O'Connor S., Pillai S.C., Ehimen E., Bartlett J. (2020) Production of Biodiesel Using Ionic Liquids. In: Inamuddin, Asiri A. (eds) Nanotechnology-Based Industrial Applications of Ionic Liquids. Nanotechnology in the Life Sciences. Springer, Cham. https://doi.org/10.1007/978-3-030-44995-7_12

Chapter 1
Production of biodiesel using ionic liquids

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Abstract

Several threats in the form of climate change, future oil supplies, and energy security have created a need for the development of large-scale alternatives to fossil fuel based fuels. One such alternative fuel developed from bio-renewable resources, which has generated considerable interest, is biodiesel, mainly produced via the transesterification of animal fats vegetable oils.

Organic and inorganic solvents have been commonly applied to improve the efficiency of the biodiesel production process. However, because of the undesirable properties of conventional solvents such as their hazardous nature, the need for greener alternatives is apparent. Over the last decade, ionic liquids (ILs) have garnered considerable attention for both their process improvement and environmental benefits to the biodiesel production process. In this chapter, a compressive overview is provided of the versatility of ILs as solvents in both the reaction and purification steps in the biodiesel production process, acting as catalysts, co-solvents, and extracting solvents. In addition, this study explores the use of deep eutectic solvents (DESs), which are considered to be the next generation of solvents in the biodiesel production process.

Keywords: • Biodiesel • Ionic liquid • Biodiesel production • Co-solvent • Catalyst • Extracting solvent • Pretreatment • Purification • Deep eutectic solvent

Abbreviations:

FFAs, free fatty acids; IL, ionic liquid; DES, deep eutectic solvent; FAME, fatty acid methyl ester; H_2SO_4, sulfuric acid; $BSP_y.CF_3SO_3$, 1-4-sulfonic acid butylpyridinium trifluoromethanesulfonate; $BMIm.CH_3SO_3$, 1-butyl-3-methylimidazolium methanesulfonate; DAIL, dicationic brønsted acidic ionic liquid; BMIm.OH, 1-butyl-3-methylimidazolium hydroxide; wt, weight; C, conversion; Y, yield; ChOH, choline hydroxide; ChOMe, choline methoxide; EMIm.TfO, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate; $BMIm.PF_6$, 1-butyl-3-methylimidazolium hexafluorophosphat; $EMIm.PF_6$, 1-ethyl-3-methylimidazolium; BF4, tetrafluoroborate; EMIm, 1-ethyl-3-methylimidazolium methyl sulfate; BMIm.MeSO4; 1-butyl-3-methylimidazolium methyl sulfate; BMIm.DCA, 1-butyl-3-methylimi-dazolium dicyanamide; HPyrBr, 1-hexylpyridinium bromide; ASTM, American Society for Testing and Materials; uFAME, unsaturated fatty acid methyl ester; $AgBF_4$, silver tetrafluoroborate; SBA-15, mesoporous silica; PF_4, tetrafluorophosphite; PUFA, polyunsaturated fatty acids; LGCPO, low grade crude palm oil; CaO; calcium oxide.

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1. Introduction

There is an immediate threat of climate change, where the average global temperature has increased by 1.1°C since pre-industrial levels because of human activity (IPCC, 2013, 2014, 2018). If current trends continue, the temperature will likely surpass 1.5°C between 2030 and 2052, resulting in potentially disastrous consequences, including the mass die-off of coral reefs, worsening food shortages, more frequent wildfires, and an increase in extreme weather events (IPCC, 2018). The release of harmful and hazardous exhaust gases from the combustion of petroleum-based fuels has contributed significantly to the advancement of climate change, representing 98% of carbon emissions released into the atmosphere (Aransiola EF *et al.*, 2012). Therefore, the need to pursue and develop alternative, environmentally friendly sources of fuel is apparent (Farrell *et al.*, 2006; Semelsberger, Borup and Greene, 2006).

One alternative energy source is biodiesel, which has a chemical composition similar to that of diesel, with the added benefit of being biodegradable, non-toxic, renewable, and environmentally friendly (Demirbas, 2008). Biodiesel is an oil-based diesel-type fuel consisting of long-chain alkyl (ethyl, methyl, or propyl) esters typically obtained by the transesterification of lipids, either animal fats or vegetable oils, with short-chain alcohols to produce fatty acid monoesters (Gerpen, 2005; Leung, Wu and Leung, 2010; Zhao and Baker, 2013). This reaction is usually catalyzed using acids or bases (homogenous or heterogeneous), or via enzymatic routes, i.e. using lipases. This conversion process is required to produce a fuel product which allows for its direct combustion in modern diesel engines, as the viscosity of the starting feedstock is often too high (Dupont *et al.*, 2009). Various parameters can affect the process and subsequently influence the biodiesel yield, including the moisture content, free fatty acids (FFAs), loading time, reaction temperature, type of catalysts, and the molar ratio of alcohol to oil (Parawira, 2010; Highina, Bugaje and Umar, 2011). Biodiesel is considered carbon-neutral, i.e. the amount of carbon spent on the formation of biomass (processed into fuel) is equal the amount of carbon returned to the atmosphere as a result of fuel combustion (Mathews, 2008). This therefore allows for the reduction in the release of polluting emissions including hydrocarbon, particulate matter, and carbon monoxide, while having a comparable fuel economy to diesel fuels. (Gashaw and Tesita, 2014).

Homogeneous catalysts are conventionally used for the preparation of biodiesel, despite having serious disadvantages, such as issues regarding its corrosivity, energy-intensive operations, product purification difficulties and production of a high amount of wastewater (Antolín *et al.*, 2002; Qin Wu *et al.*, 2007; Liang *et al.*, 2009; Stojković *et al.*, 2014; Veljković, Stamenković and Tasić, 2014; Khan *et al.*, 2015). Therefore, because of the limitations associated with these solvents, the need for a viable alternative becomes a priority. One environmentally friendly alternative to conventional chemical transesterification is the enzymatic transesterification method, because it involves milder operating conditions, lower energy demand, reduced excess volumes, reusability of enzymes, and permits a minor volume of water in substrates (Akoh *et al.*, 2007; Troter *et al.*, 2016). However, this method has several difficulties, such as leftover impurities, inactivation of lipase, and the high cost of enzymes, which have greatly limited the potential of this approach (Troter *et al.*, 2016).

In recent years, ionic liquids (ILs) have emerged as a promising alternative solvent group, extracting solvent or catalyst in the production of biodiesel. ILs have generated significant attention as an adjustable (task-driven) and budding ‘green’ solvent, with the promise of being a low-cost alternative to conventional volatile organics. Additionally, a new generation of ILs, called deep eutectic solvents (DESs), have generated significant interest among researchers, as they have the major advantages of potentially being a more cost-effective and environmentally friendly approach. The properties of DESs can be finely tuned, similar to those of ILs, by selecting different cation and anion combinations. Many benefits can be therefore be gained, such as being high purity, easily prepared, non-toxic, biodegradable, requiring mild reaction conditions, and being insensitive to water (Andrew P. Abbott *et al.*, 2004). As a result, researchers have predicted DESs to progressively replace ILs in the biodiesel production processes in the near future (Troter *et al.*, 2016).

The purpose of this chapter is to present an overview of the reported use of ILs and DESs in the production of biodiesel. This review focuses on the application of ILs as either a catalyst, co-solvent components, or for extracting solvents from numerous biodiesel feedstocks. In addition, the work critically examines and discusses the potential replacement of ILs with DESs in biodiesel synthesis. The work highlights progress in the field, problems and difficulties faced, and future research outlook.

2. Ionic liquids

ILs are defined as a class of organic salts, comprised of organic cations and either organic or inorganic anions with a melting temperature of less than 100 °C. The process of IL synthesis consists of cation formation and anion exchange. The study of ILs date back to 1914, by Walden (1914) who recorded the physical properties of ethyl ammonium nitrate, which was formed by reacting ethylamine with concentrated nitric acid. However, the discovery did not generate significant attention, as its explosive nature limited widespread application. In general, ILs continued to receive little attention until their use as a chemical synthesis in the 1990s, producing ILs with unique physical-chemical properties (Seddon, 1997).

In recent years, ILs have gained significant interest as a promising green chemical solvent, where the abundance of structures available and their adjustable nature have allowed their application in various commercial segments. This second generation of ILs has garnered significant attention as their properties can be optimised for the reaction through the careful selection of the cation and anion (Vancov *et al.*, 2012). Researchers have taken advantage of this characteristic by developing ILs finely tuned to meet the desired needs of specific applications. These needs have included specific melting points, viscosities, volatility, or both thermal and electrochemical stability (Wasserscheid and Welton, 2002; MacFarlane *et al.*, 2014). A variety of processes have used and applied the benefits of ILs, including the substituting high volatility solvents, biomass pre-treatment, gas purification, reaction media, catalysis, cellulose dissolution, and elimination of heavy metal traces (Keskin *et al.*, 2007; Tadesse and Luque, 2011).

Today, a third-generation of ILs is being developed to achieve specific desirable biological properties, such as enzyme stabilization and activation as seen in Figure 1 (Farra *et al.*, 2015). Based on these developments, various enzymatic reactions have been examined using a variety of ILs (Rantwijk *et al.*, 2007; Moniruzzaman *et al.*, 2010; Zhao, 2010; Tang, Baker and Zhao, 2012). Additionally, ILs have generated interest in different processes as a "green solvent" because of their low vapour pressure, minimising the negative impact on humans and the environment (Passos, Freire and Coutinho, 2014). Even though previous studies have reported some ILs as having poor biodegradability and relative toxicity, recent studies have found specific mixed strain consortia have the potential to biodegrade (Troter *et al.*, 2016). Owing to their environmentally friendly and tunable properties, ILs are considered a promising replacement for conventional solvents. Such studies, which have explored the use of ILs in biodiesel production are shown in Table 1. The properties of ILs are particularly advantageous for the production of biodiesel as they can replace conventional solvents in the reaction and purification processes, by acting as co-solvents, catalysts, extracting solvents, or enzyme supports. Immediate benefits include a reduction in the volume of wastewater in comparison to conventional catalysts and fewer steps for product separation and purification (Yoo, Pu and Ragauskas, 2017). However, many practical challenges must be overcome to realise wide-scale commercialisation, such as increased expenditures, high viscosities, toxicity, undesirable water tolerance, small solids loading and complex recycling (Niedermeyer *et al.*, 2013; Reddy, 2015).

The following sections discuss the ILs application, recent progress, challenges, and future outlook in regard to the production of biodiesel.

Figure 1. Chemical structures of common ionic liquids. Reprinted with permission from Farra, A. et al. (2015) 'Green solvents in carbohydrate chemistry: From raw materials to fine chemicals', Chemical Reviews, 115(14), pp. 6811–6853. Copyright 2015 American Chemical Society.

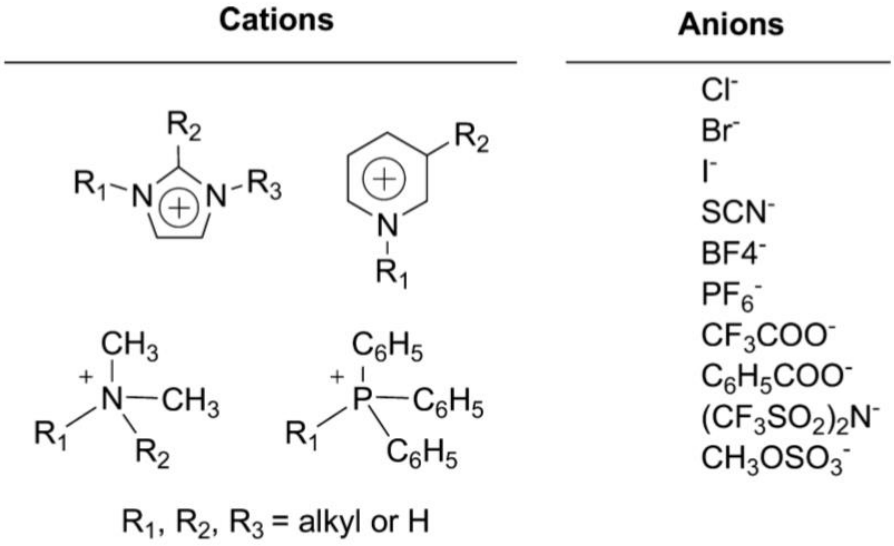


Table 1. Biodiesel production using ionic liquids. Reprinted with permission from Liu, C,-Z. et al. (2015) 'Ionic liquids for biofuel production: Opportunities and challenges, Applied Energy, 92, pp. 406-414. Copyright 2012 Applied Energy.

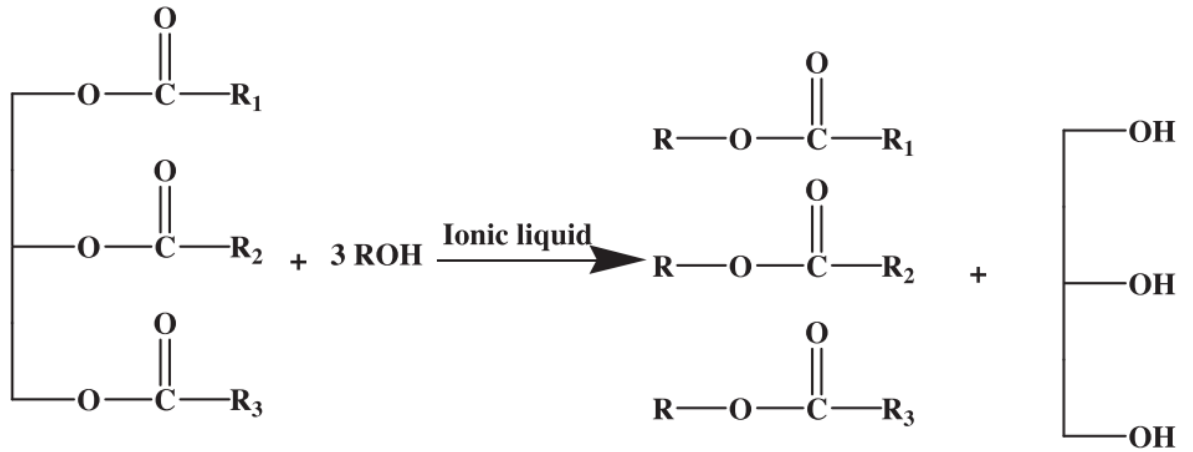
Ionic Liquid	Catalyst	Oil source	Reaction conditions	Biodiesel yield (%)	References
$[BMIm]PF_6$	Sn(3-hydroxy-2-methyl-4-pyrone)$_2$(H_2O)$_2$	Soybean	60°C, 1 h	55	(Abreu *et al.*, 2005)
$[BMIm]InCl_4$	Sn(3-hydroxy-2-methyl-4-pyron)$_2$(H_2O)$_2$	Soybean	80°C, 4 h	83	(DaSilveira Neto *et al.*, 2007)
$[Et_3NH]Cl$	$ALCl_3$	Soybean	70°C, 3 h	98.5	(Liang *et al.*, 2009)
$[BMIm]NTf_2$	K_2CO_3	Soybean	70°C, 1.5 h	98	(Lapis *et al.*, 2008)
$[BMIm]NTf_2$	H_2SO_4	Soybean	70°C, 24 h	93	(Lapis *et al.*, 2008)
[EMIm]TfO	Lipase	Soybean	50°C, 12 h	80	(Ha *et al.*, 2007)
$[BMIm]NTf_2$	Lipase	Soybean	25°C, 30 h	96.3	(Gamba, Lapis and Dupont, 2008)
$[BMIm]PF_6$	Lipase	Corn	40°C, 25 h	69.7-86	(Yang *et al.*, 2010; Zhang *et al.*, 2011)
$[BMIm]PF_6$	Lipase	Triolein	48-55°C, 6 h	80	(Ruzich and Bassi, 2010)
$[C_{16}MIM]$ NTf_2	Lipase	Triolein	60°C, 3 h	90.29	(De Diego *et al.*, 2011)
$[C_{18}MIM]$ NTf_2	Lipase	Triolein	60°C, 6 h	96	(Lozano *et al.*, 2010)
1-(4-Sulfonic acid) butyl-pyridinium hydrogen sulfate	1-(4-Sulfonic acid) butyl-pyridinium hydrogen sulfate	Cotton seed	170°C, 9 h	92	(Qin Wu *et al.*, 2007; Wu *et al.*, 2007)
$[BSPy]CF_3SO_3$	$[BSPy]CF_3SO_3$	Jatropha	100°C, 5 h	92	(Li *et al.*, 2010)
$[BMIm]HSO_4$	$[BMIm]HSO_4$	Free fatty acid	120°C, 2 h	91.2	(Elsheikh *et al.*, 2011)
$[NMP]CH_3SO_3$	$[NMP]CH_3SO_3$	Free fatty acid	70°C, 8 h	93.6-95.3	(Zhang *et al.*, 2009)

3. Ionic liquids as catalysts in biodiesel synthesis

Several catalyst types are used in the biodiesel production process from vegetable oils or animal fats such as alkalines (Vicente, Martínez and Aracil, 2004; Dupont *et al.*, 2009; Liang *et al.*, 2009) acid (Zheng *et al.*, 2006; Dupont *et al.*, 2009; Liang *et al.*, 2009), and enzymes (Iso *et al.*, 2001; Gamba, Lapis and Dupont, 2008; Ranganathan, Narasimhan and Muthukumar, 2008). Notwithstanding their high adoption, serious disadvantages still exist with the use of such catalysts. For example, negatives associated with acid catalysis include the risk of corrosion, long retention times, and a large amount of alcohol required (Liang *et al.*, 2009). Alkalines are the preferred catalysts because of the lower costs and higher reaction rates achievable (Dupont *et al.*, 2009; Atabani *et al.*, 2012). However, to be used successfully, water or high levels of FFAs cannot be present in the reagent because of the possibility of saponification (Dupont *et al.*, 2009). Subsequently, oils must undergo an often costly and time-consuming pre-treatment.

Alternatively, enzymes can be used which are capable of overcoming the disadvantages of traditional catalyses, such as high energy demand and equipment corrosion (Andreani and Rocha, 2012). However, many negatives are still associated with the process, including high costs, deactivation in the presence of alcohol, and the potential for reduced enzyme immobilisation. ILs have shown promise as an alternative mechanism in the biodiesel preparation process as shown in Figure 2.

Figure 2. Mechanism of biodiesel preparation via ionic liquid catalyzed process. Reprinted with permission from Liu, C,-Z. et al. (2015) 'An overview of the role of ionic liquids in biodiesel reaction, Journal of Industrial and Engineering Chemistry, 21, pp. 1-10. Copyright 2015 Applied Energy.



3.1 Acidic ionic liquid catalysts

Many acidic ILs have been explored by researchers as potential catalysts in biodiesel production such as bronsted acidic ILs. These catalysts contain sulfonic acid groups in their cations and have been found effective in the transesterifion of various oils or esterifying FFAs. Qin Wu (2007) carried out one of the earliest studies, using ILs as catalysts in the transesterification of cottonseed oil with methanol. Three cations with different acidity strengths were applied to produce the ILs, these included N-methylimidazole and trimethylamine, in combination with the HSO_4- ion. Among the ILs evaluated, 1-(4-sulfonic acid) butyl pyridinium hydrogen sulfate achieved the highest yield of fatty acid methyl esters (FAME), reaching 92% under optimum conditions (oil/methanol/IL = 1:12:0.057 [molar ratio] at 170 °C for 5 hours). In comparison, concentrated sulfuric acid (H_2SO_4) was used under the same reaction conditions. The FAME yield after 3 hours of the IL catalyst was 81% with a H_2SO_4 concentration of 86%. It was concluded that the yields of IL catalysts were comparable to other studies. Another study performed the transesterification of Jatropha oil using $(BSP_y)(CF_3SO_3)$ resulting in FAME yields of up to 92% and consistent catalytic activity after seven successive cycles (Li *et al.*, 2010). Similarly, (Guo *et al.*, 2011) examined a mixture of $(BMIm)(CH_3SO_3)$ and $FeCl_3$ for the conversion of Jatropha oil to biodiesel. In this mixture, metal ions acted as Lewis acidic sites resulting in a high FAME yield of 99.7% under optimal conditions.

Other ILs which have generated considerable attention as catalysts in biodiesel production processes are single and multi-SO_3H functionalised Bronsted acidic ILs (Wu *et al.*, 2007; HAN *et al.*, 2009; Fan *et al.*, 2012). Liang and Yang (2010) investigated the effectiveness of a multi-SO3H ILs, with high polarity and acidity, as a catalyst in the preparation of biodiesel through transesterification from rapeseed oil. The high polarity increases the ease of IL recovery, while the high acidity increases the amount of catalytic activity. Using this catalyst, a biodiesel yield of 98% was achieved after 7 hours under optimized conditions. The catalyst showed good water-resistant ability, with the yield only decreasing by 3% after the water content had been enlarged to 2.0% from 0.3%.

Dicationic Brønsted acidic ionic liquids (DAILs) with propyl sulfonic acid groups on their cations have shown promise by demonstrating high catalytic activity and reusability in biodiesel synthesis (Zhou *et al.*, 2011). Fang (2011) examined the esterification of FFAs into biodiesel using low alcohols catalysed by both monocationic and dicationic ILs. The results found that higher conversion rates were obtained with the addition of the DAILs in the reaction (93 - 96%) in comparison to the monocationic IL (85–87%). Furthermore, high catalytic activity was demonstrated over six runs with minor losses.

3.2 Basic ionic liquid catalysts

In addition to acidic ILs, basic ILs have also been applied to biodiesel synthesis such as imidazolium-and choline-based ILs, but not as regularly (Zhou *et al.*, 2012; Luo *et al.*, 2013; Ren *et al.*, 2014). In most basic ILs, a substrate with a small FFA content is required to evade soap formation.

Studies involving basic ILs for the esterifications and transesterifications of animal fats and vegetable oils are limited in the academic literature, as shown in Table 2. One such study was by Liang (2010) who explored the use of five basic binuclear functional ILs with an imidazolium structure as catalysts in the transesterification of cottonseed oil. The catalytic activity of the five ILs differed based upon the lengths of the carbon chain in the cations. Using a bis-(3-methyl-1-imidazolium-)-ethylene dihydroxide catalyst concentration of 0.4%, the fraction and selectivity of the FAME in the substrate reached 98.5 and 99.9% under optimum conditions (oil/methanol = 1:12 (molar ratio) at 55°C for 4 hours). Thus demonstrating the applicability of basic ILs as catalysts in the biodiesel synthesis of cottonseed oil. In addition, numerous imidazolium hydroxides have been invested for their use as recoverable catalysts in the transesterification of glycerol trioleate with methanol. Zhou (2012) used 1-butyl-3-methylimidazolium hydroxide ([BMIm]OH) to achieve a methyl ester yield of 87% and the capability to be reused up to six times without a substantial reduction in yields.

Table 2. Application of basic ionic liquids as catalysts in transesterification. Reprinted with permission from Troter, D. Z. et al. (2016) 'Application of ionic liquids and deep eutectic solvents in biodiesel production: A review', Renewable and Sustainable Energy Reviews, 66, pp. 473–500. Copyright 2016 Elsevier.

Feedstock	Type, volume of reactor, cm^3/type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst/loading, wt% (to oil)	Temperature, °C	Optimal reaction conditions	Conversion (C) or yield (Y), %/time, h	Reference
Cottonseed oil	Three-neck flask, 100	Methanol 4:1 – 16:1	4:1 – 16:1	IMC_2OH/0.10 – 1.25 wt%	35 – 65	12:1; 0.4 wt%; 55°C	98.5 (Y)/4	(Vafaeezadeh and Hashemi, 2014)
Glycerol trioleate		Methanol 3:1-9:1	3:1 – 9:1	(BMIm)(OH)	Room - 120	9:1; 120°C	87.2 (Y)/8	(Zhou *et al.*, 2012)
Rapeseed oil	Three-necked flask, 500/mechanical	Methanol 3:1 – 8:1	3:1 – 8:1	(BMIm)(Im)/ 1.0 – 10.0 wt%	30 – 70	6:1; 6.0 wt% 60°C	~95.0 (Y)/l	(Luo *et al.*, 2013)
Soybean oil Sunflower oil Soybean oil	Flask/magnetic	Methanol 6:1-18:1	6:1 – 18:1	ChOH/2.0 – 10.0 wt% ChOMe/4.0 wt%	30 – 65	9:1; 4.0 wt%; 60°C	>95.0 (Y)/1 >95.0 (Y)/l 95.0 ± 1.7 (Y)/2.5	(Fan *et al.*, 2013)
Jatropha oil	Round-bottom flask/mechanical	Methanol 3:1 – 18:1	3:1 – 18:1	ChOH/1.0 – 5.0 wt%	30 - 70	9:1; 4.0 wt%; 60°C	88.3±1.8 (Y)/2.5 76.9±1.9 (Y)/2.5 95.0 ± 1.0 (Y)/4	(Reddy *et al.*, 2014)

4. Ionic liquids as solvents and co-solvents

Conventionally, organic solvents (such as methanol) have been used with enzymes as catalysts in the biodiesel preparation process. However, many issues can arise from their use, such as poor miscibility with oils and fats, enzyme inactivation, and disruption of intra-protein hydrophobic interactions (Akoh *et al.*, 2007). ILs are a promising alternative, where their beneficial properties such as hydrophobicity, hydrogen bond, and polarity provide enzyme stabilisation, while avoiding environmental concerns (Zhao, 2016). Moreover, because of the mild reaction conditions, ILs offer reusability while requiring a low energy demand.

Many groups have demonstrated the use of co-solvents for the chemical preparation of biodiesel (Rantwijk *et al.*, 2007; Moniruzzaman *et al.*, 2010; Tang, Baker and Zhao, 2012; Zhao and Baker, 2013). For example, Ha (2007) used immobobilised *Candida Antarctica* lipase as catalysts to test the applicability of twenty-three different ILs for the methanolys of soybean oil. Hydrophilic IL (EMIm)(TfO) achieved the highest FAME yield of 80% after 12 hours at 50◦C. Moreover, the yield was higher than the solvent-free alternative, and other widely used solvent. Another study by Sunitha (2007) reported yields as high as 98% from FAME within 10 hours of methanolys is of sunflower oil in hydrophobic 1-butyl-3-methylimidazolium (BMIm)(PF_6) and 1-ethyl-3-methylimidazolium (EMIm)(PF_6) with Novozym acting as the catalyst. An interesting observation is hydrophilic BF4-based ILs under the same conditions returned low yields.

5. Ionic liquids as extraction solvents in biodiesel synthesis

A promising application of ILs is as an extraction solvent in the various steps of the biodiesel production process. Although ILs hold attractive properties, such as thermal stability, synthetic flexibility, non-volatility, non-flammability, and recyclability, there are still considerable obstacles that must be overcome for widespread use in large-scale applications.

5.1 Extraction of lipids

Lipid extraction from biomass is one of the essential steps among the various operations in the production of biodiesel, particularly for new promising oil feedstocks. One such feedstock is microalgae, which has gathered considerable attention in recent years, due to its attractive properties as a biofuel, including high lipids content, photosynthetic efficiency, production rate, and large abundance (Chisti, 2007; Passos, Freire and Coutinho, 2014). Lipid extraction can be carried out after the microalgae biomass has been harvested and dewatered. Extraction may be achieved from the dried biomass powder (dry route) or directly from the wet concentrated biomass (wet route) (Xu *et al.*, 2011). Solvents play a crucial role in both of these routes by facilitating cell disruption, increasing the efficiency of lipid extraction by improving the biomass mass transfer properties (Ehimen et al, 2012). The most common extraction techniques are Soxhlet extraction and Bligh and Dyer's method with various solvents used to enhance extraction such as petroleum ether, n-hexane, ethanol mixture and hexane–ethanol mixture (Bligh and Dyer, 1959; Ahmad *et al.*, 2011). However, there are major disadvantages to using these solvents, including volatility, toxicity, flammability, and non-miscibility with water (except ethanol) (Mata, Martins and Caetano, 2010).

ILs have garnered much attention as a medium to enhance the efficiency of lipid extraction, primarily because of their ability to either auto-partition the lipids or improve access of co-solvents to the intracellular lipids. Other advantages ILs possess over conventional solvents include non-volatility, thermal stability, and synthetic flexibility. Subsequently, numerous ILs have been investigated, often using ILs and organic solvents such as methanol, acetic acid, chloroform, acetone, dimethyl sulfoxide, and iso-propyl alcohol (Troter *et al.*, 2016).

Young (2010) investigated the capability of 1-ethyl-3-methylimidazolium methyl sulfate (EMIm) and methanol (mass ratio 1.2:1) to extract lipids from microalgae. Using a co-solvent enables the auto-partition of the lipids to a separate immiscible phase, therefore increasing the harvesting efficiency. The lipids extracted included microalga' biomass (Chlorella species and Duniella species), Kamani oil seed, Pongamia oil seed, and Jatropha oil seed using an EMIm-methanol co-solvent and a number of polar covalent molecule types. The highest reported yield of lipids was obtained from Jatropha oil seed at 49.9% with all other experimental yields within the ranges reported in the literature.

A similar study by Kim (2012) trailed several IL-methanol co-solvents to extract lipids from Chlorella vulgaris micro-algae to determine their effectiveness in comparison to the more commonly used Bligh and Dyer's method. The IL co-solvents used include (BMIm)(MeSO4),

(EMIm)($MeSO_4$), and (BMIm)(CF_3SO_3), extracting 11.84%, 11.88%, and 12.54% respectively, achieving higher yields than Bligh and Dyer's extraction method at 10.6%. This suggests that the extraction efficiency of the lipids was influenced by the anion structure, and the hydrophobicity or hydro-philicity of the ILs. Additionally, Choi (2014) compared the influence of twelve ILs on the lipid extraction yield of Chlorella vulgaris microalgae. The results showed that ILs with organic solvents and ILs mixtures generally displayed higher lipid yields because of the synergistic effects with different anions.

While ILs have proved promising for the effective extraction of lipids, more progress still needs to be made in order to achieve the economic and environmental standards for industrial-scale applications (Zhang, Bakshi and Demessie, 2008; Harris *et al.*, 2018). Although ILs are advantageous in many aspects, many difficulties still exist in their practical application such as the multiple steps required for synthesis, the use of potentially toxic or volatile solvents, and the environmental concerns related to their production. Much research is being conducted to overcome these issues: development of simpler and more efficient syntheses; improved methods for lipid extraction (Yang *et al.*, 2017); the use of potentially cheaper to synthesize ILs such as pyridinium, ammonium, and phosphonium; and the use of DESs with the potential of increasing efficiency and yields while reducing costs.

5.2 Extraction of free fatty acids

Biodiesel derived from vegetable oil have should considerable potential but conversion is significantly reduced by the presence of FFAs. The conventional conversion process used is via transesterification with an alcohol. However, elevated levels of FFAs can greatly reduce the effectiveness of transesterification because of the reaction with the alkaline catalyst forming soap which subsequently reduced the ester yield. Conventional methods utilised for the removal of FFAs include caustic stripping, hydrolysis, and glycerolysis. Although these methods have proved to be effective, considerable drawbacks are associated with their use, such as the added complexity of an additional step and the harsh conditions required in operation (high temperatures and vacuum). ILs are one such option being explored by researchers to overcome these difficulties.

Manic, Najdanovic-Visak and Ponte (2015) studied the use poly(ethyleneglycol) solvents with different molar masses and ILs for the extraction of FFA (linoleic acid) from soybean oil. The ILs investigated included 1-butyl-3-methylimidazolium dicyanamide (BMImDCA) and AMMOENG100, which are both miscible with the linoleic acid used. In the study AMMOENG100 was reported to having the highest values of linoleic acid distribution coefficient. Based on these findings, it can be concluded that ILs hold considerable potential in the biodiesel deacidification process.

A similar study by Grimes and Kewcharoenwong (2017), explored the use of a duel system with the purpose of using ILs (HPyrBr and Brønsted acid) to extract FFAs from waste vegetable oils and conversion to biodiesel. Thus allowing the ILs to be used for extraction and catalytic functionality without the uninhibited presence of the other. Of the 18 properties tested using

ASTM standard methods, 14 of them met biodiesel fuel quality standards. Further research and innovation are required in this area to fully explore the potential role of ILs.

5.3 Extraction of unsaturated fatty methyl acid esters

The removal of unsaturated fatty acid methyl esters (uFAMEs) is often necessary in biodiesel production to reduce the fuel's sensitivity to oxidation. In addition, this step is often necessary to meet the European standards for biodiesel such as EN 14214 and EN 14213, because they limit the total unsaturated biodiesel to 120 and 130 g iodine/100g respectively (European Committee for Standardization [DIN], 2003). Traditional methods employed for the removal of uFAMEs from biodiesel include urea inclusion complexation (Liu *et al.*, 2006; Alavi Talab *et al.*, 2010), low-temperature fractional crystallisation (Mudhaffar and Salimon, 2010), molecular distillation (Jiang *et al.*, 2006), supercritical fluid extraction (Rubio-Rodríguez *et al.*, 2008, 2012) lipase concentration (Shimada, Sugihara and Tominaga, 2001; Lee *et al.*, 2011). Although effective, these methods have several inherent drawbacks which limit yields and application. ILs have garnered attention in a number of studies as an alternative mechanism to overcome such difficulties.

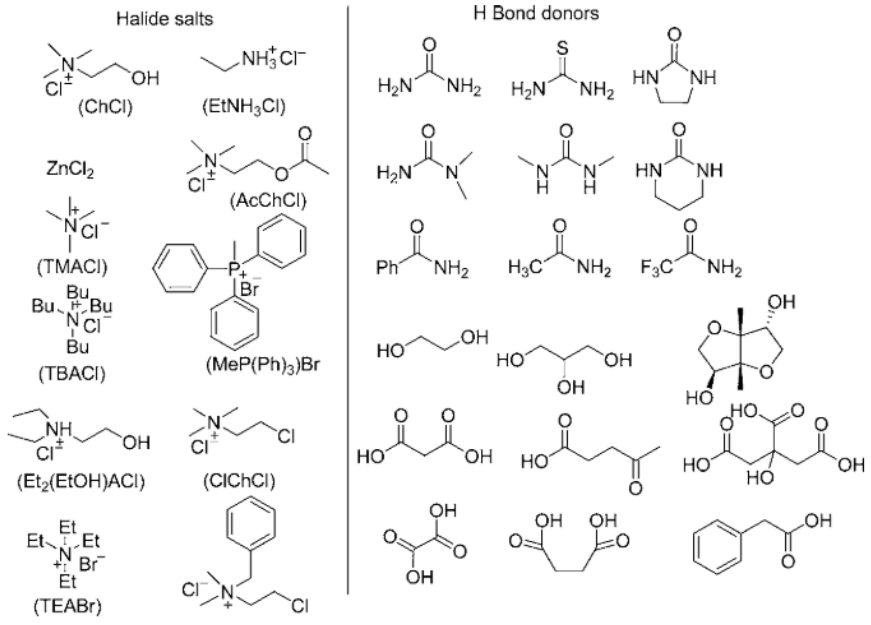
Several studies have explored the separation of uFAMEs in the biodiesel production process with ILs as extractants. Li (2009) extracted FAMEs in the form of methyl linoleate (18:2) and methyl linolenate (18:3) from soybean derived biodiesel using novel π-complexing sorbents. The preparation of these π-complexing sorbents involved the covalent immobilisation of ILs onto silica followed by coating the silica-supported ILs with silver salts. The $AgBF_4$/SBA-15-IL-PF_4 sorbent produced exhibited a higher extraction capacity and greater reusability with eight sorption successive cycles. Building on this work, Li (2009) investigated the use of a IL-cosolvent mixture to improve upon the difficulties associated with using silver salts in the extraction process, including added cost, a larger viscosity and an increased likelihood of losing activity. The study used novel π-complexing sorbents by covalently immobilising ILs onto mesoporous SBA-15 for separating polyunsaturated FAMEs, and prepared π-complexing sorbents by covalently immobilising ILs onto silica, followed by coating these silica-supported ILs with silver salts. Positive benefits were reported in the form of satisfactory extraction capacities and reusability. A similar study by Pham (2009) used an adsorbent based on mesoporous silica for separating the polyunsaturated triacylglycerols, resulting in high selectivity. Additionally, Cheong (2011) investigated the use of ILs comprised of aromatic rings for the extraction and enrichment of n-3 polyunsaturated fatty acids (PUFA) and ethyl esters through reversible ππ complexation. The use of ILs resulted in higher purity and increased extraction capabilities, strongly suggesting a correlation between the n-3 PUFA extractions and the aromatic/delocalised cation structure of the ILs.

6 Deep eutectic solvents: A new generation of ionic liquids

The latest generation of ILs, named deep eutectic solvents (DESs), have garnered considerable interest in recent years, with predictions that they could potentially replace conventional ILs in biodiesel production. Figure 3 depicts the most common DESs used today. DESs are generally composed of a mixture of solid organic salt and a complexing agent that are liquid below temperatures of 100◦C (Zhao and Baker, 2013). In such solvents, the complexing agent reacts with the anion which increases its effective size and reduces anion interaction with the cation, which results in a reduction in the mixtures freezing point (Zhao and Baker, 2013). Abbott (2003) was the first to demonstrate such solvents by reporting a series of DES from the mixture of a solid organic salt and a complexing agent can form a liquid at temperatures below 100◦C.

There has been much debate within the research community to whether DESs can be considered as ILs, mainly because of the molecular component in their structure (Zhao and Baker, 2013). Much of the debate is centered around ILs being salts composed of one type of discrete anion and cation, whereas DESs are mixtures, potentially containing several anionic and/or cationic species, as well as nonionic species. However, ILs and DESs do share many attractive solvent features, including their tunable nature. Considering the vast variety of possible combinations that can be used in the preparation of DESs the development of inexpensive, environmentally friendly solvents is therefore possible. Hence, it is now realistic to predict that DESs will play a significant role, and potentially replace ILs in biodiesel production.

Figure 3. Most common deep eutectic solvents. Reprinted with permission from Farra, A. et al. (2015) 'Green solvents in carbohydrate chemistry: From raw Materials to Fine Chemicals', Chemical Reviews, 115(14), pp. 6811–6853. Copyright 2015 American Chemical Society.



6.1 Removal of glycerol from crude biodiesel

One of the most crucial step in the production of biodiesel is the purification process, which has proven to be one of the most process intensive and economically costly steps. Before the fuel output can be classified as biodiesel, it must meet the specifications set by the international standards (i.e. EN 14214 and ASTM D6751) (European Committee for Standardization [DIN], 2003; ASTM D6751-19, 2019). These standards outline the quality requirements for the fuel to be classified as alkyl ester-based biodiesel, contributing between 60 to 80% of the process costs (Atadashi, Aroua and Aziz, 2011). This involves the removal of unwanted impurities and by-products such as glycerol, which can have several consequences on the diesel engine such as, fuel system clogging, injector fouling, engine corrosion, build-up in fuel tanks, valve deposits, and emission of harmful acrolein into the environment (Abbott *et al.*, 2007; Berrios and Skelton, 2008; Hayyan *et al.*, 2010). The traditional methods used for the commercial removal of glycerol are through dry and water washing, and membrane extraction (Berrios and Skelton, 2008; Santori *et al.*, 2012). However, there are numerous difficulties associated with the use of these purification techniques in the industry, mainly because of the cost and complexity involved. DES has received significant attention as an alternative non-toxic, inexpensive, and environmentally benign extraction media.

Abbott (2007) showed that DESs can be used for the extraction of glycerol from biodiesel using a mixture of quaternary ammonium salts and glycerol. In addition, Hayyan (2010) demonstrated that for the purpose of removing glycerol both a 1:1 DES to biodiesel molar ratio and a 1:1 (salt:glycerine) DES molar composition was the most effective. Similarly, Shahbaz (2010) showed effective glycerol extraction from palm oil-based biodiesel from two different DESs. The DESs used comprised of quaternary ammonium salt (choline chloride) with two different hydrogen-bond donors (ethylene glycol and 2,2,2-trifluracetamide). Shahbaz (2011) improved this work, indicating that binary DESs synthesised using methyl triphenylphosphonium bromide and ethylene glycol can remove all free glycerol from the palm oil-derived biodiesel. Similar to Abbott (2007), the study showed that the optimal molar ratio was 1:1 (DES:biodiesel) with no significant change after that point.

6.2 Deep eutectic solvents as catalysts

Researchers have prepared various DESs for their use as co-solvents or catalyst for biodiesel preparation as presented in Table 3. Hayyan (2013) investigated the use of an ammonium-based DES as a novel catalyst in the transesterification of low-grade crude palm oil with a high FFA content. The DES utilised comprised of a salt (N-diethyl ethanol ammonium chloride) and a hydrogen bond doner (p-toluenesulfonic acid monohydrate). The results showed a reduction from 9.5% to less than 1% in the FFA content in the low-grade crude palm oil under optimum conditions. Hayyan (2013) also studied the use of a two-stage process using a phosphonium-based DES followed by an alkali treatment for the esterification of LGCPO with different dosages of DESs in the presence of alcohol, the FFA content was reduced to

satisfactory levels for alkaline transesterification. The study demonstrated the efficient conversion of LGCPO to biodiesel using an alkali pretreatment. In addition, the DES was recycled four times without a significant loss in its activity. For the transesterification of soybean oil, Long (2010) used a Lewis acidic catalyst comprising of choline chloride and zinc chloride and methanol with a molar ratio of 1:2. The tests were carried out showed a 55% conversion after 72 hours under optimum conditions (10% catalyst, methanol/oil molar ratio 16:1, and 70◦C). In a similar study by Isahak (2011), using choline chloride: metal chloride and ILs as a catalyst in the transesterification of palm oil, resulting in ester yields of 70.4% and 67.4%. In addition, adding H2SO4 (95 vol%), further raised yields to 92.0%.

Some studies have explored combining DESs with other catalysts to improve the biodiesel production process. Huang (2013) used DESs comprised of choline chloride and glycersol (1:2 molar ratio) as solvents in the CaO-catalysied transesterification of rapeseed oil. The solvent proved to be an efficient in activating CaO through the removal of the inactive layers (calcium, carbonate, and calcium hydroxide) from the surface of the catalyst. The results showed a high ester yield of 91.9% in comparison to the low yield of 4.0% without the addition of the DES.

Table 3. Application of deep eutectic solvents as catalysts in biodiesel production. Reprinted with permission from Troter, D. Z. et al. (2016) 'Application of ionic liquids and deep eutectic solvents in biodiesel production: A review', Renewable and Sustainable Energy Reviews, 66, pp. 473–500. Copyright 2016 Elsevier.

Feedstock	Type, volume of reactor, cm^3/type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol or ml.mg oil	DES/loading, wt% or ml/g oil	Other catalyst/loading, wt% (to oil weight)	Temperature, °C	Optimal reaction conditions	Conversion (C) or yield (Y)/time, h	Reference
Soybean oil	Round-bottom flask/100	Methanol	10:1 - 30:1	ChCI:$ZnCI_2$ (1:2)/10.0 wt%	-	50-90	16:1; 10.0 wt%; 70°C	54.52 (C)/72	(Long *et al.*, 2010)
Palm oil	Three-neck flask	Methanol	10:1 - 15:1	ChCI:$ZnCI_2$ (1:2)/0.5-2.5 wt% ChCI:$FeCI_3$ (1:2)/0.5-2.5 wt% ChCI:$ZnCI_2$ (1:2)/2.5 wt% ChCl:$FeCl_2$ (1:2)/2.5 wt%	- - 95.0% H_2SO_4/20.0 wt%	65	15:1; 2.5wt% DES; 65°C	70.4 (Y)/4 67.4 (Y)/4 92.0 (Y)/4 89.5 (Y)/4	(Isahak *et al.*, 2011)
Palm oil, low grade (9.5% FFA)	Batch multi-unit reactor system/mechanical, 100-500	Methanol	4:1-20:1	DEAC:PTSA (1:3)/0.25-3.5 wt%	-	40-80	1 step: 8:1; 0.75 wt% DES; 60°C; 200rpm	97.0 (Y)/0.5	(Hayyan, Ali Hashim, *et al.*, 2013)
Esterified oil (0.7% FFA)			10:1	-	KOH/1.0 wt%	60	II step: 10:1; 1.0 wt% KOH; 60°C; 400 rpm	84.0 (Y)/1	
Palm oil, low grade (9.3% FFA)		Methanol	1:1-20:1	P-DES (1:3)/0.25-3.5 wt%	-	40-80	I step: 10:1; 1.0 wt% 1.0 wt% DES; 60°C; 300 rpm	96.0 (Y)/0.5	(Hayyan *et al.*, 2014)
Esterified oil (0.88% FFA)			10:1	-	KOH/1.0 wt%	60	II step: 10:1; 1.0 wt% KOH; 60°C; 400 rpm	89.84 (Y)/1	
Palm oil, crude (9.0% FFA)	Reactor	Methanol	3:1-20:1	ChCI:PTSA (1:3)/0.25-3.50 wt%	-	40-70	I step: 10:1, 0.75 wt% DES, 60°C	97.0 (Y)/0.5	(Hayyan *et al.*, 2014)
Esterified oil (<1% FFA)	Batch reactor with a reflus condenser, 1500/stirrer, 400		10:1	-	KOH/1.0 wt%	60	II step: 10:1, 1.0 wt% KOH, 60°C	92.0 (Y)/1	
Rapeseed oil	Round-bottom flask/vertical blender, 400	Methanol	14.28:1	ChCI:glycerol (1:2)/10.74 wt%	8.07 wt% CaO (commercial)	65	14.28:1; 10.74 wt% DES; 8.07 wt% CaO;65°C	91.9 (Y)/3	(Huang *et al.*, 2013)

Midlyol 812	Micro-reaction vessel, 5/gentle	Methanol /20.0 vol%		ChOAc:glycerol (1:1.5)	Novozym 435/27.3 wt%	50	20.0 vol% methanol; 1.0 mL mixture of DES and methanol; 27.3 wt% lipase; 1.0 vol% water; 50°C	97.0 (C)/3	(Zhao, Baker and Holmes, 2011)
Soybean oil	Micro-reaction vessel, 5/gentle	Methanol/20.0-50.0 vol% (to IL)		ChCI:glycerol (1:2)	Novozym 435/20.0-60.0 wt%	50	7:3 (v/v) of DES and methanol, 40.0 wt% lipase, 0.2 vol% water	88.0 (C)/24	(Zhao, Zhang and Crittle, 2013)
M. pinnata seed oil	Flask/shaker, 220	Methanol	3 mL/mg oil	ChOAc:glycerol (1:2)/7 mL DES/g oil	P. expansum lipase/1.0 wt% Novozym 435/1.0 wt% Lipozyme TLIM/1.0 wt%	50	3 mL methanol/mg oil; 7 mL DES/g oil; 1.0 wt% lipase; 50°C	7.6 (C)/48 54.8 (C)/48 44.8 (C)/48	(Huang *et al.*, 2014)

7. Summary and future perspectives

ILs, as ''green'' tunable solvents, have significant potential in the biodiesel production process. From this review, it can be seen that ILs have already been shown to be promising as catalysts, co-solvents and extracting solvents in biodiesel production. They offer substantial benefits including high product yields, negligible vapour pressure, high thermal stability, non-flammability, odourless, compatibility with facile post-synthesis separation and enzyme catalysts. Furthermore, ILs can be designed for a specific applications through the careful selection of the appropriate cation and anion combination.

Regardless of the recent progress made in the field, there are several shortcomings associated with the use of ILs in biodiesel production. One such shortcoming is the compromise often required between enzyme compatibility and solubilizing power in the selection of an IL.

Another key obstacle to be overcome is the high costs associated with ILs, particularly for the achievement of industrial-scale widespread use. However, when considering the overall advantages provided, this drawback can be justified in most cases. Alternatively, the costs associated with common ILs such as imidazolium and pyridiniums may be avoided by deriving its composition from low-cost alternatives. Moreover, the possibility of using inexpensive DESs comprised of choline salts allows for the development of new economic and environmentally friendly biodiesel production processes. An additional weakness is the high viscosity, typical in many ILs, which hinder mass-transfer kinetics and lead to poor performance. Significant research has been conducted to reduce this issue by designing 'viscosity-reducing' anions, such as dicyanamide, tricyanomethanide, and tetracyanoborate.

From the studies presented in this work, it is clear that ILs and DESs have already made a significant contribution to improving the overall biodiesel production process for a range of feedstock's by increasing yields, aiding ease of preparation and lowering costs. It is hoped that the continued research of such technology will greatly aid the advancement of biodiesel as an alternative green fuel source.

Acknowledgements

The authors are thankful for the funding received from the European Union's INTERREG VA Programme for the Renewable Engine project, managed by the Special EU Programmes Body (SEUPB), with match funding provided by the Department for the Economy and Department of Jobs, Enterprise and Innovation in Ireland.

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