbling was observed. Not all NaBH_4 dissolved, and a sample of the viscous, foggy mixture was collected for ^{11}B NMR. To the reaction flask, used cooking oil (3.23 g oil, 3.5 mmol oil; 10 mmol fatty acids) was added and the septum with needle was returned to the flask. The mixture was then brought to 80°C and allowed to react for two hours with strong stirring. The unpurified mixture was a clear, viscous yellow-orange mixture. Hexanes (4×10 mL) were used to extract the butyl fatty acid alkyl ester and added to a centrifuge tube. The mixture was then centrifuged without noticeable liquid separation. Additional hexanes (3×10 mL) were added to the mixture and after centrifugation a small phase separation was discernible. The liquid layer was decanted into a round-bottom flask and the hexanes were removed by evaporation at 80°C under vacuum (20 Torr). The final product

was a yellow, highly viscous material. A sample of the product and the byproduct were collected for ^1H and ^{11}B NMR analysis.

[0096] As shown in FIG. 12, the ^{11}B NMR spectra show the starting borate-alkoxide/alcohol slushies contained unreacted NaBH_4 . The presence of unreacted NaBH_4 did not affect the transesterification reaction. Its presence was expected to be troublesome, since NaBH_4 could react with EtOH , PrOH and BuOH to form $\text{NaBH}_3(\text{OEt})$, $\text{NaBH}_3(\text{OPr})$ and $\text{NaBH}_3(\text{OBu})$, respectively. These species are intermediates of $\text{NaB}(\text{OEt})_4$, $\text{NaB}(\text{OPr})_4$, and $\text{NaB}(\text{OBu})_4$. The hydrides of these intermediate species are more reactive than those of NaBH_4 and can reduce the ester groups of vegetable oils and prevent transesterification. However, ^1H NMR showed transesterification did proceed to produce the ethyl, propyl and butyl FAAEs as shown in FIGS. 13A-13D. Reaction success is evident by the complete disappearance of the glycerol signals of the used cooking oil centered at about 4.20 ppm and the emergence of new signals at about 4.1 ppm (quartet) for the ethyl fatty acid alkyl ester and about 4.0 ppm (triplet) for the propyl and butyl FAAEs. Unlike closely related FAMES, the ethyl, propyl and butyl esters are quite difficult to separate from the glyceroxide byproduct. This is because the emulsions present with EtOH , PrOH and BuOH are much harder to break up than with MeOH .

EXAMPLE 10

[0097] This example describes synthesis of FAMES from cooking oil obtained from a commercial fast-food chain.

[0098] The use of edible virgin oils for biodiesel production would not only divert important food resources away from consumers, but it would also result in uncompetitive prices when compared to fossil fuel derived diesel. Used cooking oils are currently a highly abundant waste that can pose

as an environmental pollutant. Used cooking oil as a feedstock for biodiesel eliminates the need for virgin cooking oils and makes the biodiesel process potentially competitive to those of fossil fuel diesel. For these reasons, the possibility of biodiesel production using NaBH_4 in MeOH with used cooking oil from a big chain fast food restaurant was investigated. When the used oil was added to a $\text{NaB(OMe)}_4/\text{MeOH}$ slurry at 80 °C and allowed to react for one hour with stirring, pure biodiesel was produced as the exclusive product as shown in FIG. 9. As an added bonus, the byproduct existed as a solid on the bottom of the flask and the product biodiesel could easily be separated by a simple decantation. ^1H and ^{11}B NMR showed the collected biodiesel is free of boron impurities as shown in FIG. 9.

EXAMPLE 11

[0099] This example describes synthesizing FAMES from different oils.

[00100] The presently disclosed method works with industrially realistic feedstock oils, such as used cooking oil from a fast-food chain. If the presently disclosed method were to be limited only to virgin edible oils, practical applications would be a far stretch. For completeness, virgin oils were also used to investigate the workings of this novel reaction since they are readily available.

[00101] While used cooking oils are typically a mixture of vegetable oils, the synthesis of FAMES using a variety of common edible oils was investigated to ensure this method of biodiesel production is applicable to a variety of pure oils. When $\text{NaB(OMe)}_4/\text{MeOH}$ is combined with either corn, olive, sesame, soybean oil or pig lard, biodiesel is produced as a separate, liquid layer with the byproduct existing as a solid on the bottom of the flask. This allowed for a simple separation of biodiesel from the glycerol-boron byproducts and the excess NaB(OMe)_4 starting

material. A small amount of this undesired solid contaminated the biodiesel but at such a small quantity that it is not detected by ^{11}B NMR spectroscopy. However, the biodiesel appeared slightly hazy due to this contaminant. To get the purest biodiesel, the initially decanted FAMES were extracted with hexanes to remove any excess MeOH and the entire mixture was centrifuged to remove the small amount of solid byproduct. The hexanes were then evaporated from the decant and the resulting liquid is pure, clear biodiesel, with a yellow orange to colorless appearance. ^1H NMR of these solutions are identical to those seen previously for biodiesel samples. Yields across all oils were about 85%.

[00102] Alternate embodiments may be devised without departing from the spirit or the scope of the present technology. Additionally, well-known elements of embodiments of the systems, apparatuses, and methods have not been described in detail or have been omitted so as not to obscure the relevant details of the systems, apparatuses, and methods.

[00103] The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting. The terms “comprises,” “comprising,” or any other variation thereof are intended to cover a non-exclusive inclusion, such that a process, method, article, or apparatus that comprises a list of elements does not include only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. An element preceded by “comprises ... a” does not, without more constraints, preclude the existence of additional identical elements in the process, method, article, or apparatus that comprises the element. The terms “including” and/or “having,” as used herein, are defined as comprising (i.e., open language). The terms “a” or “an”, as used herein, are defined as one or more than one. The term “plurality,” as used herein, is defined as two or more than two. The term “another,” as used herein, is defined as at least a second or more. The description may use the

terms "embodiment" or "embodiments," which may each refer to one or more of the same or different embodiments.

[00104] For the purposes of the description, a phrase in the form "A/B" or in the form "A and/or B" or in the form "at least one of A and B" means (A), (B), or (A and B), where A and B are variables indicating a particular object or attribute. When used, this phrase is intended to and is hereby defined as a choice of A or B or both A and B, which is similar to the phrase "and/or". Where more than two variables are present in such a phrase, this phrase is hereby defined as including only one of the variables, any one of the variables, any combination of any of the variables, and all of the variables, for example, a phrase in the form "at least one of A, B, and C" means (A), (B), (C), (A and B), (A and C), (B and C), or (A, B and C).

[00105] Various operations may be described as multiple discrete operations in turn, in a manner that may be helpful in understanding embodiments; however, the order of description should not be construed to imply that these operations are order dependent.

[00106] As used herein, the term "about" or "approximately" applies to all numeric values, whether or not explicitly indicated. These terms generally refer to a range of numbers that one of skill in the art would consider equivalent to the recited values (i.e., having the same function or result). In many instances these terms may include numbers that are rounded to the nearest significant figure.

[00107] From the foregoing, it will be appreciated that specific embodiments of the disclosure have been described herein for purposes of illustration, but that various modifications may be made without deviating from the scope of the disclosure. Accordingly, the disclosure is not limited except as by the appended claims.

WHAT IS CLAIMED IS:

1. A method of transesterification of triglycerides, the method comprising:
combining tetraalkoxyborate with a triglyceride composition to form a reaction mixture;
and
heating the reaction mixture above 40 °C to form fatty acid alkyl esters.
2. The method according to claim 1, wherein the tetraalkoxyborate is selected from the group consisting of tetramethoxyborate, tetraethoxyborate, tetrapropoxyborate, and tetrabutoxyborate.
3. The method according to claim 1, wherein the fatty acid alkyl esters are selected from the group consisting of fatty acid methyl esters, fatty acid ethyl esters, fatty acid methyl esters, fatty acid propyl esters, and fatty acid butyl esters.
4. The method according to claim 1, wherein heating occurs from about 1 hour to about 24 hours.
5. The method according to claim 1, further comprising:
making the tetraalkoxyborate in a reaction vessel; and
adding the triglyceride composition to the reaction vessel.
6. The method according to claim 5, wherein making the tetraalkoxyborate includes:
combining borohydride with an alcohol.

7. The method according to claim 6, wherein the alcohol and the tetraalkoxyborate include the same alkoxy group.
8. The method according to claim 7, wherein the alkoxy group is selected from the group consisting of a methoxy group, an ethoxy group, an epoxy group, and a butoxy group.
9. The method according to claim 5, wherein making the tetraalkoxyborate includes:
combining trialkoxyborane with an alkoxide salt.
10. The method according to claim 9, wherein the trialkoxyborane, the alkoxide salt, and the tetraalkoxyborate include the same alkoxy group.
11. The method according to claim 10, wherein the alkoxy group is selected from the group consisting of a methoxy group, an ethoxy group, an epoxy group, and a butoxy group.
12. The method according to claim 1, further comprising:
hydrogenating fatty acid alkyl esters.
13. The method according to claim 12, wherein hydrogenation is performed using hydrogen collected during making of the tetraalkoxyborate.

14. A method of making biodiesel, the method comprising:
combining tetramethoxyborate with a triglyceride composition to form a reaction mixture, wherein the triglyceride composition includes at least one of a vegetable oil or an animal fat; and
heating the reaction mixture above 40 °C to form a diesel fuel including fatty acid methyl esters.
15. The method according to claim 14, wherein heating occurs from about 1 hour to about 24 hours.
16. The method according to claim 14, further comprising:
making the tetramethoxyborate in a reaction vessel; and
adding the triglyceride composition to the reaction vessel.
17. The method according to claim 16, wherein making the tetramethoxyborate includes:
combining borohydride with methanol.
18. The method according to claim 14, wherein making the tetramethoxyborate includes:
combining trimethylborane with a methyl oxide salt.
19. The method according to claim 14, further comprising:
hydrogenating fatty acid methyl esters.

20. The method according to claim 19, wherein hydrogenation is performed using hydrogen collected during making of the tetramethoxyborate.