

Green synthesis of biodiesel using ionic liquids*

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Abstract: This paper is a hybrid starting with an overview and history of biodiesel synthesis and finishing with a description with some of our latest unpublished data. Initially, we examine “green” ways of obtaining biodiesel using ionic liquids, which can have an acidic or basic functionality, and can function both as a solvent and catalyst for the (trans)esterification reaction to obtain biodiesel. Both animal and vegetable resources can be utilized as a resource for (trans)esterification reactions depending on the geographical area. Biodiesel is of great interest because it enables motor vehicle transport using a renewable resource, while reducing the amount of carbon dioxide from fossil fuels being released into the environment.

Keywords: biodiesel; biofuels; green chemistry; ionic liquids; transesterification.

OVERVIEW AND HISTORY OF BIODIESEL

Biodiesel and its history

Biodiesel is quite a fashionable word nowadays, due to the fact that it is purportedly environmentally friendly and is made from renewable resources [1,2]. Biodiesel is a term “applied to a fuel derived from the transesterification of used vegetable oils or animal fats. In the production of biodiesel, the triglycerides in the fats and oils are reacted with methanol to make methyl esters and glycerine. The glycerine produced can be sold as a by-product, however, due to large supplies of glycerine produced during soap manufacture, the income from the sale is likely to be small” [3]. The history of biodiesel has been well summarized elsewhere [4].

The recent interest in biodiesel is explained by the rise in oil prices and the vanishing resources of fossil fuels (a presentation to a House of Commons All-Party Committee on 7 July 1999 forecasts a major crisis for fossil fuel availability and price in 2010–2020 [5]), which is why biodiesel made from both animal and vegetable fats has received considerable attention. Intensive usage of petroleum is an important factor in air pollution: the problem of pollution is critical, as mankind is now facing a global warming crisis [6].

What is biodiesel?

Diesel or diesel fuel in general is any fuel used in diesel engines [4]. Biodiesel is the name of a relatively clean-burning alternative fuel, produced from domestic, renewable resources [4]. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend.

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It can be used in compression-ignition (diesel) engines with little or no modification. Biodiesel is simple to use, biodegradable, and essentially free of sulfur and aromatics (that are contained in fossil fuels). Biodiesel is a light to dark yellow liquid. It is practically immiscible with water and has a high boiling point and low vapor pressure. Typical methyl ester biodiesel has a flash point of ca. 150 °C. Biodiesel has a viscosity similar to petrodiesel, the industry term for diesel produced from petroleum. It can also be used as an additive in formulations of diesel to increase the lubricity of pure ultra-low sulfur diesel (ULSD) fuel, although care must be taken to ensure that the biodiesel used does not increase the sulfur content of the mixture above 15 ppm.

How is biodiesel made?

Biodiesel (fatty acid methyl esters, or FAMES) is made through the esterification or transesterification of animal fat or vegetable oils (Fig. 1). Lard is a typical animal fat, a triglyceride, being a mixture of triesters of glycerol. The major component is based around oleic acid (containing one double bond per chain), but it is in admixture with smaller amounts of saturated chains (of varying lengths) and some doubly unsaturated chains (linoleic acid). For fatty esters (animal fats and many vegetable oils are usually the glycerol ester), both the acid- and base-catalyzed transesterifications occur readily. The base-catalyzed transesterification to methyl or ethyl esters usually requires slightly higher reaction temperatures.

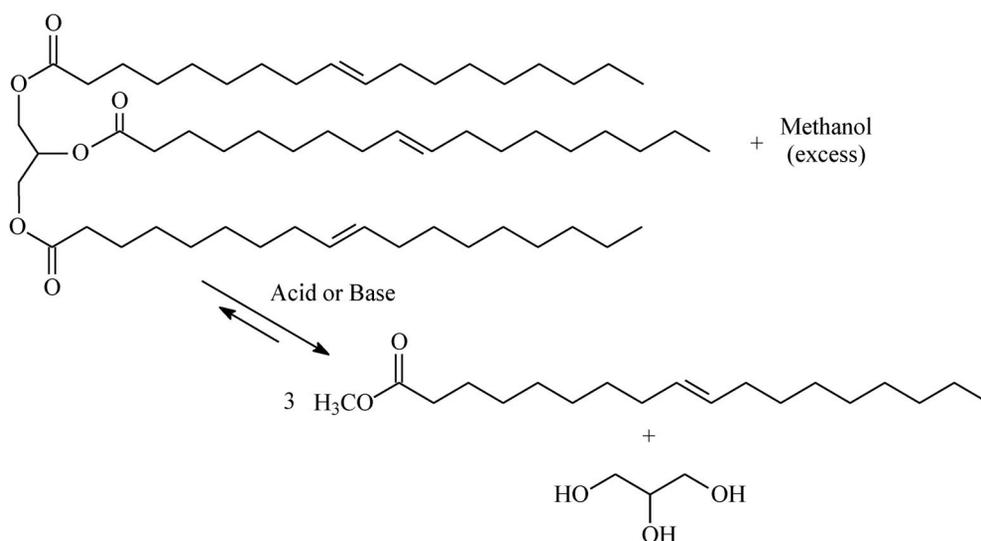


Fig. 1 Acid- and base-catalyzed transesterification of triglycerides, and the esterification of fatty acids to FAMES. The *trans*-isomers are shown in the diagram for convenience, but in reality they are a mixture of *cis*- and *trans*-isomers. It should be noted that most naturally occurring fatty acids are *cis*-isomers and double bonds can occur in various positions in the chains. The methyl ester of *cis*-octadec-9-enoic acid is normally referred to as methyl oleate.

Biodiesel is also made through esterification of free fatty acids (FFAs) derived from vegetable oils, wherein the water by-product is separated from the FAME (Fig. 2). For fatty acids (usually from vegetable sources), the acid-catalyzed esterification reaction is preferred. The base-catalyzed esterification to methyl and ethyl esters usually fails because the catalyst is deactivated by reaction with the carboxylic acid group to form a carboxylic acid salt, often referred to as soap.

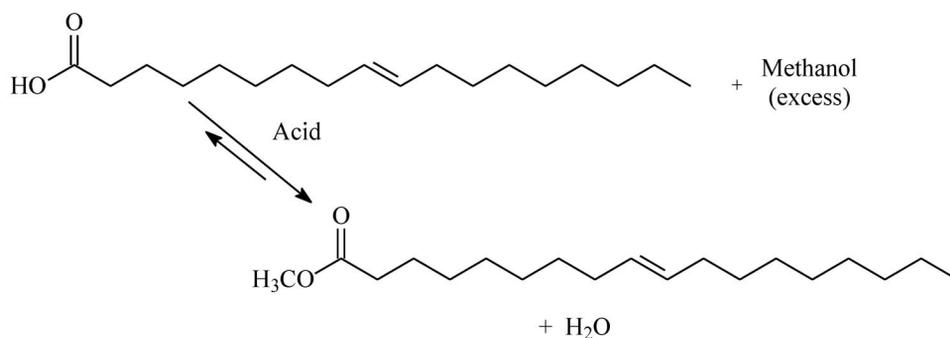


Fig. 2 Acid-catalyzed esterification of fatty acids to FAMES. The *trans*-isomers are shown in the diagram for convenience, but in reality they are a mixture of *cis*- and *trans*-isomers. It should be noted that most naturally occurring fatty acids are *cis*-isomers.

Methods for biodiesel production

A review by Marchetti et al. gives a comparison between the methods for biodiesel production using different catalysts [7] (see Table 1). High conversion has been observed in the base-catalyzed reaction process [7]. The basic catalyst is sensitive to the purity of reactants, especially to water and FFAs, so the raw materials must be refined (moisture level no more than 0.06 wt %, and the FFA no more than 0.5 wt %) [8]. Soyabean oils were found by Nouredini et al. [9] to have good transesterification kinetics under acid-catalyzed reaction. Esterification when using supercritical alcohol was shown to have a higher reaction rate than transesterification when using the same supercritical alcohol [7]. A benefit of the process is that esters are produced from the FFA. Producing ester from different sources of grease and oil using lipase is a viable method, but this involves large volumes of water [7].

Table 1 Comparison of the different technologies to produce biodiesel [7].

Variable	Alkali catalysis (NaOH or KOH)	Lipase catalysis [10]	Supercritical alcohol [11,12]	Acid catalysis (H ₂ SO ₄ [13–15] or H ₂ SO ₃ [16])
Reaction temperature/°C	60–70 25–120 [2,9,13,14,17–21]	30–40	239–385	55–80
Free fatty acid in raw materials	Saponified products	Methyl esters	Esters	Esters
Water in raw materials	Interference with reaction	No influence		Interference with reaction
Yield of methyl esters ^a	Normal	Higher	Good	Normal
Recovery of glycerol	Difficult	Easy		Difficult
Purification of methyl esters	Repeated washing	None		Repeated washing
Production cost of catalyst	Cheap	Relatively expensive	Medium	Cheap
Amount of catalyst used	0.5–1 % w/w [17,22] or 0.005–0.35 % w/w [2]			0.5–1 mol % 3.5 mol % [21,23]

^a The terms “normal”, “higher”, and “good” are undefined in [7].

Table 1 lists Brønsted acidic and basic catalysts, lipase catalysts, and supercritical alcohol catalysts. In regards to Lewis basic and acidic catalysts, there are several examples in the literature [24–28].

What role can ionic liquids play?

Ionic liquids have been used in a large number of chemical reaction types. Examples can be found in the two-volume book by Wasserscheid and Welton [29] and a review on the industrial applications of ionic liquids [30]. The principal reasons for attempting reactions in ionic liquids is that these solvents are involatile except at low pressures and high temperatures [31], and their properties can be designed to suit a particular need (“designer” solvents) [32]. An example of design is to alter the structure of ionic liquid such that it phase separates from the product of a reaction, making product isolation easier [33]. Another approach is to make either the cation or anion or both of the ionic liquids acidic or basic (either Lewis or Brønsted) [34]. Specific examples of ionic liquids which exhibit Brønsted acidity due to functionalized cations include sulfonic acid derivatives of the imidazolium cation, e.g., 4-(3-methylimidazolium)butanesulfonic acid [35]. This last approach could be used to enable the ionic liquid to catalyze esterification, transesterification, and specifically biodiesel forming reactions. Also, it is possible to design the ionic liquid in such a way that it can be recovered intact at the end of a reaction, thus not creating any ionic liquid waste, and recycled (one of the issues with ionic liquids is that they can be more expensive than some of the simpler catalysts, and somewhat more expensive than conventional solvents).

Esterification reactions in ionic liquids

Esterification reactions readily occur in certain ionic liquids. A simple example is reactions catalyzed by the Franklin basic [36,37] 1-butylpyridinium ionic liquid, $[C_4py]Cl-AlCl_3$ [38,39]. Unfortunately, the ionic liquid is consumed in the reaction. It is known that the $[PF_6]^-$ anion dissociates to phosphate and fluoride ions under aqueous conditions, and this could lead to catalyst being turned into an inactive fluoride salt [40]. Despite this, Tang et al. used the 1-methylimidazolium tetrafluoroborate ionic liquid ($[Hmim][BF_4]$) as a solvent and catalyst for the reaction [41]. Another example is the reaction of primary, secondary, and tertiary alcohols that were ethanoylated with ethanoic acid and ethanoic anhydride in 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$) using metal catalysts [42]. These reactions work well initially, but the catalyst becomes ineffective when the ionic liquid/catalyst are recycled. Because of the decomposition of these ionic liquids, stable Brønsted acidic ionic liquids, where the acid group is in the cation or anion, were used. An example is the use of [3-(triphenylphosphonium)propanesulfonic acid][tosylate] in the formation of ethyl ethanoate [43].

Biodiesel syntheses in ionic liquids

The first ionic liquid–biodiesel reactions were presented by John Verkade at the 2004 ICPC (International Conference on Phosphorus Chemistry) [44]. This involved suspending sodium methoxide in an ionic liquid such as 1-butyl-3-methylimidazolium tetrafluoroborate. This combination of sodium methoxide dissolved in a neutral ionic liquid was used in the conversion of soyabean oil to its methyl esters. It should be pointed out that this ionic liquid–reagent combination is not stable due to methanolysis of the tetrafluoroborate anion and release of fluoride ions.

Apart from this early conference presentation [44], which has not yet been fully published, the next report was in the patent literature by the authors of this review [45], and will be expanded on *vide infra*.

The literature publications on biodiesel synthesis in ionic liquids can be classified as follows:

- Brønsted acid-catalyzed reactions
- Brønsted base-catalyzed reactions
- Lewis acid-catalyzed reactions
- Enzyme-catalyzed reactions

Brønsted acid-catalyzed reactions

The simplest reported way to carry out biodiesel synthesis is to add an acid or base directly to an ionic liquid [46]. The addition of acids, such as triflic acid or 4-toluenesulfonic acid, to a range of ionic liquids (neutral, basic, or acidic) was found to catalyze the reaction of FFAs with ethanol [47]. The patent fails to mention that some of the ionic liquid/acid combinations are unstable and could lead to the formation of hydrofluoric acid, which is a dangerous material to work with. Dupont et al. [48] added either K_2CO_3 or H_2SO_4 to 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide ($[C_4mim][NTf_2]$) to transesterify soyabean oil with primary and secondary alcohols. This resulted in a two-phase system at the end of the reaction of biodiesel and a glycerol-methanol-ionic liquid-catalyst phase. It was noted that the use of tetrafluoroborate and hexafluorophosphate ionic liquids should be avoided due to their decomposition.

One of the more popular methods in the literature for making biodiesel in ionic liquids is to use acid-catalyzed chemistry based on an intrinsically acidic ionic liquid. The ionic liquids can have acidic functional groups in either the anion or cation. A patent [49] in 2006 claimed a method for subjecting fat and short-chained alcohols to transesterification in the presence of an ionic liquid catalyst, where the cation of the ionic liquid had a SO_3H group (viz. sulfoalkylimidazoliums, sulfoalkylpyridiniums, sulfoalkyltriphenylphosphoniums, or sulfoalkylammoniums salts). The top layer contained the product, and the catalyst remained in the bottom layer. This work also appeared as three papers [50–52]: these patents and papers are very similar to the earlier procedures described in the above text [45]. The same ionic liquids were also used to transesterify waste oil [53] or soyabean oil [54] with methanol to give biodiesel. An acidic anionic ionic liquid, 1-H-3-methylimidazolium hydrogensulfate, was shown to catalyze the reaction of rapeseed oil with methanol to give biodiesel [55].

Base-catalyzed reactions

Less common are base-catalyzed transesterification reactions in ionic liquids. It should be generally noted that base-catalyzed reactions are only suitable for transesterification reactions [56]. Hydroxide salts of ammonium cations or sodium hydroxide dissolved in ionic liquids have been used in the conversion of animal or vegetable fats to biodiesel [46]. Sodium methoxide and lithium diisopropylamide have also been investigated as bases for transesterification reactions [57]. Abbot et al. catalyzed the reaction of triglycerides with ethanol with KOH, and used the ionic liquid eutectic mixtures to extract the glycerol by-product [58]. Protocols to separate the glycerol from the ionic liquids were also investigated [58].

Lewis acid-catalyzed reactions

Lewis acidic ionic liquids or ionic liquids containing metal complexes can be used in biodiesel synthesis, but suffer from the disadvantage that they can lead to metal wastes. Generally, they will perform similar chemistry to Brønsted-acidic ionic liquids. The tin complex $[Sn(3\text{-hydroxy-2-methyl-4-pyrone})_2(H_2O)_2]$, immobilized in 1-butyl-3-methylimidazolium tetrachloroindate $[bmim][InCl_4]$ ionic liquid, forms an effective biphasic catalytic system for the production of biodiesel from the alcoholysis of soyabean oil [59]. However, it should be noted that indium halide ionic liquids are Lewis acid catalysts

in their own right and can be the active catalytic species in this reaction. Aluminum(III) chloride ionic liquids have also been found to promote transesterification reactions [60]. However, it must be pointed out that these ionic liquids are not stable in the presence of alcohols and liberate HCl.

Enzyme-catalyzed reactions

Enzyme-catalyzed esterification and transesterification reactions have the advantage that strong acids/bases are not required, resulting in safer and noncorrosive processes. An example is the production of biodiesel from oils or fats in what is described as a salt solution or substantially saturated salt solution. This method involves using an immobilized enzyme to catalyze the reaction [61]. Another very similar patent describes ionic liquids that were used as solvent and additive in the reaction of alcohols with plant or animal fats and oils with enzyme catalysis. It is claimed that this can resolve the problems of low stability of enzyme, and decrease of enzyme activity in organic solvents [62]. The production of biodiesel in ionic liquids with immobilized *Candida antarctica* lipase-catalyzed methanolysis of soyabean oil was demonstrated [63]. Twenty-three ionic liquids were tested, and the highest FAME production after 12 h at 50 °C was achieved in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([C₂mim][OTf]) in 80 % yield [63]. *Pseudomonas cepacia* lipase supported in the 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ionic liquid is another related method for the production of biodiesel from the alcoholysis of soyabean oil [64]. The transesterification reaction catalyzed by this ionic liquid-supported enzyme can be performed at room temperature, in the presence of water and without the use of organic solvents. The biodiesel is separated by simple decantation, and the recovered ionic liquid/enzyme catalytic system can be re-used at least four times without loss of catalytic activity and selectivity [64].

Free acids or bases contaminate product streams. In this work, we have investigated the acid and base functionalization of cations and anions, preventing the acid or base from being leached into the biodiesel: although being fully reported in 2008, this work was filed as a patent in May 2005 [45].

EXPERIMENTAL

Animal fat (specifically lard; 1.0 g), methanol (2.0 g), and an ionic liquid (0.25 g; selected from **1** to **7**) (see Fig. 3 for structures) were placed in a microwave tube with a magnetic stirrer, and heated to the desired temperature (see Tables 2–4) for 30 min in a CEM Discover microwave reactor. The mixture was then cooled to room temperature and was observed to be biphasic. The two layers were each analyzed by ¹H NMR spectroscopy: the upper (product) layer was dissolved in CDCl₃ and the lower layer was obtained in methanol; the lower methanol layer was isolated, the methanol removed in vacuo, and CD₃OD added. The yield was determined by comparing the integration of the –OCH₂– group in the glyceryl residue in the triglyceride with the –OCH₃ group in the FAME (biodiesel). The upper methyl oleate (product) layer was decanted, and the dissolved methanol was removed by distillation at 120 °C or by heating to 60 °C at 1 mm Hg pressure. The product was found to be free of ionic liquid catalyst by ¹H NMR spectroscopy.

Table 4 Base-catalyzed transesterification of animal fat {lard (0.5 g)} with methanol (1.0 g) and catalyst (0.25 g) for 30 min in a microwave oven.

Run	Catalyst	Temperature/°C	% Yield
11	(5)	100	98
12	(6)	100	54
13	(7)	140	8
14	(7)	150	18
15	(7)	160	32

All NMR spectra were recorded at ambient temperature on Bruker Avance spectrometers DPX 300. ^1H and ^{13}C NMR spectra were referenced with respect to tetramethylsilane (TMS). The NMR solvents d^1 trichloromethane and d^4 -methanol (Euriso-top) were used. The estimated error was $\pm 3\%$.

RESULTS AND DISCUSSION

The work described incorporates the Brønsted acid or base functionality into the ionic liquids (see Table 5), such that the ionic liquid functioned as both a solvent and catalyst (Fig. 4). The advantage of this approach is that the ionic liquid will not decompose and is fully recyclable. The system applied here also uses a single type of ionic liquid.

Table 5 Types of different Brønsted acidic and basic ionic liquids in the synthesis of biodiesel used in this work. These function as both solvents and catalysts. X – Brønsted acidic ionic liquids; 0 – Brønsted basic ionic liquids.

	Brønsted acidic cation	Neutral cation	Brønsted basic cation
Brønsted acidic anion	X	X	
Neutral anion	X		0
Brønsted basic anion		0	0

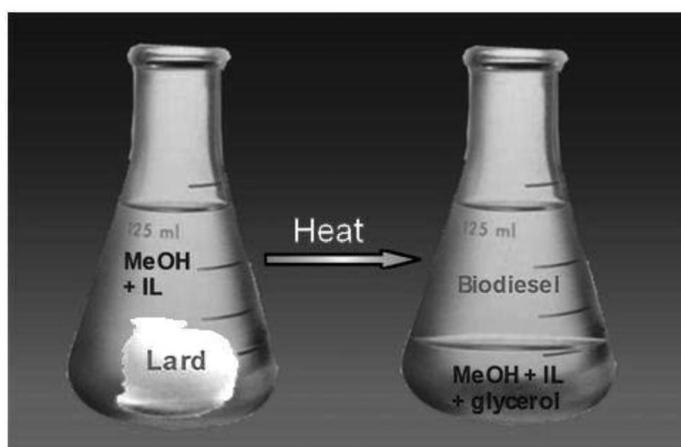


Fig. 4 Formation of biodiesel from lard by treatment with a mixture of an excess of methanol and an acidic ionic liquid.

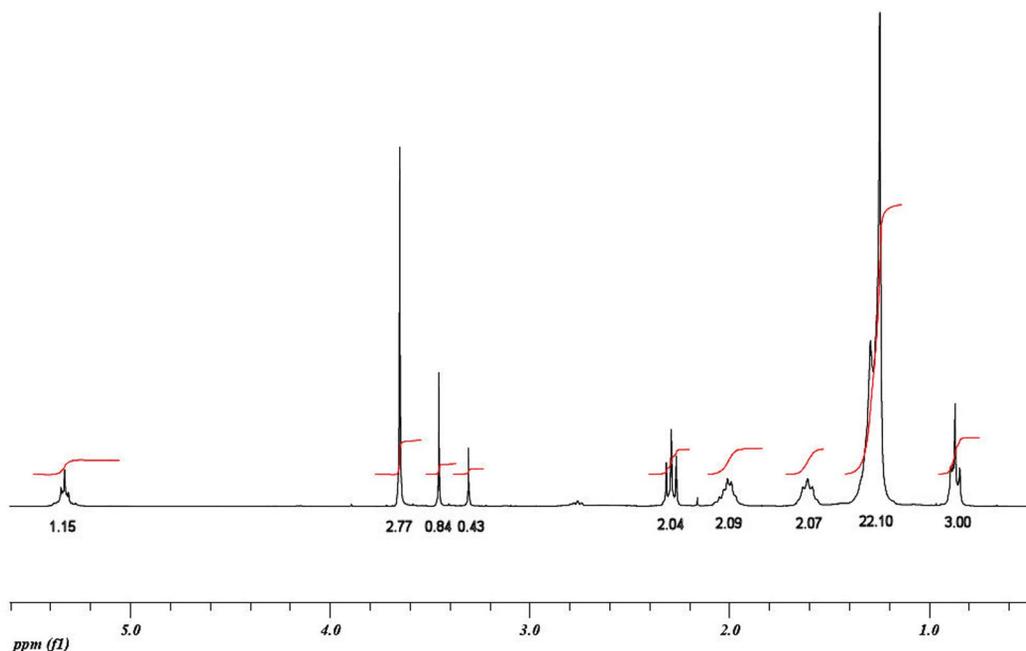


Fig. 7 ¹H NMR spectrum (300 K, 300 MHz, *d*¹-trichloromethane) of biodiesel.

number of C=C double bonds per “molecule” of biodiesel is 0.55, corresponding to an integrated number of =CH protons of 1.1.

As can be seen, catalysts **1** and **3** catalyze the reaction well at 120 °C (Table 2). These gave similar results to the conventional acid 4-toluenesulfonic acid. The ionic liquids have the advantage that they are not volatile and remain in the methanol/glycerol layer. The acid catalysts **2** and **4** are less effective and require higher reaction temperatures to catalyze the reaction, despite having acidic anions. These are presumably both weaker acids, one being a dihydrogenphosphate salt and the other being a hydrogensulfate salt. In the case of the dihydrogenphosphate salt (**2**), the hydrogen-bonding capability of the dihydrogenphosphate anion may be interacting with the sulfonic hydrogen, reducing its acidity. Thus, highly acidic conditions are required for an efficient catalysis.

Table 3 shows that the reaction is temperature-dependent and at least 120 °C is needed to obtain the required 95 % conversion to meet the biodiesel specification. The product forms a separate layer on the surface of the methanol/glycerol layer/ionic liquid layer as seen in Fig. 4.

Base-catalyzed reactions

The base-catalyzed reactions (see Table 4) were carried out by adding the ionic liquid catalyst to the alcohol and triglyceride mixture, followed by heating at the required temperature. A disadvantage of the base-catalyzed reactions is that, when applied to fatty acids (as opposed to esters), a salt is formed which renders the base catalyst inactive. For transesterification, however, the ionic liquid, methanol, and glycerol form a separate phase from the biodiesel. The ionic liquid catalyst can then be separated from the alcohols (methanol and glycerol) by distillation or vacuum distillation. The catalyst could be then recycled and reused.

Synthesis of biodiesel from fatty acids

The esterification reaction is an equilibrium process driven toward the right by using an excess of methanol (see Fig. 8) with water as the only by-product. The advantage of this method is that the ionic liquid, water, and methanol mixture obtained at the end of the reaction is immiscible with the FAME product and forms a separate phase, allowing gravity separation of the biodiesel. Another advantage of this reaction is that the reaction occurs at room temperature and hence no energy input is required in this step.

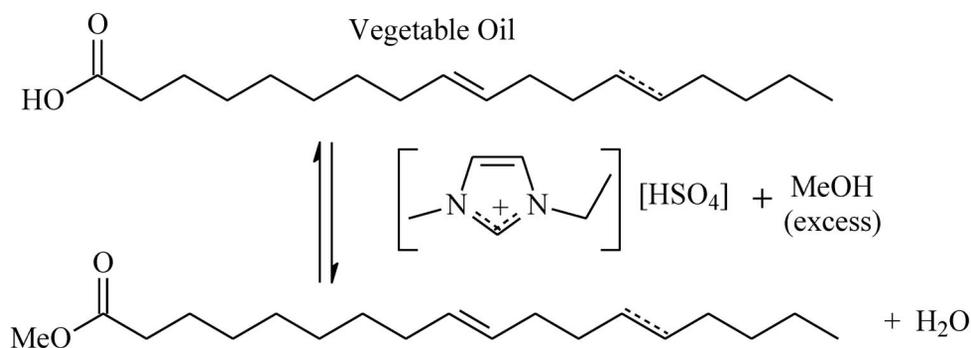


Fig. 8 Esterification of vegetable oil (Priolene 6927) with [emim][HSO₄].

As can be seen in Table 6, the reaction proceeds smoothly to give the expected products. With 1 % [emim][HSO₄] catalyst, the equilibrium yields (Table 6) are close to those expected from a statistical analysis of the reaction (60, 80, and 90 % yields for 2.5, 5, and 10 molar excess of methanol, respectively). As the amount of catalyst is increased, the final yields rise to 98 % (by ¹H NMR spectroscopy).

Table 6 Final equilibrium yields (144 h reaction time, 20 °C) determined by ¹H NMR spectroscopy analysis.

Molar excess of MeOH	1 % [emim][HSO ₄]	2.5 % [emim][HSO ₄]	5 % [emim][HSO ₄]
2.5	50	57	61
5	76	–	81
10	90	92	98

Ionic liquid recycling

Methanol can be separated from the mixture by stripping with warm air, which is cheaper than distillation. There are several ways to separate the ionic liquid from glycerol:

- vacuum distillation, as the ionic liquids normally have their boiling points much higher than glycerol (b. pt.: 250 °C);
- solvent extraction: mixtures of organic solvents (*n*-butanol, ethyl ethanoate, or dichloromethane) and water can be used: the ionic liquid would preferentially dissolve in the organic solvents (especially if it is a hydrophobic ionic liquid) and glycerol would prefer the aqueous phase; and
- finally, the best approach is to design an ionic liquid in such a way that it is not soluble in either biodiesel or glycerol, so that the triphasic system is obtained at the end of the reaction. More work is required in this direction.

CONCLUSION

The specification for biodiesel in Europe (EN 14214) [65] is for a material that is composed of 96.5 % fatty acid methyl (or ethyl) esters. Using the ionic liquid process, ca. 5 mol % catalyst and 10-fold excess of methanol are required to produce a biodiesel that meets this specification for the acidic ionic liquid catalyst at room temperature. For the acid- or base-catalyzed transesterification of animal fat with methanol, higher reaction temperatures are needed (typically 90–160 °C) for rapid reactions. Lower temperatures can be used, but they take longer. As the United Kingdom, and Northern Ireland in particular, have a substantial supply of waste fat and oils, these could form the basis of a local industry for the synthesis of biodiesel.

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