



## Application of ionic liquids and deep eutectic solvents in biodiesel production: A review

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**Abbreviations:** [BHSO<sub>3</sub>MIM][HSO<sub>4</sub>], 1-sulfobutyl-3-methylimidazolium hydrosulfate; [BIM][HSO<sub>4</sub>], 1-butylimidazolium hydrosulfate; [BMIM][BF<sub>4</sub>], 1-butyl-3-methylimidazolium tetrafluoroborate; [BMIM][CF<sub>3</sub>SO<sub>3</sub>], 1-butyl-3-methylimidazolium trifluoromethanesulfonate; [BMIM][Cl], 1-butyl-3-methylimidazolium chloride; [BMIM][ClO<sub>4</sub>], 1-butyl-3-methylimidazolium perchlorate; [BMIM][DCA], 1-butyl-3-methylimidazolium dicyanamide; [BMIM][FeCl<sub>4</sub>], 1-butyl-3-methylimidazolium tetrachloroferrate; [BMIM][HSO<sub>4</sub>], 1-butyl-3-methylimidazolium hydrogen sulfate; [BMIM][Im], 1-butyl-3-methylimidazolium imidazolidine; [BMIM][MeSO<sub>4</sub>], 1-butyl-3-methylimidazolium methyl sulfate; [BMIM][NTf<sub>2</sub>], 1-butyl-3-methylimidazolium trifluoromethanesulfonate; [BMIM][OH], 1-butyl-3-methylimidazolium hydroxide; [BMIM][PF<sub>6</sub>], 1-butyl-3-methylimidazolium hexafluorophosphate; [BMIM][TS], 1-butyl-3-methylimidazolium tosylate; [BnMIM][HSO<sub>4</sub>], 1-benzyl-3-methylimidazolium hydrosulfate; [BSAIM][OTf], 1-allyl-3-(butyl-4-sulfonyl)imidazolium trifluoromethanesulfonate; [BSIM(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>CH<sub>3</sub>][HSO<sub>4</sub>], amphiphilic Brønsted acidic IL with an alkane sulfonic acid group and a polyether group, through polyethylene glycol monomethylether; [BSMIM][Cl], 1-(1-butylsulfonic)-3-methylimidazolium chloride; [BSO<sub>3</sub>HMIM][HSO<sub>4</sub>], 1-butylsulfonic-3-methylimidazolium hydrogen sulfate; [BSPIM][HSO<sub>4</sub>], 1-butyl-3-(3-sulfopropyl)-imidazolium hydrosulfate; [BSPy][CF<sub>3</sub>SO<sub>3</sub>], 1-(4-sulfonic acid) butylpyridinium trifluoromethanesulfonate; [(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HPy][HSO<sub>4</sub>], 1-(4-sulfonic acid) butylpyridinium hydrogen sulfate; [(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>H][HSO<sub>4</sub>], *N,N,N*-triethyl-*N*-(propanesulfonic acid) ammonium hydrosulfate; [(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>H]<sup>+</sup>, *N,N,N*-triethyl-*N*-(propanesulfonic acid) ammonium cation; [ClEtMe<sub>3</sub>N]Cl:glycerol, (2-chloroethyl)trimethylammonium chloride:glycerol; [C<sub>16</sub>MIM][NTf<sub>2</sub>], 1-hexadecyl-3-methylimidazolium trifluoromethanesulfonate; [C<sub>18</sub>MIM][NTf<sub>2</sub>], 1-methyl-3-octadecylimidazolium bis(trifluoromethylsulfonyl) imide or 1-octadecyl-3-methylimidazolium trifluoromethanesulfonate; [C<sub>18</sub>MIM][PF<sub>6</sub>], 1-methyl-3-octadecylimidazolium hexafluorophosphate; [C<sub>2</sub>MIM][OH], 1-ethyl-3-methylimidazolium hydroxide; [C<sub>3</sub>SO<sub>3</sub>HMIM][HSO<sub>4</sub>], 1-(3-sulfonic acid) propyl-3-methylimidazolium hydrogen sulfate; [DDPA][Tos], 3-(*N,N*-dimethyldodecylammonium) propanesulfonic acid *p*-toluenesulfonate; [DSIM][HSO<sub>4</sub>], 1,3-disulfonic acid imidazolium hydrogen sulfate; [EMIM][BF<sub>4</sub>], 1-ethyl-3-methylimidazolium tetrafluoroborate; [EMIM][Cl], 1-ethyl-3-methylimidazolium chloride; [EMIM][DEP], 1-ethyl-3-methylimidazolium diethylphosphate; [EMIM][EtOSO<sub>3</sub>], 1-ethyl-3-methylimidazolium ethyl sulfate; [EMIM][HSO<sub>4</sub>], 1-ethyl-3-methylimidazolium hydrogen sulfate; [EMIM][MeSO<sub>4</sub>], 1-ethyl-3-methylimidazolium methyl sulfate; [EMIM][OAc], 1-ethyl-3-methylimidazolium acetate; [EMIM][PF<sub>6</sub>], 1-ethyl-3-methylimidazolium hexafluorophosphate; [EMIM][SCN], 1-ethyl-3-methylimidazolium thiocyanate; [EMIM][Tf<sub>2</sub>N], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [EMIM][TfO], 1-ethyl-3-methylimidazolium trifluoromethanesulfonate; [EPy][Br], 1-ethylpyridinium bromide; [EPy][HSO<sub>4</sub>], *N*-ethylpyridinium hydrosulfate; [Et<sub>3</sub>N][HSO<sub>4</sub>], triethylammonium hydrosulfate; [Et<sub>3</sub>NH]Cl-AlCl<sub>3</sub> (x(AlCl<sub>3</sub>)=0.7), chloroaluminate-based ionic liquids derived from triethylammonium chloride; [EtNH<sub>3</sub>]Cl:glycerol, ethylammonium chloride and glycerol; [HDSSBD][HSO<sub>4</sub>], 3,3'-(hexane-1,6-diyl) bis(6-sulfo-1-(4-sulfofenyl)-1*H*-benzimidazolium) hydrosulfate; [HMIM][BF<sub>4</sub>], 3-methylimidazolium tetrafluoroborate; [HMIM][HSO<sub>4</sub>], 1-methylimidazolium hydrosulfate; [Hnmp][HSO<sub>4</sub>], 1-methyl-2-pyrrolidonium hydrogen sulfate; [Me(OEt)<sub>3</sub>-Et<sub>3</sub>N][HCOO], triethyl (2-(2-methoxyethoxy)ethoxy)ethylammonium formate; [Me(OEt)<sub>3</sub>-Et<sub>3</sub>N][OAc], triethyl (2-(2-methoxyethoxy)ethoxy)ethylammonium acetate; [Me(OEt)<sub>3</sub>-Et-Im][OAc], 1-ethyl-3-(2-(2-methoxyethoxy)ethoxy)ethylimidazolium acetate; [Me(OEt)<sub>3</sub>-Et-Im][Tf<sub>2</sub>N], 1-ethyl-3-(2-(2-methoxyethoxy)ethoxy)ethylimidazolium bis(trifluoromethylsulfonyl)imide; [MIM][HSO<sub>4</sub>], 1-methylimidazolium hydrosulfate; [MIM-PSH]<sub>2</sub>0HPW<sub>12</sub>O<sub>40</sub>, polyoxometalate-based sulfonated IL; [MorMeA][Br], 4-allyl-4-methylmorpholin-4-ium bromide; [MSBIM][HSO<sub>4</sub>], 1-methyl-3-(4-sulfofenyl)-imidazolium hydrosulfate; [MSBP][HSO<sub>4</sub>], 1-methyl-2-(4-sulfofenyl) pyrazolium hydrosulfate; [MSIM][HSO<sub>4</sub>], 3-methyl-1-sulfonic acid imidazolium hydrogen sulfate; [MSPP][HSO<sub>4</sub>], 1-methyl-2-(3-sulfofenyl) pyrazolium hydrosulfate; [NMP][CH<sub>3</sub>SO<sub>3</sub>], *N*-methyl-2-pyrrolidonium methyl sulfonate; [OMIM][NTf<sub>2</sub>], 3-octyl-1-methylimidazolium bis(trifluoromethylsulfonyl)sulfonyl imide; [OMIM][PF<sub>6</sub>], 3-octyl-1-methylimidazolium hexafluorophosphate; [OMIM][TfO], 1-methyl-3-octylimidazolium trifluoromethanesulfonate; [OMPy][BF<sub>4</sub>], 1-octyl-3-methylpyridinium tetrafluoroborate; [SBP][HSO<sub>4</sub>], 2-(4-sulfofenyl) pyrazolium hydrosulfate; [SO<sub>3</sub>H-(CH<sub>2</sub>)<sub>3</sub>-HIM][HSO<sub>4</sub>], 1-(propyl-3-sulfonate) imidazolium hydrogen sulfate; [SO<sub>3</sub>H(CH<sub>2</sub>)<sub>3</sub>VI][HSO<sub>4</sub>], 1-(3-sulfofenyl)-3-vinylimidazolium hydrogen sulfate; [SO<sub>3</sub>H(CH<sub>2</sub>)<sub>3</sub>VPy][HSO<sub>4</sub>], 1-(3-sulfofenyl)-4-vinylpyridinium hydrogen sulfate; [SO<sub>3</sub>H-Plm-CPMS][HSO<sub>4</sub>], 1-(propyl-3-sulfonate)-3-(3-trimethoxysilylpropyl) imidazolium hydrogen sulfate; [SPPy][HSO<sub>4</sub>], 2-(3-sulfofenyl) pyrazolium hydrosulfate; [TEAm][Cl], tetraethylammonium chloride; [TEAm][HSO<sub>4</sub>], tetraethylammonium hydrosulfate; [TEPSA][HSO<sub>4</sub>], 3-(*N,N,N*-triethylamino)-1-propanesulfonic hydrogen sulfate; [TMEDAPS][HSO<sub>4</sub>], *N,N,N,N*-tetramethyl-*N,N'*-dipropanesulfonic acid ethylenediammonium hydrogen sulfate; Ammoeng 100, alkyl pentaethoxymethyl ammonium methylsulfate; Ammoeng 102, tetraalkyl ammonium sulfate; Ammoeng 120, quaternary ammonium sulfate; BMI · InCl<sub>4</sub>, 1-*n*-butyl-3-methylimidazolium tetrachloro-indate; BMI · NTf<sub>2</sub>, 1-*n*-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; BPSIM, 1-butyl-3-(propyl-3-sulfonate)-imidazolium; BSPs, biomass support particles; ChCl, choline chloride; ChCl:PTSA (1:3), choline chloride:*p*-toluenesulfate acid (1:3); ChIm, Choline imidazolium; ChOAc, choline acetate; ChOH, choline hydroxide; ChOMe, choline methoxide; DEAC:PTSA (1:3), *N,N*-diethanol ammonium chloride:*p*-toluenesulfate acid (1:3); DES, deep eutectic solvent; DVB, Divinylbenzene; EtOH, Ethanol; FAME, Fatty acid methyl esters; Fe SBA-15, Fe-incorporated SBA-15, (SBA: Santa Barbara Amorphous); Fe<sub>3</sub>O<sub>4</sub> · SiO<sub>2</sub>, silica-coated magnetite; FFA, free fatty acid; H<sub>6</sub>Si<sub>6</sub>O<sub>12</sub>(OH)<sub>2</sub>, hydroxylated cage-like nano-cluster; HMTA, hexamethylenetetramine; HPW, phosphotungstic acid; IL4B, 3,3'-(butane-1,4-diyl)-bis(4-sulfofenyl-1*H*-imidazol-3-ium) hydrosulfate; IL6B, 3,3'-(hexane-1,6-diyl)-bis(4-sulfofenyl-1*H*-imidazol-3-ium) hydrosulfate; IL8B, 3,3'-(octane-1,8-diyl)-bis(4-sulfofenyl-1*H*-imidazol-3-ium) hydrosulfate; ILB2, 3-butyl-6-sulfo-1-(4-sulfofenyl)-1*H*-imidazolium hydrogen sulfate; ILH2, 3-hexadecyl-6-sulfo-1-(4-sulfofenyl)-1*H*-imidazolium hydrogen sulfate; IL, ionic liquid; IMC<sub>2</sub>OH, bis-(3-methyl-1-imidazolium)-ethylene dihydroxide; MB3B, bentonite modified with 3,3'-(butane-1,6-diyl)bis(6-sulfo-1-(4-sulfofenyl)-1*H*-benzimidazolium) hydrosulfate; MBIL8B, bentonite modified with 3,3'-(octane-1,8-diyl)bis(4-sulfofenyl-1*H*-imidazol-3-ium) hydrosulfate; MeOH, methanol; MIM-PS, SO<sub>3</sub>H-functionalized zwitterion ionic complex 3-(1-methylimidazolium-3-yl) propane-1-sulfonate; MPEG-350-IL, ionic liquids with polyethylene glycol monomethylether molecular weight of 350; MPS-SiO<sub>2</sub>, sulfhydryl-group-modified SiO<sub>2</sub>; MTPB, methyl triphenyl phosphonium bromide; Novozym 435, *Candida antarctica* lipase B; OMR, ordered mesoporous resin; OMR-[C<sub>4</sub>HMTA][SO<sub>4</sub>H], ordered mesoporous resin with hexamethylenetetraminium hydrogen sulfate; OMR-[HMTA], ordered mesoporous resin with hexamethylenetetramine; OMR-IL, ordered mesoporous ionic liquid; P-DES (1:3), allyltriphenylphosphonium bromide:*p*-toluenesulfonic acid monohydrate (1:3); PDVB, polydivinylbenzene; PEL, *Penicillium expansum* lipase; PIL, ionic liquid polymer; scCO<sub>2</sub>, supercritical carbon dioxide; TAG, triacylglycerol; w-ROL, wild type *Rhizopus oryzae* producing triacylglycerol lipase

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## ABSTRACT

Developing technologies for the production of alternative fuels from biorenewable resources is a field of interest for many researchers. Adequate substitute to diesel fuel is biodiesel that is synthesized through the transesterification of vegetable oils or animal fats and fulfilled the international standards. Ionic liquids (ILs) and deep eutectic solvents (DESs) have gained tremendous attention for their use in biodiesel production because of environmental benefits and process improvements. The present work overviews the use of ILs and DESs in the reaction and purification steps of biodiesel production processes where they are used as catalysts, cosolvents and extracting solvent. In addition, the possibilities of recycling and reusing of ILs and DESs are pointed out. Moreover, optimization and kinetic studies of biodiesel synthesis in the presence of ILs or DESs are discussed. The use of novel technologies combined with ILs or and DESs are also considered. Therefore, the present paper highlights the promising uses of ILs and DESs in biodiesel production in the future.

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## 1. Introduction

Biodiesel is a promising alternative energy source with properties similar to mineral diesel fuel. This biofuel is commonly made by transesterification (alcoholysis) of vegetable oils or animal fats with a primary aliphatic alcohol, usually methanol or ethanol. Catalysts used for this reaction can be acids, bases or lipases. Homogeneous catalysts are mostly used despite their serious disadvantages such as corrosive nature, difficult removal from the reaction mixture after the reaction and generation of huge wastewater amount [1–3]. Acid-catalyzed reactions are usually slower than base-catalyzed ones and require a large excess of alcohol and high pressure. When basic catalysts are used, oily or fatty feedstocks should have a low content of free fatty acids (FFAs) since there is a risk of fatty acid saponification. Heterogeneous catalysts can easily be separated from the final product, but low reaction rate and catalyst deactivation are problematic. A greener alternative to chemical transesterification is enzyme-catalyzed transesterification as it requires mild reaction conditions, demands less energy, reduces waste treatment and allows a small amount of water to be present in substrates. Also, the ability of reusing the lipases and possibility of choosing various enzymes for different substrates make this process acceptable. High cost and inactivation of lipase by methanol as well as impurities in crude and waste oils represent disadvantages of this type of transesterification.

To overcome the disadvantages of existing biodiesel production processes, novel technologies are emerging. The use of ionic liquids (ILs) as a catalyst, a cosolvent or an extracting solvent have recently attracted attention in the biodiesel production [4]. ILs are organic salts that consist of ions and remain liquid at temperatures below 100 °C [5]. Cations in ILs are organic, while anions can be organic or inorganic. The most common ILs are nitrogen-containing (such as alkylammonium, *N,N'*-dialkylimidazolium, *N*-alkylpyridinium and *N,N'*-pyrrolidinium) or phosphorous-containing (such as alkylphosphonium) [6]. The common choice of anions include  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{CH}_3\text{CO}_2^-$ ,  $\text{CF}_3\text{CO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{Tf}_2\text{N}^-$ ,  $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ ,  $[\text{RSO}_4]^-$  and  $[\text{R}_2\text{PO}_4]^-$ , where Tf and R stand for bis (trifluoromethylsulfonyl)imide anions and alkyl group, respectively. These nonaqueous solvents possess favorable physical and chemical properties, like wide liquid range, high chemical and thermal stabilities, negligible vapor pressure, low flammability, high ionic conductivity, high thermal conductivity, wide electrochemical potential window and are successful in dissolving a wide range of organic and inorganic compounds [5]. Some ILs are considered to be “green” because of their minimal toxicity to humans and to the environment, and have received great attention in different processes, including catalysis, electrochemistry, separation, etc. Many ILs are proven to be poorly biodegradable and relatively toxic but Markiewicz et al. [7] have recently found that certain mixed strain consortium still has the potential to biodegrade ILs.

A new generation of ILs, called deep eutectic ILs or deep eutectic solvents (DESs), became a target of interest for many researchers studying biodiesel production due to their advantages and environmentally-friendly nature. In fact, some researchers show ambivalence on whether DESs could formally be classified as ILs since they have a molecular component. Because of their complex synthesis and expensive starting reactants, ILs are more and more replaced with DESs that are formed from the mixture of organic halide salts with an complexing organic agent (usually a H-bond donor). By mixing these two components in proper ratios, eutectic mixtures are formed, which are in liquid state at temperatures below 100 °C [8,9]. The complexing agent interacts with the anion and increases its effective size, which results in decreasing the interaction between anion and cation. As a final result, freezing point depression of the mixture occurs. One

example of DES is choline chloride (ChCl):urea (1:2 M ratio) with melting point of 12 °C, which is much lower than those of ChCl and urea (302 °C and 133 °C, respectively) [8].

The properties of DESs as tunable solvents are comparable to those of ILs. In addition, DESs have some advantages over ILs, such as easy preparation, high purity, low cost, no reactivity with water, non-toxicity and biodegradability [9]. Therefore, it is realistic to expect that DESs will replace ILs completely in biodiesel production. Since benign and cheap components are used for preparation of DESs, various combinations of organic salts and complexing agents are possible. Quaternary ammonium salts, like ChCl, are frequently used for these purposes, combined with a wide spectrum of complexing agents (amides, amines, carboxylic acids, alcohols, sugar-based polyols and metal salts). DESs are able in dissolving various compounds, such as metal salts, aromatic acids, amino acids, glucose, citric acid, benzoic acid and glycerol, and are used in various chemical and enzymatic reactions, including biodiesel synthesis [8–10].

The present work overviews the use of ILs and DESs in the reaction and purification steps of biodiesel production processes. In the synthesis of biodiesel, they are used as catalysts and cosolvents, while in the purification of crude biodiesel they are employed as extracting solvents. Therefore, at first we discuss the use of ILs as catalysts, cosolvents and extracting solvents in biodiesel production from various feedstocks. Then, we focused our attention on the use of DESs as they tend to replace ILs for the same uses in biodiesel production. In addition, optimization and kinetic studies of biodiesel synthesis in the presence of ILs and DESs as well as the use of novel technologies combined with ILs and DESs are discussed. Finally, we highlight the possibility of recycling and reusing of ILs and DESs.

## 2. ILs as catalysts in biodiesel production

Both acidic and base ILs can be used as catalysts in one- or two-step processes of biodiesel production. The former processes consists of either esterification of FFAs or transesterification of triacylglycerols (TAGs), depending on the type of feedstock (basically on FFA content), and the latter ones include the esterification pretreatment of the feedstock riched with FFAs, followed by the transesterification of TAGs. The application of ILs in biodiesel production as catalysts is increasing in recent years at least for two advantages: the possibility of their recovery and the reduced risk of contaminating the final products with them.

### 2.1. Acidic IL catalysts

Acidic ILs can catalyze both esterification of FFAs and transesterification of TAGs. These ILs are made of various combinations of cations and anions, and the higher the acidity of the compound, the higher the product yield is reported. Multi-functionalized ILs are proved to be the best choice [11]. However, type of feedstock and alcohol has an impact on achieving higher conversion rates. The literature summary on acidic ILs as catalysts in esterification and transesterification of various feedstocks along with reaction conditions applied are given in Tables 1 and 2.

#### 2.1.1. Acidic ILs in esterification

Zhang et al. [12] used acidic ILs with imidazolium and pyrrolidonium groups as catalysts in esterification of various FFAs. *N*-methyl-2-pyrrolidonium methyl sulfonate,  $[\text{NMP}][\text{CH}_3\text{SO}_3]$ , is the best catalyst under mild reaction conditions.  $[\text{NMP}][\text{CH}_3\text{SO}_3]$  is able to convert a wide range of FFAs (stearic, myristic and palmitic) into alkyl esters, with the efficiency of 93.6–95.3%. In comparison with traditional acidic catalysts, this IL is more efficient. Fang et al.

**Table 1**  
Application of acidic ILs as catalysts in esterification.

Feedstock (FFA)	Type, volume of reactor, cm <sup>3</sup> /type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst/loading, <i>n</i> (catalyst): <i>n</i> (oil) or wt% (to oil) or mol% (to oil)	Temperature, °C	Optimal reaction conditions	Conversion (C) or yield (Y), %/time, h	Reference
Oleic acid	Flask/magnetic, vigorous	Ethanol	1:1–3.5:1	[NMP][CH <sub>3</sub> SO <sub>3</sub> ]/0.213:1 <sup>a</sup>	30–70	2:1; 0.213:1 <sup>a</sup> ; 70 °C	95.0 (C)/8	[12]
		Methanol	2:1		70		95.3 (C)/8	
		<i>n</i> -Propanol					94.1 (C)/8	
		<i>n</i> -Butanol					93.9 (C)/8	
Stearic acid		Ethanol					93.6 (C)/8	
Myristic acid							94.3 (C)/8	
Palmitic acid							94.2 (C)/8	
Oleic acid	Flask/magnetic, vigorous	Ethanol	1:1–3:1	[TMEDAPS][HSO <sub>4</sub> ]/2:50–14:50 <sup>a</sup>	20–80	1.8:1; 0.2:1 <sup>a</sup> ; 70 °C	96.0 (C)/6	[13]
		Methanol	1.8:1	[TMEDAPS][HSO <sub>4</sub> ]/0.2:1	70	1.8:1; 0.2:1 <sup>a</sup> ; 70 °C	95.0 (C)/6	
		<i>n</i> -Propanol					94.0 (C)/6	
		<i>n</i> -Butanol					93.0 (C)/6	
Stearic acid		Ethanol					94.0 (C)/6	
Myristic acid							94.0 (C)/6	
Palmitic acid							95.0 (C)/6	
Oleic acid	Three-neck flask/magnetic	Methanol	10:1	MPEG-350-IL/0.017:1 <sup>a</sup>	68	10:1, 0.017:1 <sup>a</sup> , 68 °C	> 90.0 (C)/4	[14]
Oleic acid	Flask/magnetic, vigorous	Methanol	2:1	[DDPA][Tos]/0.2:1 <sup>a</sup>	80	2:1; 0.2:1 <sup>a</sup> ; 80 °C	97.9 (C)/1	[15]
		Methanol	1.5:1		60	1.5:1; 0.1:1 <sup>a</sup> ; 60 °C	96.5 (C)/3	
		Ethanol	1.5:1				94.6 (C)/3	
		<i>n</i> -Propanol	1.5:1				93.2 (C)/3	
		<i>n</i> -Butanol	1.5:1				92.5 (C)/3	
Linoleic acid		Methanol	1.5:1				95.8 (C)/3	
Palmitic acid							95.2 (C)/3	
Oleic acid	Flask, 25/vigorous	Methanol	2:1	IL4B/10.0 mol%	22–60	2:1; 10.0 mol%; 22–60 °C	67.4–78.0 (Y)/5	[16]
				IL6B/10.0 mol%	22–60		70.2–79.2 (Y)/5	
				IL8B/10.0 mol%	22–60		75.6–85.5 (Y)/5	
Lauric acid				IL8B/7.5 mol%	50	2:1; 7.5 mol%; 50 °C	97.6 (Y)/6	
Palmitic acid							94.5 (Y)/6	
Stearic acid							88.2 (Y)/6	
Oleic acid							95.0 (Y)/6	
		Ethanol					95.4 (Y)/6	
		<i>n</i> -Butanol					97.3 (Y)/6	
Lauric acid	Flask/magnetic, vigorous	Methanol	3:1	[HMIM][HSO <sub>4</sub> ]/5.0 wt%	100	3:1; 5.0 wt%; 100 °C	62.83 (C)/4	[17]
			6:1	[Hnmp][HSO <sub>4</sub> ]/5.0 wt%	70	6:1; 5.0 wt%; 70 °C	96.78 (C)/4	
				[Hnmp][HSO <sub>4</sub> ]/5.0 wt%			97.41 (C)/2	

<sup>a</sup> *n*(Catalyst):*n*(oil).

[13] compared the esterification of FFAs with different short alkyl-chain alcohols for biodiesel production by using monocationic and dicationic ILs. Dicationic IL *N,N,N',N'*-tetramethyl-*N,N'*-dipropylsulfonic acid ethylenediammonium hydrogen sulfate, [TMEDAPS][HSO<sub>4</sub>] shows the best catalytic activity. Wu et al. [14] synthesized a few water-stable, bifunctional, temperature-sensitive, amphiphilic Brønsted acidic ILs, [BsIM(CH<sub>2</sub>CH<sub>2</sub>O)<sub>*n*</sub>CH<sub>3</sub>][HSO<sub>4</sub>], with an alkane sulfonic acid group and a polyether group. Its polyethylene glycol monomethylether unit has different polymerization degree and molecular weight. The IL with polyethylene glycol monomethylether unit having molecular weight of 350 shows the best catalytic activity in the esterification of oleic acid by methanol, which is similar to the catalytic activity of concentrated sulfuric acid. The activity of the catalyst depends on polymerization degree of polyether cation and decreases as the polyether chain becomes longer. Besides the acidity of the anions, the length of the carbon chain in the cations is also important for the acidity of ILs [15]. ILs with longer carbon chain promotes more efficient esterification because these carbon chains facilitate mass transfer in the reaction system. In the esterification of oleic acid with methanol, 3-(*N,N*-dimethyldodecylammonium) propanesulfonic acid *p*-toluenesulfonate, [DDPA][Tos], gives the highest conversion under the

optimum conditions. This IL is also successfully used for the esterification of oleic acid with other short-chain alcohols, as well as for the esterification of linoleic and palmitic acid with methanol. Low cost, thermal stability and efficiency make this IL a good candidate for biodiesel production from cheap feedstocks (waste and non-edible oils). In the esterification of oleic acid with methanol, Aghabarari et al. [16] observed the best catalytic efficiency of 3,3'-(octane-1,8-diyl)-bis(4-sulfobenzyl-1*H*-imidazol-3-ium) hydrogensulfate (IL8B). Since IL8B has the lowest steric hindrance and the highest space between sulfonic groups for approaching of fatty acid to the active sites, the number of Brønsted acidic functions and steric hindrance are responsible for the catalytic activity of this IL. Testing of various FFAs (lauric, palmitic, stearic and oleic) in the esterification with methanol under the same conditions shows that FFAs with shorter carbon chain give better ester yield. Also, when oleic acid reacts with ethanol or *n*-butanol, the ester yield is high. Zhang et al. [17] examined the efficiency of 1-methylimidazolium hydrogen sulfate, [HMIM][HSO<sub>4</sub>], and 1-methyl-2-pyrrolidonium hydrogen sulfate, [Hnmp][HSO<sub>4</sub>], as catalysts in the esterification of lauric acid with methanol. Under the same reaction conditions [Hnmp][HSO<sub>4</sub>] is more productive. Keeping in mind the low cost and the route for

**Table 2**

Application of acidic ionic liquids as catalysts in transesterification.

Feedstock	Type, volume of reactor, cm <sup>3</sup> /type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst/loading, <i>n</i> (catalyst): <i>n</i> (oil) or wt% (to oil) or mol% (to oil) or mmol catalyst/g oil	Temperature, °C	Optimal reaction conditions	Conversion (C) or yield (Y), %/Time, h	Reference
Cottonseed oil	Cylindrical stainless steel reactor, 250/ mechanical, vigorous	Methanol	3:1–18:1	[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HPy][HSO <sub>4</sub> ]/0.029:1–0.115:1 <sup>a</sup>	150–180	12:1; 0.057:1 <sup>a</sup> ; 170 °C	92.0 (Y)/5	[18]
Waste oil	Cylindrical stainless steel reactor, 250/ mechanical, vigorous	Methanol	3:1–18:1	[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HPy][HSO <sub>4</sub> ]/0.03:1–0.115:1 <sup>a</sup>	80–180	12:1; 0.06:1 <sup>a</sup> ; 170 °C	93.5 (Y)/4	[19]
Soybean oil	Flask/magnetic	Methanol	8:1	[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> Hpy][HSO <sub>4</sub> ]/5.0 wt%	120	8:1; 5.0 wt%; 120 °C	94.5 (Y)/8	[20]
Rapeseed oil	Three necked round bottomed flask/ magnetic	Methanol	12:1	Multi –SO <sub>3</sub> H functionalized strong Brønsted acidic IL/0.4 mmol/g oil	70	12:1; 0.4 mmol IL/g oil; 70 °C	98.2 (Y)/7	[11]
Jatropha oil	Cylindrical stainless steel reactor, 100/ mechanical stirring	Methanol	10:1	[BSPy][CF <sub>3</sub> SO <sub>3</sub> ]/0.05:1–0.18:1 <sup>a</sup>	80–100	10:1; 0.12:1 <sup>a</sup> ; 100 °C	92.0 (Y)/5	[21]
Canola oil	Round-bottomed flask, 25/vigorous	Methanol	10:1	[BSPy][HSO <sub>4</sub> ]/0.12:1 <sup>a</sup>	100	10:1; 0.12:1 <sup>a</sup> ; 100 °C	88.6 (Y)/6	[25]
		Methanol	3:1–12:1	[HDSSBD][HSO <sub>4</sub> ]/1.0–10.0 mol%	40–80	9:1; 5.0 mol%; 60 °C	95.1 (C)/5	
		Ethanol					94.3 (C)/5	
		<i>n</i> -Butanol					88.7 (C)/5	
		Methanol					84.5 (C)/5	
Palm oil							91.9 (C)/5	[22]
Soybean oil							93.3 (C)/5	
Sunflower oil							89.5 (Y)/6	
Bitter apple oil	2-necked round bottom flask batch reactor, 250/ 300–1000 rpm	Methanol	3:1–21:1	[SBP][HSO <sub>4</sub> ]/5.0–6.0 wt%	120–200	15:1; 5.2 wt%; 170 °C; 800 rpm		
Soybean oil	Round-bottomed flask, 50/magnetic, vigorous stirring	Ethanol	1.2–54.3 (eq.)	[NMP][CH <sub>3</sub> SO <sub>3</sub> ]/10.0 mol%	78	5.4 eq. ethanol; 10.0 mol%; 78 °C	> 96.0 (C)/8	[23]
<i>N sativa</i> seed oil	Round-bottomed flask	Methanol	6:1	ILB2/5.0 mol%	45–75	6:1, 5.0 mol%; 75 °C	65.5 (C)/5	[26]
				ILH2/5.0 mol%	45–75		73.0 (C)/5	
			3:1–12:1	ILH2/1.0–10.0 mol%	45–75	9:1; 7.5 mol%; 60 °C	93.2 (C)/6	
		Ethanol	9:1	ILH2/7.5 mol%	60		93.3 (C)/6	
		<i>n</i> -Butanol	9:1				88.5 (C)/6	
Canola oil		Methanol					97.7 (C)/6	
Safflower oil							96.8 (C)/6	
Sunflower oil							97.0 (C)/6	
Soybean oil							96.2 (C)/6	
Palm oil							85.6 (C)/6	

<sup>a</sup> *n*(Catalyst):*n*(oil).



its synthesis,  $[\text{Hnmp}][\text{HSO}_4]$  could be a very promising catalyst in the future biodiesel production.

### 2.1.2. Acidic ILs in transesterification

Both single- and multi- $\text{SO}_3\text{H}$  functionalized Brønsted acidic ILs have been used as catalysts in biodiesel synthesis [18–20]. Wu et al. [18] tested several Brønsted acidic ILs with a sulfonic group in the methanolysis of cottonseed oil and the most acidic 1-(4-sulfonic acid) butylpyridinium hydrogen sulfate,  $[(\text{CH}_2)_4\text{SO}_3\text{HPy}][\text{HSO}_4]$ , was chosen as the best catalyst. The catalytic activity of this IL is higher than that of concentrated sulfuric acid. Han et al. [19] used the same IL as a catalyst in the methanolysis of waste oil and obtained high biodiesel yield under the optimized conditions. This catalyst is also successful in the biodiesel synthesis from soybean oil [20]. Liang and Yang [11] studied the methanolysis of rapeseed oil, catalyzed by a multi- $\text{SO}_3\text{H}$  functionalized strong Brønsted acidic IL. The catalyst is water and acid resistant, very acidic, polar and cheap. This IL efficiently catalyzes the reaction even though the water content in raw oil is 0.9%.

Several research groups have reported the efficient catalytic activity of ILs based on pyridinium, pyrazolium and pyrrolidonium complexing agents [21–23]. Li et al. [21] reported that 1-(4-sulfonic acid) butylpyridinium trifluoromethanesulfonate,  $[\text{BSPy}][\text{CF}_3\text{SO}_3]$ , showed the best catalytic activity in the transesterification of *Jatropha* oil. The reaction system is biphasic, and the higher acidity of the anion  $[\text{CF}_3\text{SO}_3]^-$  is probably responsible for higher catalytic activity of the IL. Elsheikh [22] examined the methanolysis of bitter apple oil (FFA content of 3.18%) over the selected ILs of pyrazolium type and obtained the highest biodiesel yield with 2-(4-sulfobutyl) pyrazolium hydrogensulfate,  $[\text{SBP}][\text{HSO}_4]$ . Zanin et al. [23] based their research on the soybean oil ethanolysis with *N*-methyl-2-pyrrolidonium methyl sulfonate,  $[\text{NMP}][\text{CH}_3\text{SO}_3]$  as catalyst.

A few imidazolium ILs are also effective catalysts in transesterification reactions [24–26]. Zhou et al. [24] reported an efficient biodiesel synthesis from tung oil catalyzed by 1-(3-sulfonic acid) propyl-3-methylimidazolium hydrogen sulfate,  $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ . Ghiaci et al. [25] noted that 3,3'-(hexane-1,6-diyl) bis(6-sulfo-1-(4-sulfobenzyl)-1*H*-benzimidazolium) hydrogensulfate,  $[\text{HDSSBD}][\text{HSO}_4]$  showed the highest catalytic activity in the transesterification of canola oil. The ester yield decreases with the increase in the length of alkyl chain of the alcohol used. The transesterifications of palm, soybean and sunflower oils with methanol are also successful. The saturation degree of the oil has an inverse effect on the conversion since the oil with a higher saturation degree has smaller chance to approach the active site of the catalyst. Hence, the palm oil with largest saturation degree (46.7%) gives the lowest conversion. This is confirmed for the methanolysis of *Nigella sativa* seed oil catalyzed by 3-butyl-6-sulfo-1-(4-sulfobenzyl)-1*H*-imidazolium hydrogen sulfate (ILB2) and 3-hexadecyl-6-sulfo-1-(4-sulfobenzyl)-1*H*-imidazolium hydrogen sulfate (ILH2) [26].

### 2.1.3. Acidic ILs combined with other catalysts, supported or used as supporting material

Besides being used as a single catalyst in biodiesel syntheses, some researchers reports good catalytic activity when ILs are combined with other catalysts (metal chlorides and bentonite). Some ILs can be used as a support such as  $[\text{BMIM}][\text{PF}_6]$  [27],  $\text{BMI} \cdot \text{InCl}_4$  [28] and  $\text{BMI} \cdot \text{NTf}_2$  [29] or they can be supported onto other materials, like Fe-SBA-15 [30],  $\text{Fe}_3\text{O}_4 \cdot \text{SiO}_2$  [31], sulfhydryl-group-modified  $\text{SiO}_2$  ( $\text{MPS-SiO}_2$ ) [32], or polymers, such as divinylbenzene (DVB) [33,34] or polydivinylbenzene (PDVB) [35]. Uses of acidic ILs combined with other catalysts or used as supporting material are reviewed in Table 3.

Different ILs are utilized as catalyst support in biodiesel synthesis and some of these catalytic systems are recycled with great success

[27–29]. Abreu et al. [27] used  $[\text{Sn}(3\text{-hydroxy-2-methyl-4-pyrone})_2(\text{H}_2\text{O})_2]$  immobilized onto 1-butyl-3-methylimidazolium hexafluorophosphate ( $[\text{BMIM}][\text{PF}_6]$ ) in the soybean oil methanolysis. DaSilveira Neto et al. [28] immobilized the same tin complex on 1-*n*-butyl-3-methylimidazolium tetrachloro-indate ( $\text{BMI} \cdot \text{InCl}_4$ ) to produce the catalyst which was more efficient in the same reaction. The same system was also successful in the soybean oil transesterification with different alcohols. Lapis et al. [29] performed the immobilization of  $\text{K}_2\text{CO}_3$  and  $\text{H}_2\text{SO}_4$  on 1-*n*-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide,  $\text{BMI} \cdot \text{NTf}_2$ , for the soybean oil conversion into ethyl esters. This IL is an ideal medium for increasing the ester yield, stabilizing the inorganic acid and removing glycerol. After 1.5 h at 70 °C under the basic conditions the ester yield was 97.0%. Under the acidic conditions at 70 °C, the ester yield was 95.0% within 24 h. With both IL-supported catalysts under the same reaction conditions, high ester yield are reported with different alcohols (methanol, *n*-butanol, isoamyl alcohol and *n*-decanol) but within longer reaction time.

Some researchers add different metal chlorides to the IL since metal ions in IL can supply Lewis acidic sites during the reaction [36,37]. Liang et al. [36] observed that chloroaluminate-based ionic liquids derived from triethylammonium chloride,  $[\text{Et}_3\text{NH}][\text{Cl-AlCl}_3]$  ( $x(\text{AlCl}_3)=0.7$ ), gave a high ester yield in the methanolysis of soybean oil. The advantages of this method are low catalyst price, high yield and low possibility of the saponification. Guo et al. [37] combined 1-butyl-3-methylimidazolium tosylate,  $[\text{BMIM}][\text{TS}]$ , with metal chlorides for the biodiesel synthesis from oleic acid (acid value 186.0 mg KOH/g) or *Jatropha* oil (acid value 13.8 mg KOH/g). In the oleic acid esterification,  $[\text{BMIM}][\text{TS}]$  provided the conversion degree of 93.0% in 5 h. Among the metal chlorides,  $\text{FeCl}_3$ ,  $\text{CuCl}_2$  and  $\text{AlCl}_3$  show the highest catalytic activity in combination with the IL. On the other hand, when *Jatropha* oil was used, the ester yield of only 63.7% was achieved with the IL alone, even at the enhanced reaction temperature of 200 °C. When different transition metal chlorides were added to the IL ( $\text{MnCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{CoCl}_2$  or  $\text{ZnCl}_2$ ), higher catalytic activities were observed (yields over 80.0%) than that achieved with the combination of  $\text{AlCl}_3$  and the IL (64.0%). Catalytic activity order of metal chlorides is as follows:  $\text{Zn}^{2+} > \text{Mn}^{2+} > \text{Fe}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+}$ . The highest biodiesel yield of 92.5% was achieved with  $[\text{BMIM}][\text{TS}]\text{-ZnCl}_2$  used at 180 °C. When the reaction temperature was raised to 220 °C,  $[\text{BMIM}][\text{TS}]\text{-ZnCl}_2$  and  $[\text{BMIM}][\text{TS}]\text{-FeCl}_3$  were less active, providing lower biodiesel yields (below 75.0%). Decreased catalytic activity of transition metal salts in transesterification is explained by the reaction of transition metal ions with  $\text{H}_2\text{O}$  generated in the esterification reaction at higher temperature (200–220 °C). For the same reason,  $[\text{BMIM}][\text{TS}]\text{-AlCl}_3$  gives the highest conversion degree in esterification at 80 °C (91.0%), but it is less active in transesterification (ester yield of 64.0% at 200 °C).

Modified bentonite seems to be a promising catalyst for the esterification of oleic acid and alcohols [38,39]. Ghiaci et al. [38] used bentonite modified with 3,3'-(butane-1,6-diyl)bis(6-sulfo-1-(4-sulfobenzyl)-1*H*-benzimidazolium) hydrogensulfate (MB3B) to catalyze the esterification of oleic acid with different alcohols. The ester yield decreases with the increase in alkyl chain of the alcohol. Since the alcohols with longer alkyl chains are less nucleophilic, they are less successful in attacking the activated carbonyl group of the fatty acid on the surface of catalyst. The catalytic activity of MB3B is also tested in the esterification of other fatty acids. Under the optimized reaction conditions, the yield of alkyl esters decreases with increasing the alkyl chain of the fatty acid. This can be a result of increased steric hindrance near the acid sites on the catalyst surface. In addition, the presence of a double bond in the fatty acid results in higher yield, probably because the stronger electronic interaction between the double bond and the aromatic ring of the IL on the surface of the catalyst speeds up the

**Table 3**

Application of acidic ionic liquids combined with other catalysts, supported or used as supporting material.

Feedstock	Type, volume of reactor, cm <sup>3</sup> /type of agitator, agitation speed, rpm	Alcohol	Alcohol:oil molar ratio or wt% (to oil)	Catalyst/loading, wt% (to oil) or mL/g oil or <i>n</i> (catalyst): <i>n</i> (oil) or mol% (to oil) or mmol catalyst/g feedstock	Temperature, °C	Optimal reaction conditions	Conversion (C) or yield (Y), %/Time, h	Reference
Soybean oil	Batch reactor, 50/magnetic	Methanol	15.0 wt%	[BMIM][PF <sub>6</sub> ] and Sn(3-hydroxy-2-methyl-4-pyrone) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> /0.2 mL/g oil	60	15.0 wt%; 0.2 mL catalyst/g oil; 60 °C	55.0 (Y)/1	[27]
Soybean oil	Batch reactor, 50/magnetic	Methanol	30.0 wt%	[BMIM][InCl <sub>4</sub> ]/0.3 mL/g oil and Sn(3-hydroxy-2-methyl-4-pyrone) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> /1.0 wt%	80	30.0 wt%; 0.3 mL IL/g oil; 1.0 wt% Sn (3-hydroxy-2-methyl-4-pyrone) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ; 80 °C	83.0 (Y)/4	[28]
Soybean oil	Round-bottomed flask, 50	Ethanol	7.5:1	[BMIM][NTf <sub>2</sub> ]/1 mL/g oil and K <sub>2</sub> CO <sub>3</sub> /0.63 wt%	70	7.5:1; 1 mL IL/g oil; 0.63 wt% K <sub>2</sub> CO <sub>3</sub> ; 70 °C	97.0 (Y)/1.5	[29]
			21.25:1	[BMIM][NTf <sub>2</sub> ]/1 mL/g oil and H <sub>2</sub> SO <sub>4</sub> /0.178 mL/g oil		21.25:1; 1 mL IL/g oil; 0.178 mL H <sub>2</sub> SO <sub>4</sub> /g oil; 70 °C	95.0 (Y)/24	
Soybean oil	Round bottomed flask/magnetic	Methanol	6:1–24:1	[Et <sub>3</sub> NH]Cl-AlCl <sub>3</sub> (x(AlCl <sub>3</sub> )=0.7)/0.01:1–0.09:1 <sup>a</sup>	70	12:1; 0.05:1 <sup>a</sup> ; 70 °C	98.5 (Y)/9	[36]
Oleic acid	Flask	Methanol	1:1–5:1	[BMIm][TS]/0.071–0.355 mmol/g acid	80–140	2:1; 0.213 mmol IL/g acid; 140 °C	93.0 (C)/5	[37]
			2:1	[BMIm][TS]-FeCl <sub>3</sub> /3 mmol IL ([x(FeCl <sub>3</sub> )=0.7]), 4.2 mol% (based on oleic acid) FeCl <sub>3</sub>	80	2:1; 0.071 mmol IL/g acid; 4.2 mol% FeCl <sub>3</sub> ; 80 °C	90.0 (C)/5	
				[BMIm][TS]-AlCl <sub>3</sub> /3 mmol IL ([x(AlCl <sub>3</sub> )=0.7]), 4.2 mol% (based on oleic acid) AlCl <sub>3</sub>		2:1; 0.071 mmol IL/g acid; 4.2 mol% AlCl <sub>3</sub> ; 80 °C	91.0 (C)/5	
				[BMIm][TS]-MnCl <sub>2</sub> /3 mmol IL ([x(MnCl <sub>2</sub> )=0.7]), 4.2 mol% (based on oleic acid) MnCl <sub>2</sub>		2:1; 0.071 mmol IL/g acid; 4.2 mol% MnCl <sub>2</sub> ; 80 °C	45.0 (C)/5	
				[BMIm][TS]-ZnCl <sub>2</sub> /3 mmol IL ([x(ZnCl <sub>2</sub> )=0.7]), 4.2 mol% (based on oleic acid) ZnCl <sub>2</sub>		2:1; 0.071 mmol IL/g acid; 4.2 mol% ZnCl <sub>2</sub> ; 80 °C	46.0 (C)/5	
Un-pretreated Jatropa oil	High-pressure autoclave, 350		2:1–12:1	[BMIm][TS]/0.2 mmol IL/g oil	80–220	12:1; 0.2 mmol IL/g oil; 200 °C, initial N <sub>2</sub> pressure 2.8 MPa, reaction pressure 4.8 MPa	63.7 (Y)/5	
				[BMIm][TS]-FeCl <sub>3</sub> /0.2 mmol IL/g oil, [x(FeCl <sub>3</sub> )=0.7]			85.0 (Y)/5	
				[BMIm][TS]-AlCl <sub>3</sub> /0.2 mmol IL/g oil, [x(AlCl <sub>3</sub> )=0.7]			64.0 (Y)/5	
				[BMIm][TS]-MnCl <sub>2</sub> /0.2 mmol IL/g oil, [x(MnCl <sub>2</sub> )=0.7]			87.0 (Y)/5	
				[BMIm][TS]-ZnCl <sub>2</sub> /0.2 mmol IL/g oil, [x(ZnCl <sub>2</sub> )=0.7]			88.0 (Y)/5	
						12:1; 0.2 mmol IL/g oil; 180 °C; initial/reaction pressure 2.8/4.8 MPa	92.5 (Y)/5	
Oleic acid	Round-bottomed flask, 50/vigorous	Methanol	1:1–4:1	MB3B <sup>b</sup> /1.0–12.5 wt%	60–80	2:1; 10.0 wt%; 70 °C	92.8 (Y)/6	[38]
		Ethanol	2:1	MB3B <sup>b</sup> /10.0 wt%	70		90.0 (Y)/6	
		<i>n</i> -Butanol					80.9 (Y)/6	
Lauric acid		Methanol					98.3 (Y)/6	
Palmitic acid							90.6 (Y)/6	
Stearic acid							85.5 (Y)/6	
Oleic acid	Round-bottom flask, 50/Magnetic hot plate stirrer, vigorous stirring	Ethanol	1:1–4:1	MBIL8B <sup>c</sup> /1.0–15.0 wt%	40–80	2:1; 12.5 wt%; 60 °C	93.1 (Y)/6.5	[39]
		Methanol	2:1	MBIL8B <sup>c</sup> /12.5 wt%	60		94.8 (Y)/6.5	
		<i>n</i> -Butanol					82.9 (Y)/6.5	
		Ethanol					97.3 (Y)/6.5	
Lauric acid							92.4 (Y)/6.5	
Palmitic acid							85.6 (Y)/6.5	
Stearic acid							87.7 ± 0.6 (C)/3	
Oleic acid	Round-bottom flask, 50/magnetic	Methanol	1:1–10:1	[SO <sub>3</sub> H-Plm-CPMS][HSO <sub>4</sub> •Fe-SBA-15]/0.5–10 wt %	60–110	6:1; 5.0 wt%; 90 °C		[30]
			6:1	[SO <sub>3</sub> H-Plm-CPMS][HSO <sub>4</sub> •SBA-15]/5.0 wt%	90		81.4 ± 0.4 (C)/3	
		Ethanol		[SO <sub>3</sub> H-Plm-CPMS][HSO <sub>4</sub> •Fe-SBA-15]/5.0 wt%			93.3 (C)/3	
		<i>n</i> -Propanol		[SO <sub>3</sub> H-Plm-CPMS][HSO <sub>4</sub> •Fe-SBA-15]/5.0 wt%			91.5 (C)/3	
		<i>n</i> -Butanol		[SO <sub>3</sub> H-Plm-CPMS][HSO <sub>4</sub> •Fe-SBA-15]/5.0 wt%			92.6 (C)/3	

Table 3 (continued)

Feedstock	Type, volume of reactor, cm <sup>3</sup> /type of agitator, agitation speed, rpm	Alcohol	Alcohol:oil molar ratio or wt% (to oil)	Catalyst/loading, wt% (to oil) or mL/g oil or $n(\text{catalyst}):n(\text{oil})$ or mol% (to oil) or mmol catalyst/g feedstock	Temperature, °C	Optimal reaction conditions	Conversion (C) or yield (Y), %/Time, h	Reference
Oleic acid		Ethanol	6:1	[SO <sub>3</sub> H-(CH <sub>2</sub> ) <sub>3</sub> -HIM][HSO <sub>4</sub> ]/10.8 wt%	110	6:1; 10.8 wt%; 110 °C	95.6 ± 0.3 (Y)/4	[31]
		Methanol	6:1	[SO <sub>3</sub> H-(CH <sub>2</sub> ) <sub>3</sub> -HIM][HSO <sub>4</sub> ] modified Fe <sub>3</sub> O <sub>4</sub> · SiO <sub>2</sub> /10.8 wt%	110		84.5 ± 0.4 (Y)/4	
		Ethanol	1:1–10:1	[SO <sub>3</sub> H-(CH <sub>2</sub> ) <sub>3</sub> -HIM][HSO <sub>4</sub> ] modified Fe <sub>3</sub> O <sub>4</sub> · SiO <sub>2</sub> /1.8–17.9 wt%	60–140		92.9 ± 0.4 (Y)/4	
		<i>n</i> -Butanol	6:1	[SO <sub>3</sub> H-(CH <sub>2</sub> ) <sub>3</sub> -HIM][HSO <sub>4</sub> ] modified Fe <sub>3</sub> O <sub>4</sub> · SiO <sub>2</sub> /10.8 wt%	110		91.0 ± 0.4 (Y)/4	
Soybean oil		Ethanol	12:1	[SO <sub>3</sub> H-(CH <sub>2</sub> ) <sub>3</sub> -HIM][HSO <sub>4</sub> ] modified Fe <sub>3</sub> O <sub>4</sub> · SiO <sub>2</sub> /0.6 g	160	12:1; 0.6 g; 160 °C	90.1 ± 0.2 (Y)/6	
3-Phenyl-propionic acid	Round-bottom flask/magnetic	Ethanol/1 ml		IL · silica (40 wt% [BnMIm][HSO <sub>4</sub> ]/silica gel)/10.0 mol%	25	1 ml ethanol; 10 mol%; 25 °C	48.0 (Y)/12	[32]
Palmitic acid				IL · silica	70	1 ml ethanol; 10 mol%; 70 °C	92.0 (Y)/12	
Stearic acid				[BnMIm][HSO <sub>4</sub> ]/20 mg		1 ml ethanol; 20 mg IL; 70 °C	62.0 (Y)/12	
Lauric acid				IL · silica		1 ml ethanol; 10 mol%; 70 °C	87.0 (Y)/12	
		Ethanol/1.5 ml				1.5 ml ethanol; 10 mol%; 70 °C	86.0 (Y)/12	
Brown grease	Three-necked round flask/magnetic stirrer, strong	Methanol	9:1	OMR-[C <sub>4</sub> HMTA][SO <sub>4</sub> H]/1.0–5.0 wt%	65	I step: 9:1; 1.0 wt% IL; 65 °C I step: 9:1; 5.0 wt% IL; 65 °C	86.0 (C)/1.5 99.5 (C)/1.5	[41]
Esterified grease				KOH/1.67 wt%		II step: 1.67 wt% KOH; 65 °C	~100.0 (C)/1	
Brown grease			40:1	OMR-[C <sub>4</sub> HMTA][SO <sub>4</sub> H]/5.0 wt%		40:1; 5.0 wt% IL; 65 °C	65.0 (C)/1	
Waste cooking oil	Round-bottom flask	Methanol	15:1	PIL <sup>d</sup> /1.0 wt%	70	15:1; 1.0 wt%; 70 °C	> 99.0 (Y)/12	
Waste oil		Methanol	16:1	PIL <sup>e</sup> /0.2–1.8 wt%	70	16:1; 1.0 wt%; 70 °C	99.0 (Y)/12	[42]
Waste oil		Methanol	15:1	PIL <sup>f</sup> /0.2–1.8 wt%	30–140	15:1; 1.0 wt%; 70 °C	98.2 (C)/10	[35]
Oleic acid	Round-bottom flask	Methanol	0.34 wt% (to oleic acid)	PIL <sup>g</sup> /1.0 wt%	70	0.34 wt% methanol; 1 wt%; 70 °C	99.0 (Y)/10	[34]
Rapeseed oil			0.442 wt% (to oil)	PIL <sup>g</sup> /1.0 wt%		0.442 wt% methanol; 1 wt%; 70 °C	> 99.4 (Y)/12	
Waste cooking oil			0.232–0.698 wt% (to oil)	PIL <sup>g</sup> /1.0 wt%		0.582 wt% methanol (15:1); 1 wt%; 70 °C	99.1 (Y)/12	

<sup>a</sup>  $n(\text{Catalyst}):n(\text{oil})$ .<sup>b</sup> Bentonite modified with 3,3'-(butane-1,6-diyl)bis(6-sulfo-1-(4-sulfobenzyl)-1*H*-benzimidazolium) hydrogensulfate.<sup>c</sup> Modified bentonite with 3,3'-(octane-1,8-diyl)bis(4-sulfobenzyl-1*H*-imidazol-3-ium) hydrogensulfate.<sup>d</sup> Solid acidic ionic liquid polymer made by copolymerization of [SO<sub>3</sub>H(CH<sub>2</sub>)<sub>3</sub>VPy][HSO<sub>4</sub>] oligomers and DVB.<sup>e</sup> Solid acidic ionic liquid polymer made by copolymerization of [SO<sub>3</sub>H(CH<sub>2</sub>)<sub>3</sub>VIm][HSO<sub>4</sub>] oligomers and DVB.<sup>f</sup> Acidic ionic liquid polymer made by copolymerization of [SO<sub>3</sub>H(CH<sub>2</sub>)<sub>3</sub>VIm][HSO<sub>4</sub>] with PDVB.<sup>g</sup> Obtained by copolymerization of 1-(3-sulfopropyl)triethylammonium hydrogen sulfate oligomers with DVB.



mass transfer to the acid sites. The same conclusion was reported by Aghabarari and Dorostkar [39], who chose bentonite modified with highly acidic 3,3'-(octane-1,8-diyl)bis(4-sulfobenzyl-1H-imidazol-3-ium) (MBIL8B) as catalyst for the esterification of oleic acid with ethanol.

Modified mesoporous silica materials like iron- and magnetite-silica have recently been studied in order to develop green processes for biodiesel production [30,31]. Zhang et al. [30] immobilized 1-(propyl-3-sulfonate)-3-(3-trimethoxysilylpropyl) imidazolium hydrogen sulfate,  $[\text{SO}_3\text{H-PIm-CPMS}][\text{HSO}_4]$ , onto the surface of Fe-SBA-15 (SBA: Santa Barbara Amorphous) by chemical covalent bond, which made the active component strongly attached to the support. The high surface area and ordered pore improves the contact between the active component and the reactants. In the oleic acid esterification, the conversion over IL/Fe-SBA-15 is better than that of IL/SBA-15 under the same optimum reaction conditions. The cooperation of Lewis acid brought by Fe and Brønsted acid from the IL is responsible for the best catalytic activity of IL/Fe-SBA-15. The conversion is also high with other short-chain alcohols. Wu et al. [31] immobilized dual acidic 1-(propyl-3-sulfonate) imidazolium hydrogen sulfate,  $[\text{SO}_3\text{H}-(\text{CH}_2)_3\text{-HIM}][\text{HSO}_4]$ , onto the surface of  $\text{Fe}_3\text{O}_4 \cdot \text{SiO}_2$ . With this system, both esterification of oleic acid with short-chain alcohols and transesterification of soybean oil are successfully carried out.

ILs are frequently loaded on silica materials that can be modified by organic compounds [32–40]. Zhen et al. [32] immobilized 1-allyl-3-(butyl-4-sulfonyl) imidazoliumtrifluoromethane sulfonate,  $[\text{BsAIM}][\text{OTf}]$ , on sulfhydryl-group-modified  $\text{SiO}_2$ , MPS- $\text{SiO}_2$ , via free radical addition reaction. The increase of  $[\text{BsAIM}][\text{OTf}]$  loading on  $\text{SiO}_2$  leads to the decrease of the specific surface area and pore volume of  $[\text{BsAIM}][\text{OTf}]/\text{SiO}_2$ . This acidic IL-functionalized silica system catalyzes both esterification of oleic acid and transesterification of glycerol trioleate. With increasing  $[\text{BsAIM}][\text{OTf}]$  loading, the oleic acid conversion raises and the highest conversion degree is obtained with the  $[\text{BsAIM}][\text{OTf}]$  loading of 0.13 mmol/g, i.e. using  $[\text{BsAIM}][\text{OTf}]/\text{SiO}_2 \cdot 3$ . However, the opposite effect results in the glycerol trioleate conversion. In the esterification of oleic acid, the number of activity sites in the porous solid catalyst is very important, while in the transesterification of glycerol trioleate, the narrow pore diameter has the impact on the mass transfer. Vafaezadeh and Mahmoodi Hashemi [40] dispersed  $[\text{BnMIM}][\text{HSO}_4]$  onto the high surface area silica gel via physisorbed confinement, thus producing the 40.0 wt%  $[\text{BnMIM}][\text{HSO}_4]/\text{silica}$  gel. This system is very promising in the esterification of 3-phenylpropionic acid with ethanol. The supported IL has stronger acidity than the non-supported IL. The hydrophobic nature of the IL also contributes to better catalytic activity by removing water, thus shifting the reaction equilibrium to ester production. The esterification of palmitic, stearic acid and lauric acid with ethanol are also successfully catalyzed. In addition, this catalytic system shows great water-tolerance.

Noshadi et al. [41] managed to convert almost 100.0% of raw brown grease oil into methyl esters. The treatment of hexamethylenetetramine (HMTA) with an ordered mesoporous resin (OMR) resulted in forming OMR-[HMTA], which was treated with 1,4-butanedisulfone, providing an ordered mesoporous ionic liquid (OMR-IL). The OMR-IL was lastly treated with  $\text{H}_2\text{SO}_4$ , thus giving a high activity solid acid catalyst OMR hexamethylenetetraminium hydrogen sulfate,  $\text{OMR}[\text{-C}_4\text{HMTA}][\text{SO}_4\text{H}]$ . This catalyst is also used in the two step esterification–transesterifications of brown grease oil (containing 90.0 wt% FFAs) with KOH in the second step and one step esterification–transesterification of brown grease oil (without KOH). In the former case, the conversion of 99.5% is achieved in the esterification step in 1.5 h, while it is almost complete in 1 h of transesterification of the pre-treated brown grease oil. In the latter process, the 75.0% conversion of TAG is

achieved in 5 h. Large BET surface area, strong acidity and stable and adjustable hydrophobic polymeric network of catalyst are responsible for its high catalytic activity.

Solid acidic IL polymers (PILs) are synthesized by Liang and coworkers [33–35,42] through the copolymerization of acidic IL oligomers of 1-(3-sulfopropyl)-4-vinylpyridinium hydrogen sulfate,  $[\text{SO}_3\text{H}(\text{CH}_2)_3\text{VPy}][\text{HSO}_4]$ , 1-(3-sulfopropyl)-3-vinylimidazolium hydrogen sulfate,  $[\text{SO}_3\text{H}(\text{CH}_2)_3\text{VIm}][\text{HSO}_4]$  or 1-(3-sulfopropyl) triethylammonium hydrogen sulfate with DVB or PDVB. These PILs are successful catalysts in the biodiesel production from a waste oil (acidity 45 mg KOH/g). The total ester yield achieved by simultaneous transesterification of TAGs and esterification of FFAs in the presence of the PIL obtained from  $[\text{SO}_3\text{H}(\text{CH}_2)_3\text{VPy}][\text{HSO}_4]$  or  $[\text{SO}_3\text{H}(\text{CH}_2)_3\text{VIm}][\text{HSO}_4]$  and DVB was over 99.0% within 12 h [33,42]. In the presence of another PIL synthesized from  $[\text{SO}_3\text{H}(\text{CH}_2)_3\text{VIm}][\text{HSO}_4]$  as monomer and immobilized on PDVB in the weight ratio of 1:1, the ester yield was 99.0% in shorter time (10 h) [35]. Also, the PIL obtained from 1-(3-sulfopropyl) triethylammonium hydrogen sulfate,  $[\text{SO}_3\text{H}(\text{CH}_2)_3\text{TEA}][\text{HSO}_4]$ , and DVB catalyze the esterification of pure oleic acid and the transesterification of refined rapeseed and waste cooking oils with the ester yield higher than 99.0% in 6 h, 8 h and 12 h, respectively [34]. All these catalysts possess high hydrophobic surface, which raises the efficiency of mass transfer and prevents the acid sites releasing. High acidity, stability and activity of PILs and high quality methyl esters produced under mild reaction conditions are the reasons why these catalysts might be very perspective in the future.

#### 2.1.4. Acidic ILs in two-step processes: esterification followed by transesterification

Acidic ILs are also used in two-step processes that include the IL-catalyzed esterification of oily feedstock, followed by alkaline-catalyzed transesterification of the pre-treated oily feedstock. A review on these processes is given in Table 4. Commonly, KOH is used as a catalyst in the second step. These processes are widely used in the treatment of oily feedstocks having high FFA content, and the produced alkyl esters are of high quality.

Many acidic ILs can be used to catalyze esterification of oils with large amount of FFAs [43–48].  $[\text{BMIM}][\text{HSO}_4]$ , 1-butylimidazolium hydrogensulfate ( $[\text{BIM}][\text{HSO}_4]$ ), and 1-methylimidazolium hydrogensulfate ( $[\text{MIM}][\text{HSO}_4]$ ) catalyze the esterification of crude palm oil (FFA content 3.49 wt%) [43]. By applying triethylammonium hydrogensulfate,  $[\text{Et}_3\text{N}][\text{HSO}_4]$ , in the same process, the acid value of oil is reduced from 6.98 to 1.24 mg KOH/g [44]. 1-Methyl-3-(4-sulfobutyl)-imidazolium hydrogensulfate ( $[\text{MSBIM}][\text{HSO}_4]$ ) is the best catalyst for esterification of crude *Citrus colocythis* oil (FFA content of 3.18%) [45]. Elsheikh and Akhtar [46] esterified the same oil over 1,3-disulfonic acid imidazolium hydrogen sulfate ( $[\text{DSIM}][\text{HSO}_4]$ ) or 3-methyl-1-sulfonic acid imidazolium hydrogen sulfate ( $[\text{MSIM}][\text{HSO}_4]$ ). Two sulfonic chains existing in  $[\text{DSIM}][\text{HSO}_4]$  increases its acidity, resulting in a higher catalytic efficiency. Later, Elsheikh et al. [47] reported 1-butyl-3-(propyl-3-sulfonate)-imidazolium (BPSIM) as a better catalyst than 1-butyl-3-(3-sulfopropyl)-imidazolium hydrogensulfate ( $[\text{BSPIM}][\text{HSO}_4]$ ). Das et al. [48] tested the catalytic efficiency of 1-(1-butylsulfonic)-3-methylimidazolium chloride ( $[\text{BSMIM}][\text{Cl}]$ ) in the esterification of *Jatropha curcas* oil (FFA content 8.15 wt%) with methanol. With this IL, the FFA content in the oil decreased to 0.49 wt%. The second alkali catalyzed step results in a high ester yield [43,44].

#### 2.2. Basic ILs in transesterification

Basic ILs are also used in biodiesel production, but not as frequently as acidic ILs. Mainly imidazolium-based ILs, such as imidazolium hydroxides [49,50] and imidazolidine [51], choline-based ILs such as choline hydroxide, choline methoxide and choline

**Table 4**

Application of acidic ionic liquids as catalysts in the esterification of oil, followed by alkaline-catalyzed transesterification.

Feedstock (oil)	Type, volume of reactor, cm <sup>3</sup> /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
Crude palm (3.49 wt% FFA)	Two necked round bottom flask, 250/magnetic, 600	Methanol	3:1–21:1	[BMIM][HSO <sub>4</sub> ]/4.0–6.0 wt%	130–170	I step: 12:1; 4.4 wt% IL; 160 °C; 600 rpm	91.2 (C)/2	<a href="#">[43]</a>
Esterified oil (0.3 wt% FFA)			6:1	KOH/1.0 wt%	60	II step: 6:1; 1.0 wt% KOH; 60 °C	98.4 (Y)/1	
Crude palm (3.49 wt% FFA)	Two necked round bottom flask, 250/magnetic, 600	Methanol	3:1–18:1	[Et <sub>3</sub> N][HSO <sub>4</sub> ]/4.6–5.4 wt%	120–180	I step: 15:1; 5.2 wt% IL, 170 °C	82.1 (C)/3.5	<a href="#">[44]</a>
Esterified oil (0.44 wt% FFA)			6:1	KOH/1.0 wt%	60	II step: 6:1; 1.0 wt% KOH; 60 °C	97.3 (Y)/1	
Crude palm (6.98 mg KOH/g oil)	Two-necked round bottomed flask, 250/magnetic stirrer, 600	Methanol	3:1, 6:1–21:1	[BSPIM][HSO <sub>4</sub> ]/3.0–4.4 wt%	110–180	I step: 12:1; 4.0 wt% IL; 150 °C	95.7 (C)/2	<a href="#">[47]</a>
Esterified oil (FFA 0.12 wt)			6:1	KOH/1.0 wt%	60	II step: 6:1; 1.0 wt% KOH; 60 °C	97.8 (Y)/0.83	
<i>C. colocynthis</i> (6.36 mg KOH/g)	Two necked flask, 250/magnetic, 600	Methanol	3:1–21:1	[MSBIM][HSO <sub>4</sub> ]/3.0–4.8 wt%	100–180	I step: 12:1; 3.8 wt% IL; 130 °C	96.7 (C)/2	<a href="#">[45]</a>
Esterified oil (0.23 wt% FFA)			6:1	KOH/1.0 wt%	60	II step: 6:1; 1.0 wt% KOH; 60 °C	98.8 (Y)/0.83	
<i>C. colocynthis</i> (FFA content 3.18 wt)	Three-necked flask/600	Methanol	3:1–21:1	[MSIM][HSO <sub>4</sub> ]/3.0–5.0 wt%	100–170	I step: 12:1; 4.0 wt% IL; 150 °C	90.8 (C)/3	<a href="#">[46]</a>
Esterified oil (0.29 ± 0.021 mg KOH/g oil)			6:1	[DSIM][HSO <sub>4</sub> ]/3.0–5.0 wt%	60	I step: 12:1; 3.6 wt% IL; 150 °C	95.4 (C)/1.75	
				KOH/1.0 wt%		II step: 6:1; 1.0 wt% KOH; 60 °C	98.2 (Y)/0.83	
<i>J. curcas</i> (8.15 wt% FFA)	Three-neck round-bottom flask/magnetic, vigorous	Methanol	3:1–18:1	[BSMIM][Cl]/2.5–17.5 wt%	30–90	I step: 12:1, 10.0 wt% IL, 70 °C	93.9 (C)/6	<a href="#">[48]</a>
Esterified oil (0.49 wt% FFA)			6:1	KOH/1.3 wt%	64	II step: 6:1, 1.3 wt% KOH, 64 °C	98.6 (Y)/0.33	

imidazolium [52] are used. Similarly to common basic catalysts, basic ILs require the oily feedstock with low FFA content to avoid the soap formation, although some can be used with feedstocks having a relatively high FFA content. The more basic groups in the IL, the better catalytic activity. Table 5 presents a review on the use of basic ILs in transesterification reactions.

Liang et al. [49] synthesized five basic imidazolium-based ILs and tested their catalytic activity in the methanolysis of cottonseed oil. The catalytic activity of ILs decreases with the increase of the number of carbon atoms in alkyl-chain connected with the cation. Among the tested ILs, bis-(3-methyl-1-imidazolium-)-ethylene dihydroxide (IMC<sub>2</sub>OH) is the most efficient. Several imidazolium hydroxides are also used by Zhou et al. [50] as catalysts in the methanolysis of glycerol trioleate. The highest ester yield is obtained with 1-butyl-3-methylimidazolium hydroxide, [BMIM][OH] as catalyst under the optimized reaction conditions. For methanolysis of different vegetable oils (rapeseed, soybean and sunflower), Luo et al. [51] noted 1-butyl-3-methylimidazolium imidazolate, [BMIM][Im], as an efficient catalyst. Fan et al. [52] explored the methanolysis of soybean oil with choline hydroxide (ChOH), choline methoxide (ChOMe) and choline imidazolium (ChIm), and their catalytic activities were in order ChOH > ChOMe > ChIm. Also, Reddy et al. [53] reported that ChOH was very efficient in methanolysis of not-treated *Jatropha* oil (acid value 17 mg KOH/g). The quality of the product allows it to be instantly used as fuel in existing diesel engines without any modification.

### 3. ILs as cosolvents in biocatalyzed transesterification

Some problems related to the use of lipases in biodiesel production can be overcome by using ILs as cosolvents since IL/biocatalyst systems result in higher selectivity, increased reaction rate and greater enzyme stability [54]. The hydrophobic ILs protect the lipase from the methanol-induced deactivation when included in its matrix. The same effect of amphiphilic ILs is caused by their amphiphile that enables the efficient interactions of immiscible substrates. The use of ILs as cosolvents in biocatalyzed transesterification processes is reviewed in Table 6. In most studies on enzyme-catalyzed transesterification, Novozym 435 lipase is chosen as catalyst. In biocatalyzed reactions, hydrophobic ILs with 1-butyl-3-methylimidazolium, [BMIM]<sup>+</sup>, [55–63] or 1-ethyl-3-methylimidazolium, [EMIM]<sup>+</sup>, [55,61,63,64] as cations and hexafluorophosphate, [PF<sub>6</sub>]<sup>−</sup>, [55–61,63,65], triflimide, [NTf<sub>2</sub>]<sup>−</sup>, [61,62,65–68] or tetrafluoroborate, [BF<sub>4</sub>]<sup>−</sup>, [55,63] as anions are most frequently used. Also, amphiphilic based ILs like Ammoeng 102 and 120 can be used such as in the methanolysis of rapeseed oil with Novozym 435 [69].

Hydrophobic [BMIM][PF<sub>6</sub>] is efficient with the lipases of various origin like Novozym 435 with sunflower oil [55] or triolein and waste canola oil [56,57], *Penicillium expansum* lipase (PEL) with corn oil [58,59] or *Rhizopus chinensis* and *Aspergillus niger* lipases with *Milletia pinnata* seed oil [61] and *Pseudomonas cepacia* lipase with soybean oil [62], etc. The ester yield with Novozym-435 is influenced by the type of feedstock and agitation intensity in the reactor [56,57]. A better ester yield is obtained in a flask type reactor than in a poorly stirred conical reactor; also, a higher ester yield is achieved from triolein than from waste canola oil. This IL in combination with PEL is more efficient than *tert*-butanol or *n*-hexane [58,61]. However, Novozym 435 combined with the same IL gives a much lower conversion of *M. pinnata*, compared to the enzyme/*tert*-butanol system [61]. Lipases originated from *R. chinensis* and *A. niger* are also tested in combination with [BMIM][PF<sub>6</sub>]. While the former gives a higher conversion (96.6% conversion) than PEL (93.9%), *A. niger* performs worse (61.9%). In addition, a test of nine ILs with different chain lengths attached to the cationic imidazolium ring and [TfO]<sup>−</sup> or [Tf<sub>2</sub>N]<sup>−</sup> as cosolvents in the PEL-catalyzed methanolysis of *M. pinnata* seed oil shows that the ester yield decreases with increasing the alkyl chain length of the cation in the IL. Moreover, when [Tf<sub>2</sub>N]<sup>−</sup> is the anion, yields are higher. The ester yield with PEL is somewhat higher than that with Novozym 435 in the methanolysis of *Chlorella pyrenoidosa* oil [60]. However, hydrophilic 3-methylimidazolium tetrafluoroborate, [HMIM][BF<sub>4</sub>], and 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF<sub>4</sub>] are not efficient because of the lipase deactivation by methanol [55].

Imidazolium ILs with different alkyl chain lengths (C<sub>10</sub> to C<sub>18</sub>) and different anions ([Tf<sub>2</sub>N]<sup>−</sup>, [PF<sub>6</sub>]<sup>−</sup> or [BF<sub>4</sub>]<sup>−</sup>), such as 1-hexadecyl-3-methylimidazolium triflimide, [C<sub>16</sub>MIM][NTf<sub>2</sub>], and 1-methyl-3-octadecylimidazolium, [C<sub>18</sub>MIM][NTf<sub>2</sub>], are very efficient as cosolvents in the Novozym 435- and *Pseudomonas fluorescens* lipase-catalyzed synthesis of biodiesel from triolein/methanol mixtures [66–68]. Catalytic efficiency of the lipases increases with increasing the alkyl chain length of IL, thus [C<sub>16</sub>MIM][NTf<sub>2</sub>] showing the highest activity. When different alcohols (methanol, ethanol, *n*-propanol and *n*-butanol) are used, the lipase activity decreases with increasing the alkyl chain length of the alcohol. The Novozym 435-catalyzed methanolysis of different vegetable (sunflower, olive and palm oil) and waste cooking oils in the presence of [C<sub>16</sub>MIM][Tf<sub>2</sub>N] gives high ester yields [68]. Among 1-butyl-3-methylimidazolium triflimide ([BMIM][NTf<sub>2</sub>]), [BMIM][BF<sub>4</sub>], and [BMIM][PF<sub>6</sub>], the first IL is the most active in the *P. cepacia* lipase-catalyzed production of biodiesel from soybean oil, ensuring the highest conversion degree of 96.3% at room temperature. The high conversion degree is partially achieved because of the glycerol extraction by the IL/alcohol mixture, which

**Table 5**  
Application of basic ionic liquids as catalysts in transesterification.

Feedstock	Type, volume of reactor, cm <sup>3</sup> / type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst/load- ing, 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	IMC <sub>2</sub> OH/0.10– 1.25 wt%	35–65	12:1; 0.4 wt%; 55 °C	98.5 (Y)/4	[49]
Glycerol trioleate		Methanol	3:1–9:1	[BMIM][OH]	Room – 120	9:1; 120 °C	87.2 (Y)/8	[50]
Rapeseed oil	Three-necked flask, 500/ mechanical	Methanol	3:1–8:1	[BMIM][Im]/ 1.0–10.0 wt%	30–70	6:1; 6.0 wt%; 60 °C	~95.0 (Y)/1	[51]
Soybean oil							> 95.0 (Y)/1	
Sunflower oil							> 95.0 (Y)/1	
Soybean oil	Flask/magnetic	Methanol	6:1–18:1	ChOH/2.0– 10.0 wt%	30–65	9:1; 4.0 wt%; 60 °C	95.0 ± 1.7 (Y)/2.5	[52]
				ChOMe/4.0 wt%			88.3 ± 1.8 (Y)/2.5	
				ChIm/4.0 wt%			76.9 ± 1.9 (Y)/2.5	
Jatropha oil	Round-bottom flask/ mechanical	Methanol	3:1–18:1	ChOH/1.0– 5.0 wt%	30–70	9:1; 4.0 wt%; 60 °C	95.0 ± 1.0 (Y)/4	[53]

**Table 6**  
Application of ionic liquids as solvents for biocatalyzed transesterification process.

Feedstock	Enzyme, wt% (based on oil weight)	Type, volume of reactor, cm <sup>3</sup> /type of agitator, agitation intensity, rpm	Alcohol	Alcohol:oil molar ratio, mol/mol or vol% (to IL)	Ionic liquid/loading, wt% (based on oil weight) or mL IL/g oil or mL/mol oil or v/v (with oil) or w/w (with oil)	Water/loading, vol% (to alcohol) or wt% (based on oil weight) or vol% (based on oil volume) or $\mu$ L/g oil	Temperature, °C	Optimal reaction conditions	Conversion (C) or yield (Y), %/time, h	Reference
Soybean oil	Novozym 435/2.0	Screw capped vial, 5/reciprocal shaker, 250	Methanol	2:1–10:1	[EMIM][TfO]/1:1 v/v (with oil)	–	50	4:1; 2.0 wt% lipase; IL 1:1 v/v (with oil); 50 °C	80.0 (Y)/12	[64]
Sunflower oil	Novozym 435/2.0–10.0	Flask, 25	Methanol	4:1–10:1	[BMIM][PF <sub>6</sub> ]/0.25–2.0 w/w (with oil)	–	58–60	8:1; 2.0 wt% lipase; 1.0 w/w (with oil) IL; 60 °C	97.0 $\pm$ 1.0 (C)/10	[55]
					[EMIM][PF <sub>6</sub> ]/0.25–2.0 w/w (with oil)	–	58–60		97.0 $\pm$ 1.0 (C)/6	
					[HMIM][BF <sub>4</sub> ]/2.0 w/w (with oil)	–	60	10.0 wt% lipase; 1.0 w/w (with oil) IL; 60 °C	10.0 $\pm$ 2.4 (Y)/4	
					[BMIM][BF <sub>4</sub> ]/2.0 w/w (with oil)	–			0.0 (Y)/4	
Triolein	Novozym 435	Micro-reaction vessel, 5/gentle	Methanol	30.0–70.0 vol% (to IL)	[C <sub>18</sub> MIM][NTf <sub>2</sub> ]	–	60		96.0 (Y)/6	[66] [71]
Miglyol 812	Novozym 435/36.36		Methanol		[Me(OEt) <sub>3</sub> -Et-Im][OAc]	–	50	36.36 wt% lipase; IL: methanol=7:3 (v/v); 50 °C	70.0 (C)/48	
					[Me(OEt) <sub>3</sub> -Et <sub>3</sub> N][OAc]	–	50	36.36 wt% lipase; IL: methanol=7:3 (v/v); 50 °C	70.0 (C)/1 85.0 (C)/48 98.0 (C)/96	
						–	50	36.36 wt% lipase; IL: methanol=7:3 (v/v); 50 °C	88.0 (C)/48	
Soybean oil				30.0 vol% (to IL)	[Me(OEt) <sub>3</sub> -Et <sub>3</sub> N][HCOO]	–	50	36.36 wt% lipase; IL: methanol=7:3 (v/v); 50 °C	63.64 (C)/96	[56]
				30.0 vol% (to IL)	[Me(OEt) <sub>3</sub> -Et <sub>3</sub> N][OAc]	–	50	36.36 wt% lipase; IL: methanol=7:3 (v/v); 50 °C	83.0 (Y)/24	
Triolein	Novozym 435/10.0	Shake flask reactor, 500/, 200 Conical reactor, 500	Methyl acetate	14:1	[BMIM][PF <sub>6</sub> ]/1:1 (v/v, with oil)	–	48	14:1; 10.0 wt% lipase; IL: oil=1:1 (v/v); 48 °C	54.0 (Y)/7	[57]
Waste canola oil		Conical reactor, 12/ magnetic			[BMIM][PF <sub>6</sub> ]/1:1 (v/v, with oil)	–			72.0 (Y)/24	
Triolein	Novozym 435/1.0–20.0	Jacketed reactor, 12/ magnetic	Methyl acetate	3:1–20:1	[BMIM][PF <sub>6</sub> ]/0–6 mL	–	30–70	10:1; 20 wt% lipase; 4 mL of IL or 1:1 ratio (v/v) IL: triolein; 42.5 °C	80.0 (Y)/6	[67]
Triolein	Novozym 435/10.0	Screw-capped vial, 1/vigorous shaking	Methanol	6:1	[C <sub>16</sub> MIM][NTf <sub>2</sub> ] or [C <sub>18</sub> MIM][NTf <sub>2</sub> ]/2.58:1 (v/v, with oil)	–	60	6:1; 10.0 wt% lipase; 2.58:1 (v/v, with oil) IL; 60 °C	98.0 (Y)/6	
Triolein	Novozym 435/5.0–20.0	Screw-capped vial, 1/vigorous shaking	Methanol	3:1–12:1	[C <sub>16</sub> MIM][NTf <sub>2</sub> ]/0.13:1–2.58:1 (v/v, with oil)	–	50–90	6:1; 2.58:1 (v/v, with oil) IL; 10.0 wt% lipase; 60 °C	99.39 (Y)/24 93.38 (Y)/24 92.78 (Y)/24 94.11 (Y)/24 96.91 (Y)/24	[68]
Olive oil				6:1			60			
Sunflower oil										
Palm oil										
Waste cooking oil										[69]
Rapeseed oil	Novozym 435/5.0–10.0	Capped vial, 10/ magnetic, 300	Methanol	4:1–8:1	Ammoeng 102/22.68–90.70 wt%	1.5 wt% (based on oil weight)	50	4:1; 56.69 wt% IL; 5.0 wt% lipase; water 1.5 wt%; 50 °C	98.62 $\pm$ 1.21 (Y)/24; 99.24 $\pm$ 0.34 (C)/24 94.93 $\pm$ 1.78 (Y)/24; 97.50 $\pm$ 0.97 (C)/24	
				3:1–6:1	Ammoeng 120/22.68–90.70 wt%			3:1; 56.69 wt% IL; 5.0 wt% lipase; water 1.5 wt%; 50 °C	95.21 $\pm$ 2.03 (Y)/24; 99.35 $\pm$ 0.51 (C)/24	
Sunflower oil	Novozym 435/0.05 g/ml oil	Screw-capped vial, 5/900	Methanol	10:1	[OMIM][NTf <sub>2</sub> ]/1:1 (v/v, with oil)	1.0 (v/v, with oil)		10:1, 0.05 g lipase/ml oil; 1:1 (v/v, with oil) IL; 1.0 (v/v, with oil) water; 40 °C	60.0 (C)/24	[65]
				2:1–14:1		0–4.0 (v/v, with oil)	30–50		60.0 (C)/24	

Waste cooking oil				10:1	[OMIM][PF <sub>6</sub> ]/1:1 (v/v, with oil)	1.0 (v/v, with oil)	30–65		~47.0 (C)/24	
Corn oil	<i>P. expansum</i> lipase/10.0	Capped flask, 25/ shaker, 220 rpm	Methanol	2:1	[BMIM][PF <sub>6</sub> ]/2 mL/ g oil	–	40	2:1; 2 mL IL/g oil; 10.0 wt% lipase; 40 °C	69.7 (Y)/25	[58]
Corn oil	<i>P. expansum</i> lipase/5.0–40.0	Capped bottle, 5/ 220	Methanol	0.33:1–4:1	[BMIM][PF <sub>6</sub> ]/0.5–3 ml/g oil	0–4.0 wt% (based on oil weight)	35–55	2:1; 1.5 mL IL/g oil; 20.0 wt% lipase; 3.0 wt% water; 40 °C	86.0 (Y)/24	[59]
<i>C. pyrenoidosa</i> oil	<i>P. expansum</i> lipase/20.0	Capped flask, 25/ shaker, 220 rpm	Methanol	0.5:1–5:1	[BMIM][PF <sub>6</sub> ]/1.0–6.0 mL/ g oil	0–5.0 wt% (based on oil weight)	30–60	3:1; 2 ml IL/g oil; 20.0 wt% lipase; 3.0 wt% water; 50 °C	90.7 (Y)/48	[60]
<i>M. pinnata</i> seed oil	<i>P. expansum</i> lipase/10.0–80.0	Capped vial/ 220 rpm	Methanol	0.5:1–12:1	[BMIM][PF <sub>6</sub> ]/1.0–6.0 mL IL/g oil	0–50 µL/g oil	30–70	4:1; 2 ml IL/g oil; 10.0 wt% lipase; 1.0 wt% water; 50 °C	86.2 (Y)/48	[61]
				0.5:1–12:1		0–50 µL/g oil	30–70	6:1; 1.0 mL IL/g oil; 20.0 wt% lipase; 40 µL water/g oil; 40 °C	93.5 (Y)/56	
	<i>P. expansum</i> lipase/20.0 <i>R. chinensis</i> lipase/20.0 <i>A. niger</i> lipase/ 20.0 <i>P. expansum</i> lipase/20.0			6:1		40 µL/g oil	40	3:1; 3.0 mL IL/g oil; 20.0 wt% lipase; 20 µL water/g oil; 60 °C	48.4 (Y)/56	
								6:1; 1.0 mL IL/g oil; 20.0 wt% lipase; 40 µL water/g oil; 40 °C	93.9 (Y)/54	
									96.6 (Y)/54	
									61.9 (Y)/54	
									94.7 (Y)/48	
		91.5 (Y)/48								
Soybean oil	<i>P. cepacia</i> lipase/20.0	Round-bottom flask, 250	Methanol	12:1	[BMIM][Tf <sub>2</sub> N]/0.8 mL/g oil	0–30.0 vol% water (to methanol, v/v)	20–60	12:1; 0.8 mL IL/ g oil; 20.0 wt% lipase; 30.0 vol% water (methanol: water=7:3, v/v); 30 °C	96.3 (C)/48	[62]
			Ethanol			0–15.0 vol% water (to ethanol, v/v)		0.8 mL IL/ g oil; 20.0 wt% lipase; 15.0 vol% water (ethanol:water=17:3, v/v); 30 °C	96.3 (C)/30	
Soybean oil	w-ROL (5 pieces of BSPs)	Screw-capped vial, 10/reciprocal shaker, 250	Methanol	1:1–8:1	[EMIM][BF <sub>4</sub> ]/1:1 (v/v, with oil) [BMIM][BF <sub>4</sub> ]/1:1 (v/v, with oil)	5.0 wt% (based on oil)	30	4:1; 1:1 (v/v, with oil) IL; 30 °C; 5.0 wt% water (based on oil)	~45.0 (Y)/24 ~44.0 (Y)/24	[63]



shifted the equilibrium to the ester synthesis. The system of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, [EMIM][TfO] and Novozym 435 lipase gives around 15.0% higher yield than that achieved in the reaction with *tert*-butanol [64]. Higher viscosity of [EMIM][TfO] causes lower conversion degrees in the earlier stage of the reaction, compared to the reaction in the presence of *tert*-butanol.

Continuous Novozym 435-catalyzed transesterification is rarely studied. *n*-Butanol and vinyl laurate react in a double-layer type stirred tank reactor with *in situ* separation of the fatty acid ester in 1-methyl-3-octylimidazolium trifluoromethanesulfonate, [OMIM][TfO] [70]. This water-immiscible IL is chosen because it dissolves both reactants, but not the product (butyl laurate). The productivity of butyl laurate at the flow rate of 0.75 mL/h was maintained for at least 5 days after the steady-state was reached.

Imidazolium- and ammonium-based ILs consisting of alkoxyalkyl-substituted cation like ILs 1-ethyl-3-(2-(2-methoxyethoxy)ethoxy)ethylimidazolium acetate, [Me(OEt)<sub>3</sub>-Et-Im][OAc], triethyl (2-(2-methoxyethoxy)ethoxy)ethylammonium acetate, [Me(OEt)<sub>3</sub>-Et<sub>3</sub>N][OAc] and triethyl (2-(2-methoxyethoxy)ethoxy)ethylammonium formate, [Me(OEt)<sub>3</sub>-Et<sub>3</sub>N][HCOO], can dissolve oils and facilitate the increase in the lipase activity for the synthesis of biodiesel [71]. Among these ILs, [Me(OEt)<sub>3</sub>-Et<sub>3</sub>N][OAc] and [Me(OEt)<sub>3</sub>-Et<sub>3</sub>N][HCOO] give the highest conversion. Even at high methanol concentrations in the IL-methanol mixtures (up to 50.0% v/v) different lipases show a high catalytic activity. For instance, the complete conversion of Miglyol oil 812 is obtained with the IL-methanol mixtures (70:30 v/v) in 96 h. In addition, the Novozym 435-catalyzed soybean oil transesterification using these IL/methanol mixtures is efficient.

In the methanolysis of sunflower oil or waste cooking oil with the use of 3-octyl-1-methylimidazolium hexafluorophosphate, [OMIM][PF<sub>6</sub>], or 3-octyl-1-methylimidazolium bis(trifluoromethyl) sulfonyl imide, [OMIM][NTf<sub>2</sub>], Novozym 435 activity increases with increasing hydrophobicity of the cation and with decreasing nucleophilicity of the anion [65]. The Novozym 435-catalyzed methanolysis of waste cooking oil in [OMIM][PF<sub>6</sub>] gives only the 13.0% decrease in the ester production with respect to the process with sunflower oil.

Amphiphilic tetraammonium-based ILs (Ammonoeng 102 and Ammonoeng 120) are the most efficient in the Novozym 435-catalyzed methanolysis of rapeseed oil [69]. The oil/Ammonoeng 102 system has some unique properties, such as small amount of IL needed for the reaction, low amounts of mono- and diacylglycerols (MAGs and DAGs, respectively) in the final product and protection of the enzyme from being inactivated by methanol.

Whole-cell biocatalysts are also used in the biocatalyzed biodiesel production. The soybean oil methanolysis is catalyzed by filamentous lipase-producing fungi, immobilized on biomass support particles, in the presence of 1-ethyl-3-methylimidazolium tetrafluoroborate, [EMIM][BF<sub>4</sub>], and 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF<sub>4</sub>] [63]. The highest ester yield is obtained with wild type *Rhizopus oryzae* TAG lipase (w-ROL) in [BMIM][BF<sub>4</sub>] or [BMIM][BF<sub>4</sub>]. The ILs allow a greater lipase tolerance to inhibition by methanol, even when the methanol-to-oil molar ratio is 4:1, and the activity of w-ROL is reduced after the 72 h incubation in [BMIM][BF<sub>4</sub>]. Cross-linking the biocatalyst with glutaraldehyde is recommended for increasing its stability and recycling.

#### 4. ILs in biodiesel purification

ILs have several uses in various steps of biodiesel production process such as extraction of lipids from biomass, FFAs from oily feedstocks before the reaction, as well as glycerol, unsaturated

fatty acid esters and the leftover catalyst from crude biodiesel after the reaction.

##### 4.1. Extraction of lipids from biomass

The use of microalgal oil as a feedstock for preparation of biodiesel is growing in the last decade, since microalgae have not only high abundance, photosynthetic efficiency and production rate, but also high content of lipids (more than 20.0% of dry weight) [72]. Lipid extraction from microalgal biomass is usually done by the Soxhlet extraction with *n*-hexane [73] and by the Bligh and Dyer's method [74]. Showing great extraction efficiency, ethanol, *n*-hexane-ethanol mixture and petroleum ether are common extracting solvents for recovering lipids from microalgal biomass. However, these solvents are flammable, volatile, toxic and non-miscible with water (except ethanol). In addition, ethanol also extracts undesirable proteins, pigments and sugars, which is a serious drawback [75]. Some ILs are also used for extracting lipids from algal biomass as being efficient in extraction and environmentally-friendly.

In many cases, lipid extraction from biomass by ILs is more efficient than the conventional methods. Total lipids extracted from *Chlorella vulgaris* by the Bligh and Dyer's method are 10.6%, while 1-butyl-3-methyl imidazolium trifluoromethanesulfonate, [BMIM][CF<sub>3</sub>SO<sub>3</sub>], [EMIM][MeSO<sub>4</sub>] or 1-butyl-3-methyl imidazolium methyl sulfate, [BMIM][MeSO<sub>4</sub>] extract 12.54%, 11.88%, and 11.84% of the lipids, respectively [76]. Also, the total lipid amount extracted from cultivated *C. vulgaris* by the Bligh and Dyer's method is 11.1%, while the [BMIM][CF<sub>3</sub>SO<sub>3</sub>]-methanol mixture extracts 19.0% of the lipids. Among the ILs containing [BMIM]<sup>+</sup>, the lipid extraction efficiency is influenced by the IL's anion and is in the following order: [CF<sub>3</sub>SO<sub>3</sub>]<sup>−</sup> > [MeSO<sub>4</sub>]<sup>−</sup> > [CH<sub>3</sub>SO<sub>3</sub>]<sup>−</sup> > [BF<sub>4</sub>]<sup>−</sup> > [PF<sub>6</sub>]<sup>−</sup> > [Tf<sub>2</sub>N]<sup>−</sup> > [Cl]<sup>−</sup>. Hydrophobic and water immiscible [BMIM][PF<sub>6</sub>] and [BMIM][NTf<sub>2</sub>] are less efficient than hydrophilic and water miscible ILs ([BMIM][CF<sub>3</sub>SO<sub>3</sub>], [BMIM][MeSO<sub>4</sub>] and [EMIM][MeSO<sub>4</sub>]), except 1-butyl-3-methyl imidazolium chloride, [BMIM][Cl], and 1-ethyl-3-methyl imidazolium acetate, [EMIM][OAc]. Higher solubility of lipids in hydrophobic ILs induces the partitioning of lipids to the IL-methanol mixture. Despite highly hydrophilic and completely water-miscible nature, [EMIM][OAc] shows a very high solubility for lipids.

When single ILs, organic solvents and IL mixtures are used for lipid extraction from *C. vulgaris* (initial fatty acids content 292.2 mg/g) at 120 °C for 2 h, the lipid extraction yields by *n*-hexane and a *n*-hexane-methanol mixture (7:3 v/v) are similar (about 185 mg/g) but lower than that obtained by 1-ethyl-3-methyl imidazolium diethylphosphate, [EMIM][DEP] (250.0 mg/g) [77]. Good results are also achieved with 1-ethyl-3-methyl imidazolium chloride, [EMIM][Cl], [EMIM][OAc] and [EMIM][BF<sub>4</sub>] (235.1, 223.7, and 219.7 mg/g, respectively). The fatty acids contents in the extracted lipids are very high (more than 940 mg/g lipid). Despite low lipid yields obtained using [EMIM][EtOSO<sub>3</sub>] and [EMIM][SCN] (60.5 and 42.7 mg/g, respectively), their 1:1 mixture (weight ratio) gives the yield of 158.2 mg/g. The same is noticed in the case of [EMIM][HSO<sub>4</sub>] and its 1:1 mixture with [EMIM][SCN] (yields are 35.2 and 200.6 mg/g, respectively). The lipid extraction yield is enhanced by the synergistic effects of the mixture of ILs with different anions.

A combined use of ILs and organic solvents (methanol, isopropyl alcohol, acetone, chloroform, dimethyl sulfoxide or acetic acid) improves the oil extraction efficiency. An example is the use of 1-ethyl-3-methyl imidazolium methyl sulfate, [EMIM][MeSO<sub>4</sub>], with a polar cosolvent (methanol, isopropyl alcohol, acetone, chloroform, dimethyl sulfoxide and acetic acid) for extracting oils from microalgal biomass (*Chlorella* sp. and *Dunaliella* sp.) [78]. The cosolvent interferes with the stability of the cell wall in the biomass, thus making the lipid extraction more efficient. Because of



its amphiphilic properties and the strong ionic bonding between its cation and anion, the IL facilitates transfer of lipids to the surface interface, so the extracted lipids form their own phase that can be separated. Higher lipid yield is obtained with isopropyl alcohol and methanol (8.5% and 7.9%, respectively) than with dimethyl sulfoxide and acetic acid (6.0% and 5.6%, respectively). Since acetone and chloroform extract the non-lipid components, they are not recommended as cosolvents in lipid extraction from biomass. The IL-methanol system can also be used to extract bio-oil and phorbol esters from *Jatropha* biomass [79]. The bio-oil yield of 40–45 wt% achieved with the [EMIM][MeSO<sub>4</sub>]/methanol mixture (30–50 wt% of IL) is higher than that obtained with [EMIM][OAc]/methanol mixtures. The mixture containing 30 wt% of [EMIM][MeSO<sub>4</sub>] is suggested for simultaneous extraction of bio-oil and phorbol esters. Under the optimized conditions, this extracting system extracts approximately 98.0% of the phorbol esters and almost all the bio-oil from the original biomass.

Mixtures of a molten salt and an IL can also improve the lipid extraction yield from *C. vulgaris* [80]. A high lipid extraction yield (113.0 mg/g) is obtained by molten salt FeCl<sub>3</sub> · 6H<sub>2</sub>O, while [EMIM][OAc] gives a better result (218.7 mg/g). In the case of the FeCl<sub>3</sub> · 6H<sub>2</sub>O/[EMIM][OAc] mixture (5:1 w/w) at 90 °C, the yield rises up to 227.6 mg/g within 1 h. The extracted lipid has very high fatty acid content of 981.7 mg/g lipid with less than 2% of impurities. [EMIM][HSO<sub>4</sub>] and [EMIM][SCN] gives low lipid yields (33.5 and 40.4 mg/g, respectively), but their mixtures with FeCl<sub>3</sub> · 6H<sub>2</sub>O (5:1 w/w) leads to better yields (131.9 and 158.3 mg/g, respectively). The molten salt/IL mixtures are better in lipid extraction because of the synergistic effects of two anions in the mixtures.

Since recently, a novel ultrasound-assisted method has been used for lipid extraction from biomass using ILs [81]. Since [BMIM][MeSO<sub>4</sub>] dissolves the microalgal biomass, the pretreatment step to disrupt the cellular structure is not necessary. The total lipids extracted by the Soxhlet and Bligh–Dyer's methods are 21.1 and 28.5 mg/g, respectively, while the extraction by [BMIM][MeSO<sub>4</sub>] results in 47.4 mg/g. The amount of lipids extracted using [BMIM][MeSO<sub>4</sub>] with ultrasound irradiation is even higher (74.0 mg/g) in shorter time. Also, at 60 °C the rate of extraction of total lipids from *C. vulgaris* with [BMIM][MeSO<sub>4</sub>] is 2.7 times larger than that under ultrasound irradiation. Because the lipid phase has lower density, the undissolved lipids are easily recovered.

#### 4.2. Extraction of FFAs from oily feedstocks

Manic et al. [82] studied the use of alkyl pentaethoxymethyl ammonium methylsulfate (Ammonoeng 100) and 1-butyl-3-methylimidazolium dicyanamide ([BMIM][DCA]) for the extraction of linoleic acid from soybean oil. These ILs are miscible with linoleic acid and less soluble in soybean oil. The highest values of linoleic acid distribution coefficient are obtained with Ammonoeng 100. This potential can be used in the biodiesel deacidification process.

#### 4.3. Extraction of unsaturated esters and TAGs from biodiesel

In order to reduce NO<sub>x</sub> emission and to enhance the oxidation stability of biodiesel, Li et al. [83] extracted the unsaturated fatty acid esters (methyl linolenate and methyl linoleate) from biodiesel produced from soybean oil, with the use of  $\pi$ -complexing sorbents. These new sorbents are produced through covalent immobilization of ILs (imidazolium type with PF<sub>6</sub><sup>−</sup> and BF<sub>4</sub><sup>−</sup> ions) onto silica and coating the silica-supported ILs with AgBF<sub>4</sub> or AgNO<sub>3</sub>. The produced sorbent (AgBF<sub>4</sub>/SiO<sub>2</sub> · Im<sup>+</sup> · PF<sub>6</sub><sup>−</sup>) shows a high selectivity in the extraction of 18:3 esters. Pham et al. [84] used the modified SBA-15 adsorbent (AgBF<sub>4</sub>/SBA-15 · HPSiOEtIm<sup>+</sup> · PF<sub>6</sub><sup>−</sup>) for separating the polyunsaturated TAGs. The adsorption capacity for

linolenin is around 217.0 mg/g. In addition, when this adsorbent is applied to a mixture of TAGs with varying degrees of unsaturation, good selectivity and high capacity are observed. The selectivity and capacity of the adsorbent are retained in 5 cycles.

### 5. DESs in biodiesel production

As ILs, DESs have different roles in production of biodiesel where they are used in the biodiesel synthesis step as catalyst or cosolvent and in the crude biodiesel purification step as extracting solvent. DESs are employed as catalysts in one- and two-step processes (Table 7). The second process is applied with feedstocks having high FFA content and involves oil esterification, followed by alkaline-catalyzed transesterification. In some cases, DESs are used as a cosolvent in combination with other (bio)catalysts to improve their catalytic capability. In addition, DESs might reduce the side reactions (such as saponification), and make separation and purification processes easier. Some DESs are also efficient in removing glycerol and remaining alkaline catalyst from crude biodiesel.

#### 5.1. DESs as catalysts in transesterification

The use of DESs as catalysts in transesterification has recently begun, as it can be seen in Table 7. In the study of Long et al. [85], ChCl:ZnCl<sub>2</sub> (molar ratio 1:2) was used as the Lewis acidic catalyst in the soybean oil methanolysis. This DES has many advantages such as simple preparation, low price, insensitivity to moisture and mild process conditions. In the palm oil transesterification over either ChCl:ZnCl<sub>2</sub> (1:2) or ChCl:FeCl<sub>3</sub> (1:2), the ester yield of 70.4% and 67.4% were achieved, respectively [86]. When H<sub>2</sub>SO<sub>4</sub> (95 vol%) was added into ChCl · ZnCl<sub>5</sub><sup>−</sup>, the ester yield raised up to 92.0%.

Some DESs were used in two-step processes consisted of crude palm oil (with a high FFA content) esterification, followed by KOH-catalyzed transesterification. Hayyan et al. [87] reduced the amount of FFAs in the oil from 9.5% to 0.7% after the oil pretreatment with *N,N*-diethanol ammonium chloride:*p*-toluenesulfonic acid, DEAC:PTSA (molar ratio 1:3). The same research group used allyltriphenylphosphonium bromide:*p*-toluenesulfonic acid monohydrate, P-DES (molar ratio 1:3) [88] and ChCl:*p*-toluenesulfonic acid, ChCl:PTSA (molar ratio 1:3) [89] to reduce the amount of FFAs in the oil from 9.3% to less than 2.0% and from 9.0% to less than 1.0%, respectively.

Some DESs, combined with other catalysts, are efficient in production of biodiesel. ChCl:glycerol (1:2) activates commercial CaO by removing the inactive layers of CaCO<sub>3</sub> and Ca(OH)<sub>2</sub> from the surface of the solid catalyst [90]. Methanolysis of rapeseed oil with calcinated CaO in the absence and the presence of the DES gives the ester yield of 87.3% and 95.0%, respectively. Non-calcinated CaO is not efficient in the reaction (4.0% yield), but when is used with the DES, the ester yield is 91.9%.

DESs are also efficient solvents in the biocatalyzed biodiesel production. Their advantages for this use are cheapness, non-toxicity, biodegradability and lipase-compatibility. The Novozym 435-catalyzed transesterification of ethyl sorbate in the presence of *n*-propanol and various DESs based on ChCl or ChOAc gives good results [91]. ChCl:urea (1:2), ChCl:glycerol (1:2) and ChOAc:glycerol (1:1.5) raise the selectivity of lipase to 99.0%. Also, the same DESs give the high conversion of Miglyol oil within only 1 h, but ChOAc:glycerol (1:1.5) gives the highest conversion degree under optimized conditions. In addition, ChCl:glycerol (1:2) is used as a solvent in the Novozym 435-catalyzed soybean oil transesterification by methanol where the conversion degree of 88.0% is achieved in 24 h [4]. ChCl:glycerol (1:2) and ChOAc:glycerol (1:2, 1:1 and 2:1) are efficient in producing biodiesel from *M.*

**Table 7**

Application of deep eutectic solvents as catalysts in biodiesel production.

Feedstock	Type, volume of reactor, cm <sup>3</sup> /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	ChCl:ZnCl <sub>2</sub> (1:2)/ 10.0 wt%	–	50–90	16:1; 10.0 wt%; 70 °C	54.52 (C)/72	[85]
Palm oil	Three-neck flask	Methanol	10:1–15:1	ChCl:ZnCl <sub>2</sub> (1:2)/ 0.5–2.5 wt%	–	65	15:1; 2.5 wt% DES; 65 °C	70.4 (Y)/4	[86]
				ChCl:FeCl <sub>3</sub> (1:2)/ 0.5–2.5 wt%	–			67.4 (Y)/4	
				ChCl:ZnCl <sub>2</sub> (1:2)/ 2.5 wt%	95.0% H <sub>2</sub> SO <sub>4</sub> /20.0 wt%			92.0 (Y)/4	
				ChCl:FeCl <sub>3</sub> (1:2)/ 2.5 wt%	–			89.5 (Y)/4	
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	I step: 8:1; 0.75 wt% DES; 60 °C; 200 rpm	97.0 (Y)/0.5	[87]
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% DES; 60 °C; 300 rpm	96.0 (Y)/0.5	[88]
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	ChCl: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	[89]
Esterified oil (< 1% FFA)	Batch reactor with a reflux 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	ChCl: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	[90]
Miglyol 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	[91]
Soybean oil	Micro-reaction vessel, 5/ gentle	Methanol/20.0–50.0 vol% (to IL)		ChCl: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	[4]
<i>M. pinnata</i> seed oil	Flask/shaker, 220	Methanol	3 mL/mg oil	ChOAc:glycerol (1:2)/7 mL DES/g oil	<i>P. expansum</i> lipase/ 1.0 wt%	50	3 mL methanol/mg oil; 7 mL DES/g oil; 1.0 wt% lipase; 50 °C	7.6 (C)/48	[92]
					Novozym 435/1.0 wt%			54.8 (C)/48	
					Lipozyme TLIM/1.0 wt%			44.8 (C)/48	

*pinnata* seed oil with Novozym 435 [92]. In this reaction Novozym 435 enables a better conversion than PEL with a maximal yield obtained with  $\text{CH}_3\text{OAc/glycerol}$  (1:2).

## 5.2. Extraction of glycerol and left-over catalyst from crude biodiesel

Some DESs such as  $\text{CH}_3\text{Cl:glycerol}$ ,  $[\text{ClEtMe}_3\text{N}]\text{Cl:glycerol}$ , and  $[\text{EtNH}_3]\text{Cl:glycerol}$ , all with molar ratio 1:1, are efficient in the glycerol extraction from crude biodiesel produced by the KOH-catalyzed ethanolysis of rapeseed or soybean oil [10].  $\text{CH}_3\text{Cl:glycerol}$  (molar ratio 1:1) reduces the content of glycerol in the purified product from the ethanolysis of rapeseed or soybean oil to 0.06 wt% and 0.02 wt%, respectively. Furthermore,  $\text{CH}_3\text{Cl:glycerol}$  (1:1) is efficient in extracting glycerol from crude biodiesel obtained by the KOH-catalyzed methanolysis of palm oil, achieving the highest extraction yield of 51.25 wt% at the DES:biodiesel molar ratio of 1:1 [93].  $\text{CH}_3\text{Cl:ethylene glycol}$  (1:2.5) and  $\text{CH}_3\text{Cl:2,2,2-trifluoroacetamide}$  (1:7.5) are also efficient in the glycerol extraction from the DES:biodiesel molar ratio of 3:1 [94]. Several DESs synthesized by combining methyl triphenyl phosphonium bromide (MTPB) with glycerol, ethylene glycol or triethylene glycol are successful in free glycerol removal from crude biodiesel [95]. The extraction with MTPB:glycerol (1:2) results in the free glycerol content of 0.02 wt% at DES-to-biodiesel molar ratios of 2:1, 2.5:1 and 3:1, but the ethylene and triethylene glycol DESs (molar ratios 1:3, 1:4 and 1:5) give better results in the DES-to-biodiesel molar ratios ranging from 0.75 to 3:1. In addition, these DESs reduce the amount of MAGs and DAGs. MTPB-based DESs with ethylene or triethylene glycol is the most efficient DESs in reducing the total glycerol amount in crude biodiesel [96]. The DES with ethylene glycol (mole fraction 0.66) gave the removal efficiency of 23.85% at the DES-to-biodiesel molar ratio of 3:1, while the 2,2,2-trifluoroacetamide-based DES (mole fraction 0.60) results in the removal efficiency of 29.29% (DES:biodiesel molar ratio of 2.93:1).

$\text{CH}_3\text{Cl}$ - and MTPB-based DESs are used for the removal of the remaining KOH from crude palm oil biodiesel [97]. The efficiency of KOH removal increases with increasing the DES:biodiesel molar ratio and the amount of hydrogen bond donor in the DES. Among these DESs,  $\text{CH}_3\text{Cl:glycerol}$  and MTPB:glycerol are the most efficient in the removal of KOH, with the average removal efficiencies of 98.59% and 97.57%, respectively. Also, these DESs reduce the amount of water in biodiesel. Furthermore, they can be used five times, without any significant change in their efficiencies.

## 6. Optimization of biodiesel production using ILs and DESs

In order to increase the process efficiency and to make the biodiesel product cheaper, the application of the optimal reaction conditions for the selected feedstock, alcohol and catalyst system is desired. In developing and optimizing the biodiesel production process a statistical design of experiments is important, because it allows the simultaneous analysis of the effects of many process variables and their interactions. The response surface methodology (RSM) is usually used in defining the optimal reaction conditions for achieving the maximum esters yield, although artificial neural network combined with genetic algorithm (ANN-GA) is also employed. A literature survey on the optimization of biodiesel producing reactions by statistical/mathematical methods with ILs and DESs is listed in Table 8.

Han et al. [98] conducted the esterification of palmitic acid with ethanol and a series of polyoxometalate-based sulfonated ILs as catalysts. These catalysts were formed by combining phosphotungstic acid (HPW) and  $\text{SO}_3\text{H}$ -functionalized zwitterion complex 3-(1-methylimidazolium-3-yl) propane-1-sulfonate (MIM-PS). RSM combined with the Box-Behnken design (BBD) was used in

optimizing the esterification conditions and defining the relationship between yield of biodiesel with reactant ratio, amount of IL and time. This analysis of variance showed that reaction time and amount of catalyst were the most significant parameters. Polyoxometalate-based sulfonated IL  $[\text{MIM-PSH}]_{2.0}\text{HPW}_{12}\text{O}_{40}$  was the most efficient catalyst. In addition, with this IL, the effectiveness of different alcohols in the esterification of palmitic acid follows this order: methanol > ethanol > isopropanol. Fauzi and Amin [99] optimized the oleic acid esterification with methanol and 1-butyl-3-methylimidazolium hydrogen sulfate,  $[\text{BMIM}][\text{HSO}_4]$ , as a catalyst with respect to methyl oleate yield and oleic acid conversion. The multi-objective optimization using ANN-GA had higher effectivity than the single-objective optimization by RSM. Li et al. [100] used RSM based on BBD to optimize the esterification of oleic acid with methanol and seven different acidic ILs. Introducing  $-\text{SO}_3\text{H}$  group into the IL increases its Brønsted acidity, making  $[\text{BHSO}_3\text{MIM}][\text{HSO}_4]$  the best choice as a catalyst. This IL is also successful for the palmitic acid esterification with methanol and the conversion of waste oils with high acid value (72.0% of FFAs) to biodiesel.

Yanfei et al. [101] optimized the methanolysis of soybean oil with four ILs based on *N,N,N*-triethyl-*N*-(propanesulfonic acid) ammonium cation using RSM based on the central composite rotatable design (CCRD). The order of catalytic activity for the anions in the ILs is:  $[\text{HSO}_4]^- > [\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3]^- > [\text{H}_2\text{PO}_4]^- > [\text{CF}_3\text{COO}]^-$ . The highest yield is achieved with  $[(\text{CH}_3\text{CH}_2)_3\text{N}(\text{CH}_2)_3\text{SO}_3\text{H}][\text{HSO}_4]$ . Gu et al. [102] proposed a greener biodiesel synthesis by using  $\text{CH}_3\text{Cl:glycerol}$  (1:2) as the cosolvent in the NaOH-catalyzed transesterification of rapeseed oil. Under the optimum conditions determined by RSM based on BBD, the ester yield is higher in the presence of the DES.

## 7. Novel biodiesel production technologies using ILs or DESs

ILs and DESs have frequently been used in combination with novel transesterification technologies based on the use of microwave and ultrasound irradiation, as well as supercritical fluids like  $\text{CO}_2$ . A review on novel biodiesel production technologies using ILs or DESs as catalysts is given in Table 9.

Microwave irradiation is an effective method for promoting biodiesel synthesis by increasing the reaction rate, product yield and/or purity of the products [103]. This heating system is more energy efficient for transesterification reactions than the conventional heating method [103]. In addition, some ILs have strong capacity for absorbing microwave energy, promoting IL-catalyzed reactions [104]. 4-Allyl-4-methylmorpholin-4-ium bromide,  $[\text{Mor-MeA}][\text{Br}]$ , combined with NaOH gives a better yield than that achieved with NaOH alone in the microwave-assisted biodiesel production from waste cooking oil [105]. This IL and NaOH form the  $\text{IL}_x\text{NaOH}_y$  catalyst (defined as  $x$  wt% IL +  $y$  wt% NaOH). The best results are obtained under the optimized conditions with the catalytic system  $\text{IL}_1\text{NaOH}_{0.75}$  (1.0 wt%  $[\text{Mor-MeA}][\text{Br}]$  + 0.75 wt% NaOH). The microwave-assisted methanolysis of soybean oil is also done using a basic IL/NaOH catalytic system [106]. 1-Ethyl-3-methylimidazolium hydroxide,  $[\text{C}_2\text{MIM}][\text{OH}]$ , shows the highest efficiency. Brønsted–Lewis ILs, prepared by combining 1-butylsulfonic-3-methylimidazolium hydrogen sulfate,  $[\text{BSO}_3\text{HMIM}][\text{HSO}_4]$ , with different metal sulfates like  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{CuSO}_4$ ,  $\text{ZnSO}_4$ ,  $\text{MgSO}_4$  and  $\text{CaSO}_4$  are successful catalysts in the microwave-assisted biodiesel production from acidic *Camptotheca acuminata* seed oil [107]. The activity of these catalytic systems decreases in the following order:  $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+}$ . The system  $\text{Fe}_2(\text{SO}_4)_3/[\text{BSO}_3\text{HMIM}][\text{HSO}_4]$  in the molar ratio of 3:1 shows the highest catalytic activity. Microwave and ionic liquids have also been employed to accelerate enzyme-catalyzed biodiesel reaction. For

instance, the use of microwave irradiation with [EMIM][PF<sub>6</sub>] is applied in the Novozym 435-catalyzed methanolysis of soybean oil [108]. The synergistic effect of microwaves and [EMIM][PF<sub>6</sub>] under the optimized reaction conditions leads to a high ester yield.

The use of low-frequency high-intensity ultrasonic waves in biodiesel synthesis results in higher yield, shorter reaction time or milder conditions. Ultrasonication provides the mechanical energy for mixing and increases the mass transfer rate, leading to higher rate of transesterification, compared to that induced by mechanical agitation. When applied, ultrasound reduces the viscosity of the IL because of its cavitation effect, leading to the decrease of mass transfer limitation. ILs are used in ultrasound-assisted biodiesel synthesis as catalyst and cosolvent. 3-(*N,N,N*-triethylamino)-1-propanesulfonic hydrogen sulfate, [TEPSA][HSO<sub>4</sub>], is used as a catalyst in the ultrasound-assisted methanolysis of soybean oil and ensures higher reaction rate [109]. The efficiency of 19 different ILs as cosolvents in the soybean oil ultrasound-assisted methanolysis catalyzed by *Burkholderia cepacia* lipase was tested by Liu et al. [110]. The lipase activity decreases in the following IL's anion order: [PF<sub>6</sub>]<sup>−</sup> > [Tf<sub>2</sub>N]<sup>−</sup> > [OTf]<sup>−</sup> > [BF<sub>4</sub>]<sup>−</sup> > [CH<sub>3</sub>SO<sub>3</sub>]<sup>−</sup> ~ [Cl]<sup>−</sup>. The system with 1-octyl-3-methylpyridinium tetrafluoroborate, [OMPy][BF<sub>4</sub>], enables the highest ester yield because it dissolves methanol and glycerol readily and limits direct exposure of the lipase to these compounds.

The advantage of supercritical carbon dioxide (scCO<sub>2</sub>) for mass transfer combined with the high catalytic efficiency of enzymes in ILs results in continuous clean and sustainable biocatalysis in the IL/scCO<sub>2</sub> biphasic system that provides pure products. Lozano et al. [111] combined Novozym 435 and imidazolium-based hydrophobic ILs with large alkyl side chain (from C<sub>12</sub> to C<sub>18</sub>) for the methanolysis of triolein. The catalytic activity of the lipase increases with the hydrophobicity of anions ([Tf<sub>2</sub>N]<sup>−</sup> > [PF<sub>6</sub>]<sup>−</sup> > [BF<sub>4</sub>]<sup>−</sup>). A high methyl esters yield is achieved in the [C<sub>18</sub>mim][PF<sub>6</sub>]/scCO<sub>2</sub> biphasic system at 60 °C and 180 bar.

## 8. Mechanism and kinetics of IL- or DES-catalyzed biodiesel production

The mechanism of biodiesel production catalyzed by ILs or DES can be different from that in their absence. Because of the temperature-sensitive polyether group, the hydrogen bond can be formed between alcohol and oxygen of polyether group at low temperature, making the IL hydrophilic. Upon heating, the hydrogen bond is broken and the IL can become hydrophobic. Therefore, the reaction mixture in the presence of ILs is homogeneous at high temperature, while the biphasic system is formed upon cooling [14]. For better understanding transesterification process in the presence of ILs or DESs, the study on the catalytic mechanism is very significant. The knowledge of the transesterification reaction kinetics is needed for the production process development, design, operation, scale-up, analysis and control.

### 8.1. Acidic IL-catalyzed esterification

Only Fauzi et al. [112] have performed a kinetic study of the esterification of oleic acid with methanol in the presence of [BMIM][FeCl<sub>4</sub>] as a catalyst. The reaction follows a pseudo-first order reaction, with activation energy and pre-exponential factor of 17.97 kJ/mol and 181.62 min<sup>−1</sup>, respectively. These values are comparatively lower than those reported for both homogeneously- and heterogeneously-catalyzed esterification of oleic acid.

### 8.2. Acidic IL-catalyzed transesterification

The H<sup>+</sup> of Brønsted acid is the active center in acidic catalyzed transesterifications. Since ILs can be stronger organic acids than some mineral acids, they can ionize a proton faster. The proton and carbonyl group form a carbo-cation intermediate, which reacts with alcohol through nucleophilic substitution reaction, producing DAG, FAME and proton catalyzing the following reaction.

[C<sub>4</sub>SO<sub>3</sub>Hpy][HSO<sub>4</sub>] possesses two H<sup>+</sup> of Brønsted acid as active centers that can interact with the isolated electron pair at the O atom of carbonyl group, promoting two reaction pathways. Hence, the two mechanisms for the transesterification catalyzed by this IL are postulated [20]. In the first mechanism, the carbonyl group of TAG is firstly attacked by H<sup>+</sup> of cationic group of the IL, and an intermediate with the carbocation is produced. This intermediate reacts rapidly with the nucleophilic reagent (CH<sub>3</sub>OH), producing methyl ester and DAG. Lastly, the active species are reformed after release of H<sup>+</sup>. In the second mechanism, H<sup>+</sup> of the anionic group of the IL follows the same pathway of H<sup>+</sup> of the cationic group. The presence of H<sup>+</sup>-ions of both cationic and anionic group provides two active species, making this catalyst more efficient. Also, high catalytic activity of the [BSO<sub>3</sub>HMIM][HSO<sub>4</sub>]-Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in the transesterification of *Camptotheca acuminata* seed oil is based on the synergetic effect of its Brønsted ([BSO<sub>3</sub>HMIM][HSO<sub>4</sub>]) and Lewis (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) acidic parts, with different catalytic mechanisms [107]. The first mechanism is the transesterification reaction catalyzed by the Brønsted acidic part of the catalyst. This group can support a proton, and the protonation of the carbonyl group leads to forming the carbocation that suffers the nucleophilic attack of a methanol molecule, generating a tetrahedral intermediate, which leads to the formation of ester molecule and the regeneration of the catalyst. The second mechanism is the transesterification reaction catalyzed by the Lewis acidic part of the catalyst. The attraction of an electron from TAG by the Lewis acidic cation results in forming the carbocation, and after the nucleophilic attack of the methanol molecule to this carbocation, a tetrahedral intermediate is generated, which, again, forms ester molecule and regenerates the catalyst. The transesterification was proved to be a first order reaction with respect to TAG with the activation energy of 37.68 kJ mol<sup>−1</sup>.

The best catalytic activity of [BSPy][CF<sub>3</sub>SO<sub>3</sub>] in the transesterification of Jatropha oil is due to trifluoromethane sulfonic acid [21], which is a very strong organic acid because of the negative induction effect of fluorine atoms between CF<sub>3</sub><sup>−</sup> and HSO<sub>3</sub><sup>−</sup> groups. In addition, this IL shows the best immiscibility with the synthesized esters, shifting the transesterification equilibrium to the product side.

The soybean oil ethanolysis catalyzed by [NMP][CH<sub>3</sub>SO<sub>3</sub>] is a pseudo first-order reaction with respect to TAG [23], similarly to transesterification reactions catalyzed by mineral acids [113]. The same is observed for transesterification of rapeseed, sunflower, corn, olive and waste cooking oils with the rate constant between 0.36 and 0.44 h<sup>−1</sup>. For diluted IL solutions (up to 0.17 mol/L), the rate constant is proportional to the IL concentration, suggesting that the reaction kinetics is dependent only on the IL concentration.

### 8.3. Basic IL-catalyzed transesterification

The catalytic activity of basic [BMIM][OH] in glycerol trioleate methanolysis is mainly from OH<sup>−</sup>-anion [50]. In the beginning, methanol is converted to CH<sub>3</sub>O<sup>−</sup> because H<sup>+</sup> is taken away by strongly basic OH<sup>−</sup> anion paired with imidazolium cation of the IL. Then, the nucleophilic CH<sub>3</sub>O<sup>−</sup> attacks the carbonyl group in order to complete transesterification. For this reason, [BMIM][Cl] shows the worst catalytic activity, compared to the basic ILs having OH<sup>−</sup> anion.



The alkyl chain length of imidazolium ring cation also has an influence on the efficiency of the ILs. Because of the poor solubility in glycerol trioleate and the restricted mass transfer process caused by high viscosity, [EMIM][OH] are worse catalysts than [BMIM][OH]. The C2 of imidazolium cation in the IL possesses certain acidity in virtue of the charge delocalization on the conjugated five-ring molecule. Hydrogen bond can be formed between the H atom on C2 in the imidazolium ring with O of carbonyl group. This makes the electronegativity of O atom in carbonyl group dispersive. This interaction with carbonyl group does not happen when sodium hydroxide is used as a catalyst. The nucleophilic addition activity with  $\text{CH}_3\text{O}^-$  decreases the catalytic activity of basic ILs, which explains the lower yield of methyl oleate than in the processes catalyzed by inorganic bases.

ChOH possesses better basicity in the methanol solution, where its catalytic performance is promoted [52]. The  $\text{OH}^-$  of basic ionic liquid acts as an active center in the biodiesel synthesis through the transesterification of methanol. Both  $\text{OH}^-$  groups of ChOH as active centers interact with the isolated electron pair at the O atom of the methoxyl group. First, the methoxyl group from methanol is activated by the active  $\text{OH}^-$ , and then it is attacked by carbonyl group of TAG. The intermediate with methoxyl group translates into the DAG group producing methyl ester. When methanol molecules come in contact with the catalyst, the intermediate DAG group reacts rapidly with the nucleophilic reagent ( $\text{CH}_3\text{OH}$ ), thus giving methoxyl group and DAG. At the end, the other carbonyl group of DAG is also attacked by methoxyl group after activating, producing methyl ester in the same way. The extraction of glycerol from the reaction intermediate facilitates the transesterification reaction.

#### 8.4. DES-catalyzed transesterification

DESs can act in transesterification reactions in different ways like catalyst, solvating promoter and cosolvent. For instance, low conversion rate in the transesterification catalyzed by  $\text{ChCl}:\text{ZnCl}_2$  (molar ratio 1:2) DES is explained by weak acidity of  $\text{Zn}_2\text{Cl}_5^-$ , which is the predominant species [85]. On the other side, the  $\text{ChCl}:\text{glycerol}$  (1:2)/methanol mixture dissolves inactive layers of  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$  from the  $\text{CaO}$  catalyst surface because of its strong solvation ability, thus allowing a better contact between  $\text{CaO}$  and the reactants and making the transesterification more successful [90]. Furthermore, when  $\text{ChCl}:\text{glycerol}$  (1:2) is used as a cosolvent in the  $\text{NaOH}$ -catalyzed transesterification of rapeseed oil, FAMES are insoluble in the DES/methanol mixture, so the direct contact between FAME and  $\text{NaOH}$  is significantly reduced [102]. Since FAMES become a single phase, the saponification is minimized, resulting in easier separation and purification. The DES increases the dissolution of  $\text{NaOH}$  in the DES/methanol mixture, so a higher concentration of  $\text{CH}_3\text{O}^-$  needed for the transesterification is produced. The DES also captures glycerol during the reaction, which shifts the reaction equilibrium to the product side, thus increasing the FAME yield. The DES added in higher concentration inhibits the reaction, since excess glycerol molecules in DES bind with methanol molecules, which results in some free methanol molecules for the reaction, thus reducing the FAME yield. In addition, the hydroxyl group in the concentrated DES can compete with methanol in order to react with  $\text{NaOH}$ , which decreases the  $\text{CH}_3\text{O}^-$  concentration and the FAME yield.

## 9. Recyclability of ILs and DESs

Recyclability can involve separation, purification and reuse of ILs or DESs in successive steps. At first, ILs or DESs are separated from reactants and products (recovery step), then purified

(refining step) if necessary and finally reused in the process (recycling step). It has a great impact on their exploitation in industrial processes both from economic and environmental points of view. Since ILs are usually 2–100 times more expensive than organic solvents [114], their recovering and reusing will influence the overall process cost significantly [115]. Also, disposal of waste catalyst may have a negative effect on the environment. Recycling process is greatly influenced by the type of IL. In chemical reactions, hydrophobic ILs are more favorable, since a multiphase system is created at the end of the reaction. Formation of the biphasic system is also induced after adding potassium salt [116] or sucrose [117] to the hydrophilic IL, which helps the phase separation and permits the recycling of ILs. In addition, hydrophobic ILs are recovered by membrane technology more easily than hydrophilic ones [115].

### 9.1. Recovery of ILs and DESs

Separation of ILs or DESs from reactants and products proceeds to their recycling. With respect to the possibility of recovering, ILs and DESs are more superior than traditional homogeneous catalysts and solvents. Their advantage is easy separation from alkyl esters because of their low miscibility. A variety of techniques are used for recovering ILs and DESs such as distillation,  $\text{scCO}_2$  extraction, membrane separation technology, crystallization and sorption.

Low vapor pressure and high thermal stability of ILs allow using heating-based methods for their recovery. ILs can be retrieved after removal of volatile components by distillation. Zhao et al. [118] used distillation to remove methanol and methyl butyrate after esterification of aliphatic alcohols in the presence of Brønsted acidic ILs. However, distillation cannot be used when IL should be recovered from the components with a very high boiling point. In some cases, ILs can be recovered by  $\text{scCO}_2$  extraction as being insoluble in  $\text{scCO}_2$ , while organic compounds are soluble. An example is separation of  $[\text{BMIM}][\text{PF}_6]$  from a number of organic compounds by  $\text{scCO}_2$  extraction [119]. Membrane separation method can also be used. As long as an IL has different size and charge from other components, it can be separated by a proper membrane [120,121]. Pervaporation under mild operating conditions is used for recovering  $[\text{BMIM}][\text{PF}_6]$  from solutes [122]. Nanofiltration can separate hydrophilic ILs from non-volatile products in solutions [123]. Depending on the nature of the membrane, ILs are permeated or retained. The size of the cation has a great influence on the effectiveness of the method, with higher retention value in the case of dicationic ILs.

Crystallization is also an option for IL recovery. Usually, crystal formation results from simply cooling the mixture below certain temperature. The temperature at which an IL solidifies is significant for this method. Then, IL crystals can easily be separated from the liquid mixture by filtration under vacuum. Diego et al. [67] separated an IL from organic solvent by cooling the mixture under  $20^\circ\text{C}$ . ILs with heterogeneous or homogeneous properties improve the separation of the catalyst from the solvent. Zhou et al. [124] observed a homogeneous system in the esterification over benzothiazolium-based acidic ILs, but the IL crystallized at the end of the reaction and crystals precipitated after being cooled to room temperature. Crystallization of IL can also be done with addition of an antisolvent.  $\text{ChCl}$  is separated from glycerol by adding *n*-butanol as an antisolvent and cooling the mixture to  $-20^\circ\text{C}$  [93].

Physical adsorption is an attractive option since it is simple operation and the regeneration of the adsorbent lowers the cost [125]. Activated carbon is used for separating of imidazolium-based ILs from an aqueous solution [126]. The adsorption capacity is greatly influenced by the properties of both IL (hydrophobicity and size) and adsorbent (in the terms of its surface chemistry).

**Table 8**

A literature survey on optimization of biodiesel-producing reactions with the use of IL or DES.

Feedstock	Type, volume of reactor, cm <sup>3</sup> /type of agitator, agitation intensity, rpm	Alcohol	Applied reaction conditions			Optimization			Statistical method <sup>a</sup>	Reference
			Alcohol:oil molar ratio, mol/mol	Catalyst/loading, <i>n</i> (catalyst): <i>n</i> (oil) or wt% (to oil) or mol% (to oil)	Temperature, °C	Conversion (C) or yield (Y), %/time, h	Optimal reaction conditions	Conversion (C) or yield (Y), %/time, h		
Palmitic acid	Three-neck flask including 3 A mesoporous molecular sieves, 100/magnetic	Ethanol	8:1–16:1	[MIM-PSH] <sub>2.0</sub> HPW <sub>12</sub> O <sub>40</sub> /4.0–8.0 wt%	50–80	80.4–91.5 (Y)	13:1; 7.0 wt%; 80 °C	91.8 (Y)/5	BBD	<a href="#">[98]</a>
			12:1	[MIM-PSH]H <sub>2.0</sub> PW <sub>12</sub> O <sub>40</sub> /6.0 wt%	80		12:1; 6.0 wt%; 80 °C	85.1 (Y)/4	–	
				[MIM-PSH] <sub>1.5</sub> H <sub>1.5</sub> PW <sub>12</sub> O <sub>40</sub> /6.0 wt%				87.5 (Y)/4	–	
				[MIM-PSH] <sub>2.0</sub> HPW <sub>12</sub> O <sub>40</sub> /6.0 wt%				90.4 (Y)/4	–	
				[MIM-PSH] <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub> /6.0 wt%				88.4 (Y)/4	–	
Oleic acid	Three-necked flask, 100/ stirring	Methanol	8.5–8.6	[MIM-PSH] <sub>3.0</sub> PW <sub>12</sub> O <sub>40</sub> /6.0 wt% [BMIM][HSO <sub>4</sub> ]/0.62:1–1.28:1 <sup>b</sup> 0.031–0.064 mol	86.5–87.6	69.4–99.2 (Y) (predicted) 80.1–80.9 (C) (predicted)	9:1; 1.2:1 <sup>b</sup> ; 87 °C	84.8 (Y)/4 81.8 (Y)/5.2	– CCD	<a href="#">[99]</a>
Oleic acid	Three-necked flask, 100/–	Methanol	21.9:1–26.7:1	[BMIM][FeCl <sub>4</sub> ]/0.03–0.14 <sup>b</sup>	65	69.3–85.6 (Y) (predicted) 80.3–90.7 (C) (predicted)	22:1; 0.03:1 <sup>b</sup> ; 65 °C	83.4 (Y)/3.6	CCD	<a href="#">[112]</a>
Oleic acid	Round bottom flask, 50/ magnetic, 500	Methanol	1:1–5:1	[BHSO <sub>3</sub> MIM][HSO <sub>4</sub> ]/8.0–12.0 wt%	100–140	62.0–96.6 (Y)	4:1; 10.0 wt%; 130 °C	97.7 (Y)/4	BBD	<a href="#">[100]</a>
			2:1	[BHSO <sub>3</sub> MIM][HSO <sub>4</sub> ]/10.0 wt%	80		2:1; 10.0 wt%; 80 °C	72.4 (Y)/4		
Palmitic acid			4:1	[BMIM][HSO <sub>4</sub> ]/10.0 wt% [BHSO <sub>3</sub> MIM][HSO <sub>4</sub> ]/10.0 wt%	130		4:1; 10.0 wt%; 130 °C	60.0 (Y)/4 94.7 (Y)/4		
Waste oil (72% FFA)			8:1		140		8:1; 10.0 wt%; 140 °C	88.5 (Y)/4 94.9 (Y)/6		
Soybean	Stainless-steel autoclave, 100/magnetic	Methanol	6:1–16:1	[(CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> N(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> H][HSO <sub>4</sub> ]/2.0–6.0 wt%	80–160	80.69–95.96 (Y)	14:1, 4.0 wt%, 120 °C	94.8 (Y)/8.7	CCRD	<a href="#">[101]</a>
Rapeseed oil	Round-bottom flask/vertical blender, 300	Methanol	3:1–9:1	ChCl:glycerol (1:2)/0–20.0 wt% with NaOH/0.5–1.5 wt%	65	72.0–95.0 (Y)	6.95:1; 9.27 wt% DES; 1.34 wt% NaOH; 65 °C	98.0 (Y)/2	BBD	<a href="#">[102]</a>

<sup>a</sup> BBD – Box–Behnken experimental design; CCD – central composite design; CCRD – central composite rotatable design.<sup>b</sup> mol/mol.



**Table 9**  
A literature survey on novel technologies of biodiesel production using ILs.

Feedstock	Other catalyst (if present)/wt% (to oil)	Type, volume of reactor, cm <sup>3</sup> /type of agitator, agitation intensity, rpm	Frequency/power	Alcohol	Alcohol:oil molar ratio, mol/mol	Catalyst/loading, $\eta$ (catalyst): $\eta$ (oil) or wt% (to oil) or mol% (to oil) or mmol catalyst/g oil	Temperature, °C	Optimal reaction conditions	Conversion (C) or yield (Y), %/Time, h	Reference
Waste cooking oil	–	Microwave synthesis/magnetic, 600		Methanol	6:1–12:1	1.0 wt% [MorMeA][Br] + 0.75 wt% NaOH/0.25–1.5 wt%	40–90	9:1; 1.0 wt% [MorMeA][Br] + 0.75 wt% NaOH; 70 °C	98.1 (Y)/0.1167	[105]
<i>C. acuminata</i> oil	–	Digital microwave-assisted reactor/magnetic		Methanol	3:1–7:1	[BSO <sub>3</sub> HMIM][HSO <sub>4</sub> ]-Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> /1.0–5.0 wt%	40–80	5:1; 4.0 wt%; 60 °C; molar fraction Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> : [BSO <sub>3</sub> HMIM][HSO <sub>4</sub> ] = 3:1	95.7 (Y)/1	[107]
Soybean oil	Novozym 435/1.0–10.0	Multimode microwave reactor (MCR-3) and three-neck round bottomed flask, 10/ magnetic, 0–500	160–800 W	Methanol	1:1–18:1	[BSO <sub>3</sub> HMIM][HSO <sub>4</sub> ]/5.0 wt% [EMIM][PF <sub>6</sub> ]/0–4 (IL to oil, v/v) [BMIM][PF <sub>6</sub> ] [EMIM][TfO] [OMIM][Tf <sub>2</sub> N]	60	6:1; 6.0 wt% lipase; 2:1 IL (v/v); water activity 0.33; 60 °C; 480 W microwave power; 200 rpm	578 ± 3.1 (Y)/0.5	[108]
Soybean oil	–	Reactor with a jacket	24 kHz/200 W	Methanol	3:1–15:1	[TEPSA][HSO <sub>4</sub> ]/0.25–1.0 wt%	20–80	9:1; 1.0 wt%; 60 °C; ultrasound (24 kHz, 200 W)	86.0 ± 4 (Y) 79.0 ± 3 (Y) 53.0 ± 2 (Y)	[109]
Soybean oil	<i>B. cepacia</i> lipase/4.0	Screw capped vial, 5/thermostatic shaking bed, 200	40 kHz	Methanol	41.15:1	[OmPy][BF <sub>4</sub> ]/1 mL/mol oil	50	41.15:1; 4.0 wt% lipase; 1 mL IL/mol oil; 50 °C; ultrasound (40 kHz)	93.2 (C)/1 82.2 ± 1.2 (Y)/12	[110]

Among several sorption methods, the ion exchange resin (Amberlite IRN-150) and activated carbon are the most efficient in the sorption of [BMIM] cation and recovering [BMIM][Cl] [127].

#### 9.1.1. Acidic IL catalysts used in esterification

Several methods of different complexity are employed to recover acidic ILs used in esterification. In some cases, water and alcohol in excess should previously be removed by distillation under vacuum. [NMP][CH<sub>3</sub>SO<sub>3</sub>] can be recycled after the water removal [12], [TMEDAPS][HSO<sub>4</sub>] is recovered by centrifugation [13], while MPEG-350-IL is separated from methanol by vacuum distillation [14]. After removing water and methanol, [DDPA][Tos] is recovered by centrifugation and then washed with petroleum ether to remove the organic ester [15], while 3,3'-(octane-1,8-diyl)-bis(4-sulfobenzyl-1*H*-imidazol-3-ium) hydrogensulfate (IL8B) is precipitated, washed with ethyl acetate and dried under vacuum at 70 °C [16]. After being separated, [Hnmp][HSO<sub>4</sub>] is dried by rotary evaporation [17].

#### 9.1.2. Acidic IL catalysts used in transesterification

Several different approaches are applied for recovering acidic IL catalysts used in transesterification. A simple procedure includes cooling the final reaction mixture down to room temperature in order to form two phases of methyl esters (lower layer) and a mixture of the IL and excess methanol (upper layer) that are simply separated by decantation [18,20]. The separated IL contains water, methanol and little glycerol. Usually, the excess alcohol and water are at first removed from the IL phase by atmospheric distillation at 100 °C, while crude glycerol is removed by vacuum distillation at 180–210 °C. Further procedure varies from study to study. When an IL is insoluble in the organic phase, it is simply separated by decantation [21] or centrifugation [11,100]. Sometimes, the separated IL is washed with an organic solvent like ethyl acetate [21], diethyl ether [98] or *n*-hexane [25,26,100] and dried under vacuum. Sometimes, after distillation of excess ethanol, spontaneous phase separation takes place that forms a clean biphasic system [23]. At this point, the ethyl esters can be separated from glycerol/IL mixture or the glycerol-based additive-blended biodiesel can be produced. In some cases, more simple procedures can be employed. [BMIM][HSO<sub>4</sub>] and [BMIM][FeCl<sub>4</sub>] are, after being separated from the lower layer, only heated at 105 °C up to 24 h [99,112], while [(CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>H][HSO<sub>4</sub>] is purified and dried under vacuum for 5 h at 120 °C after each transesterification reaction [101]. Also, water is removed from the used [TEPSA][HSO<sub>4</sub>] by distillation [109].

#### 9.1.3. Acidic ILs combined with other catalysts, supported or used as supporting material

This type of ILs is usually recoverable although there are catalytic systems, such as [Sn(3-hydroxy-2-methyl-4-pyrone)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] immobilized onto 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF<sub>6</sub>]), unsuitable for recycling because of catalyst leaching from the ionic phase [27]. The same tin complex immobilized on BMI · InCl<sub>4</sub> can, however, be recovered from glycerol by freezing or by water washing, but the recovered IL phase shows no catalytic activity because of decomposition [28]. The separated BMI · NTf<sub>2</sub> is washed with water and dried under reduced pressure [29]. It is worth mentioning that in the case of using BMI · NTf<sub>2</sub> under acidic conditions H<sub>2</sub>SO<sub>4</sub> is almost exclusively retained in the IL.

In several cases [32–42], after the excess methanol removal by vacuum distillation and the glycerol removal by freezing, ILs are recovered by filtration or centrifugation and then washed with organic solvents (ethyl acetate, diethyl ether, dichloromethane or *n*-hexane) or dried in the air or under vacuum. Specific properties of some catalytic systems may make their separation from the

reaction mixture easier. Because of its magnetic properties, the catalytic system  $[\text{SO}_3\text{H}-(\text{CH}_2)_3\text{-HIM}][\text{HSO}_4]/\text{Fe}_3\text{O}_4 \cdot \text{SiO}_2$  is separated by magnetic force with smaller loss, compared to filtration or centrifugation [31].

#### 9.1.4. Acidic IL catalysts used in two-step processes

After removal the excess methanol by vacuum distillation, the IL is centrifuged, washed with an organic solvent (ethyl acetate) and dried under vacuum in order to remove traces of water and methanol [45,47]. Alternatively, the final reaction mixture can at first be centrifuged to get a biphasic mixture. The lower layer is subjected to vacuum distillation to separate water and excess methanol from the IL, which is then washed with diethyl ether and dried under vacuum [48].

#### 9.1.5. Basic IL catalysts

Usually, methanol is removed by atmospheric distillation, while glycerol is separated from the IL by either vacuum distillation [49,51] or solvent extraction (dichloromethane, mixture of *n*-butanol and water 1:2) [50,52,53]. Then, the IL is centrifuged, washed with an organic (ethyl acetate) and dried under vacuum. Alternatively, the final reaction mixture is centrifuged to form a biphasic system, excess methanol in the upper phase is evaporated and the catalytic system  $\text{IL}_2\text{NaOH}_{0.75}$  is removed by adding silica gel and washed by water [105].

#### 9.1.6. ILs used as cosolvents

At the end of biocatalyzed transesterification process, the IL is separated from the enzyme by filtration, washed with organic solvents (*tert*-butanol and acetone) and dried under vacuum [108]. Sometimes, the IL is washed with water to remove glycerol and dried under vacuum [55]. In many cases, the separation of ILs is more complicated as three-layer systems are formed [67] or its formation is induced by adding water [56]. ILs are located in the bottom layer with no residual FAME and glycerol. Separation of the enzyme-IL mixture is done in steps. At first, glycerol and FAME are extracted with water and *n*-hexane, respectively. Then, the enzyme reactor is cooled to under 20 °C in order to cause the solidification of the IL. The enzyme-IL mixture is finally treated by vacuum to fully eliminate any residual organic solvent. When water is added to the final reaction mixture, a third phase is formed between the layers, allowing the simple IL removal by decantation, while Novozym 435 remained in the reactor [56]. Some amount of water left is distilled from the IL. It is recommended that the lipase and the IL remain in contact for reuse, after removing the excess methyl acetate. In a similar study [57], the bottom IL layer and the immobilized lipase are left in the system without any purification steps. According to Devi et al. [69], who used Ammoeng 102 and Ammoeng 120 in the oil/IL reaction system, the enzyme (Novozym 435) is suspended in between the two phases, forming a relatively stable cloudy interphase. After centrifugation and decantation of the esters, the Novozym 435/IL phase is separated by filtration [65]. Alternatively, the PEL-catalyzed reaction mixture is first centrifuged and then glycerol and FAMES are extracted from the liquid phase by water and *n*-hexane, respectively [59]. The resulting IL is heated at 85 °C for 7 days to remove the residual solvents. Because the PEL is in the form of fine particles, it is not suitable for recycling. After separation from  $[\text{BMIM}][\text{PF}_6]$  by decantation, the remaining Novozym 435 particles are washed 3 times with *n*-hexane and ethanol and air-dried at room temperature [61]. Alternatively, *P. cepacia* lipase is removed from the IL by filtration, washed with water and dried under vacuum [62].

#### 9.1.7. Recovery of DESs used as catalysts

When the biphasic system is formed, as in the case of the NaOH-catalyzed transesterification of rapeseed oil in the presence of ChCl:

glycerol (1:2) used as cosolvent, complete phase separation is achieved in several hours or days [102]. The formation of the separate phase containing DES can be induced by methanol evaporation [87–89] or freezing at 0 °C [86]; then DES is easily separated by centrifugation. A more complex procedure must be applied for recovering the DES (ChCl:glycerol, 1:2) from the final reaction mixture of the CaO-catalyzed reaction, which settles into three layers: the upper ester layer, the middle layer containing glycerol, the DES and excess methanol and the lower CaO layer [90]. The catalyst is filtered, washed with ethanol and dried for 24 h at 70 °C. After only 30 s, the DES-containing mixture is separated into two layers, since FAMES are not soluble in the DES/methanol/glycerol system. When the product is the reaction top phase, the bottom phase contains ChCl:glycerol (1:2), excess glycerol and methanol, while Novozym 435 is in between these layers [4]. After filtration of the reaction mixture, the enzyme is washed with water and diethyl ether and dried.

### 9.2. Reuse of ILs and DESs

No significant reduction in catalytic activity of most recycled ILs and DESs is observed, even after being used several times. The literature on catalytic activity of recycled ILs and DESs is reviewed in Table 10, where the number of successive uses and the conversion/ester yield in the first and final steps are emphasized.

#### 9.2.1. Recycled acidic IL catalysts in esterification

Generally, these ILs are reusable for several times with high ester yield in repeated cycles. After 8 cycles,  $[\text{NMP}][\text{CH}_3\text{SO}_3]$  gives the ester yield of 90.7% in the esterification of oleic acid [12]. After the separation of water under vacuum,  $[\text{TMEDAPS}][\text{HSO}_4]$  is reusable for at least 6 times with a minor decrease in the conversion [13]. Amphiphilic Brønsted acidic IL MPEG-350-IL is used 5 times in the oleic acid esterification with methanol without significant decrease of its catalytic activity, providing the conversion degree higher than 80.0% [14].  $[\text{DDPA}][\text{Tos}]$  shows a high catalytic activity in the same reaction after 9 cycles [15]. When IL8B is used in the esterification of oleic acid with methanol, no significant loss of activity is detected after 7 cycles [16].  $[\text{Hnmp}][\text{HSO}_4]$  is successfully recycled and maintained activity in the esterification of lauric acid with methanol, providing the conversion of 95.89% after the fifth cycle [17].

#### 9.2.2. Recycled acidic IL catalysts in transesterification

After the transesterification of waste oil by methanol,  $[(\text{CH}_2)_4\text{SO}_3\text{HPy}][\text{HSO}_4]$  is separated by simple decantation and exploited nine times, with a small decrease in the ester yield [19]. The same IL is used six times in the biodiesel synthesis from soybean oil with the ester yield higher than 90.0% [20]. The multi- $\text{SO}_3\text{H}$  functionalized strong Brønsted acidic IL is used 10 times in the methanolysis of rapeseed oil without any significant decrease in its catalytic activity [11].  $[\text{BSPy}][\text{CF}_3\text{SO}_3]$  is active in 7 successive cycles of the *Jatropha* oil transesterification [21]. Recyclability test of  $[\text{HDSSBD}][\text{HSO}_4]$  in the canola oil methanolysis gives good results, since after 8 runs the conversion degree is 85.9% [25]. The methanolysis of bitter apple oil over  $[\text{SBP}][\text{HSO}_4]$  is successful in 7 successive cycles [22]. The conversion degree is 90.0% in four cycles of the soybean oil ethanolysis in the presence of  $[\text{NMP}][\text{CH}_3\text{SO}_3]$  [23]. However, when this IL contaminated with glycerol is used, high conversion is achieved only until the third cycle. After 7 runs, the conversion degree in the methanolysis of *N. sativa* seed oil over ILH2 is 89.4% [26].

#### 9.2.3. Recycled acidic ILs combined with other catalysts, supported or used as supporting material

$\text{Sn}(3\text{-hydroxy-2-methyl-4-pyrone})_2(\text{H}_2\text{O})_2$  immobilized onto  $[\text{BMIM}][\text{PF}_6]$  is not suitable for recycling because of the catalyst

Recycled acidic and basic ILs and ILs combined with other catalysts, supported or used as supporting material used in biodiesel production.

Type of IL/DES	IL/DES	Feedstock	Alcohol	Number of cycles	Conversion (C) or yield (Y), %		Reference
					First cycle	Final cycle	
Acidic ILs as catalysts in esterification	[NMP][CH <sub>3</sub> SO <sub>3</sub> ]	Oleic acid	Ethanol	8	95.3 (C)	90.7 (C)	[12]
	[TMEDAPS][HSO <sub>4</sub> ]	Oleic acid	Ethanol	6	95.0–96.0 (C)	~92.0 (C)	[13]
	MPEG-350-IL	Oleic acid	Methanol	5	~85.0 (C)	~82.0 (C)	[14]
	[DDPA][Tos]	Oleic acid	Methanol	9	96.5 (C)	> 90.0 (C)	[15]
	IL8B	Oleic acid	Methanol	7	95.0 (Y)	> 85.0 (Y)	[16]
	[Hnmp][HSO <sub>4</sub> ]	Lauric acid	Methanol	5	97.41 (C)	95.89 (C)	[17]
	[MIM-PSH] <sub>2.0</sub> HPW <sub>12</sub> O <sub>40</sub>	Palmitic acid	Ethanol	6	91.8 (Y)	83.3 (Y)	[98]
	[BMIM][HSO <sub>4</sub> ]	Oleic acid	Methanol	5	81.8 (Y)	> 80.0 (Y)	[99]
	[BMIM][FeCl <sub>4</sub> ]	Oleic acid	Methanol	6	83.4 (C)	~65.0 (C)	[112]
	[BHSO <sub>3</sub> MIM][HSO <sub>4</sub> ]	Oleic acid	Methanol	10	97.7 (Y)	93.2 (Y)	[100]
Acidic ILs as catalysts in transesterification	[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HPy][HSO <sub>4</sub> ]	Soybean oil	Methanol	6	94.5 (Y)	90.1 (Y)	[20]
	Multi-SO <sub>3</sub> H functionalized Brønsted acidic IL	Rapeseed oil	Methanol	10	98.2 (Y)	~98.0 (Y)	[11]
	[BSPy][CF <sub>3</sub> SO <sub>3</sub> ]	Jatropha oil	Methanol	7	92.0 (Y)	~80.0 (Y)	[21]
	[HDSSBD][HSO <sub>4</sub> ]	Canola oil	Methanol	8	95.1 (C)	85.9 (C)	[25]
	[SBP][HSO <sub>4</sub> ]	Bitter apple oil	Methanol	7	89.5 (Y)	~89.5 (Y)	[22]
	[NMP][CH <sub>3</sub> SO <sub>3</sub> ]	Soybean oil	Ethanol	4	with glycerol 96.7 (C); without glycerol 96.9 (C)	with glycerol 71.2 (C); without glycerol 90.0 (C)	[23]
	ILH2	<i>N. sativa</i> seed oil	Methanol	7	93.2 (C)	89.4 (C)	[26]
	[(CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> N(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> H][HSO <sub>4</sub> ]	Soybean oil	Methanol	6	94.8 (Y)	> 90.0 (Y)	[101]
	[TEPSA][HSO <sub>4</sub> ] <sup>a</sup>	Soybean oil	Methanol	5	93.2 (C)	86.4 (C)	[109]
	[BMI][InCl <sub>4</sub> ] and Sn(3-hydroxy-2-methyl-4-pyrone) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	Soybean oil	Methanol	2	83.0 (Y)	25.0 (Y)	[28]
Acidic ILs combined with other catalysts, supported or used as supporting material	[Et <sub>3</sub> NH]Cl-AlCl <sub>3</sub> (x(AlCl <sub>3</sub> ) = 0.7)	Soybean oil	Methanol	6	98.5 (Y)	> 98.0 (Y)	[36]
	MB3B <sup>b</sup>	Oleic acid	Methanol	8	92.8 (C)	85.3 (C)	[38]
	MBIL8B <sup>c</sup>	Oleic acid	Ethanol	7	93.1 (Y)	80.3 (Y)	[39]
	[SO <sub>3</sub> H-PIm-CPMS][HSO <sub>4</sub> ]/Fe-SBA-15	Oleic acid	Methanol	6	87.7 (C)	80.8 (C)	[30]
	[SO <sub>3</sub> H-(CH <sub>2</sub> ) <sub>3</sub> -HIM][HSO <sub>4</sub> ]-Fe <sub>3</sub> O <sub>4</sub> ·SiO <sub>2</sub>	Oleic acid	Ethanol	8	92.9 (C)	~80.0 (C)	[31]
	[BnMim][HSO <sub>4</sub> ]·silica	3-Phenylpropionic acid	Ethanol	4	92.0 (Y)	81.0 (Y)	[40]
	OMR-[C <sub>4</sub> HMTA][SO <sub>4</sub> H]	Brown grease	Methanol	5	> 99.0 (C)	> 96.0 (C)	[41]
	PIL <sup>d</sup>	Waste oil	Methanol	6	> 99.0 (Y)	99.0 (Y)	[33]
	PIL <sup>e</sup>	Waste oil	Methanol	6	99.0 (Y)	99.0 (Y)	[42]
	PIL <sup>f</sup> , m(IL)/m(PDVB) = 1:1	Waste oil	Methanol	6	99.0 (Y)	~99.0 (Y)	[35]
Acidic ILs as catalysts in the esterification of oil, followed by alkaline-catalyzed transesterification	PIL <sup>g</sup>	Waste oil	Methanol	6	> 99.0 (Y)	> 99.0 (Y)	[34]
	IL <sub>1</sub> NaOH <sub>0.75</sub> (1 wt% [Mor-MeA][Br] + 0.75 wt% NaOH) <sup>h</sup>	Waste oil	Methanol	7	98.1 (Y)	97.7 (Y)	[105]
	[BSO <sub>3</sub> HMIM][HSO <sub>4</sub> ]-Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (molar ratio 1:3) <sup>h</sup>	<i>C. acuminata</i> seed oil	Methanol	9	95.7 (Y)	72.3 (Y)	[107]
	[BSPIM][HSO <sub>4</sub> ]	Crude palm oil	Methanol	7	95.7 (C)	> 95.0 (C)	[47]
	[MSBIM][HSO <sub>4</sub> ]	<i>C. colocynthis</i> oil	Methanol	8	> 97.0 (C)	97.0 (C)	[45]
	[DSIM][HSO <sub>4</sub> ]	<i>C. colocynthis</i> oil	Methanol	8	95.4 (C)	> 95.0 (C)	[46]
	[BSMIM][Cl]	Jatropha oil	Methanol	4	92.5 (C)	88.1 (C)	[48]
	IMC <sub>2</sub> OH	Cottonseed oil	Methanol	7	98.5 (C)	96.2 (C)	[49]
	[BMIM]OH	Glycerol trioleate	Methanol	6	> 86.0 (C)	~82.0 (C)	[50]
	[BMIM]Im	Rapeseed oil	Methanol	6	~95.0 (Y)	~95.0 (Y)	[51]
Basic ILs as catalysts in transesterification	[BMIM]Im	Soybean oil	Methanol	6	> 95.0 (Y)	> 95.0 (Y)	

Table 10 (continued)

Type of IL/DES	IL/DES	Feedstock	Alcohol	Number of cycles	Conversion (C) or yield (Y), %		Reference
					First cycle	Final cycle	
DESs as catalysts in biodiesel production	DEAC:PTSA (1:3)	Palm oil, low grade	Methanol	4	93.0 (Y)	87.0 (Y)	[87]
	P-DES (1:3)	Palm oil, low grade	Methanol	4	90.53 (C)	< 80.0 (C)	[88]
	ChCl:PTSA (1:3)	Palm oil, crude	Methanol	3	96.0 (Y)	95.0 (Y)	[89]
	ChCl:glycerol (1:2) <sup>n</sup>	Rapeseed oil	Methanol	5	91.9 (Y)	~85.0 (Y)	[90]
	ChCl:glycerol (1:2) <sup>i</sup>	Soybean oil	Methanol	4	88.0 (C)	79.0 (C)	[4]

<sup>a</sup> Ultrasound-assisted.<sup>b</sup> Bentonite modified with 3,3'-(butane-1,6-diyl)bis(6-sulfo-1-(4-sulfobenzyl)-1H-benzimidazolium) hydrogensulfate.<sup>c</sup> Modified bentonite with 3,3'-(octane-1,8-diyl)bis(4-sulfobenzyl-1H-imidazol-3-ium) hydrogensulfate.<sup>d</sup> Solid acidic ionic liquid polymer made by copolymerization of [SO<sub>3</sub>H(CH<sub>2</sub>)<sub>3</sub>VPy][HSO<sub>4</sub>] oligomers and DVB.<sup>e</sup> Solid acidic ionic liquid polymer made by copolymerization of [SO<sub>3</sub>H(CH<sub>2</sub>)<sub>3</sub>VIm][HSO<sub>4</sub>] oligomers and DVB.<sup>f</sup> Acidic ionic liquid polymer made by copolymerization of [SO<sub>3</sub>H(CH<sub>2</sub>)<sub>3</sub>VIm][HSO<sub>4</sub>] with PDVB.<sup>g</sup> Obtained by copolymerization of 1-(3-sulfopropyl)triethylammonium hydrogen sulfate oligomers with DVB.<sup>h</sup> Microwave-assisted.<sup>i</sup> With Novozym 435.<sup>j</sup> With *P. expansum* lipase.<sup>k</sup> With *P. cepacia* lipase.<sup>l</sup> With Burkholderia cepacia lipase.<sup>m</sup> With H<sub>2</sub>SO<sub>4</sub> (20.0 wt%).<sup>n</sup> With non-calcinated CaO.

leaching from the ionic phase [27]. The catalytic activity of the same tin complex immobilized in BMI · InCl<sub>4</sub> also decreases in the second recharge, providing the ester yield of only 25.0% [28]. The catalytic systems of H<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>CO<sub>3</sub> immobilized on BMI · NTF<sub>2</sub> are reused six and three times, respectively in the soybean oil conversion into biodiesel, without a significant drop in activity [29]. Also, the ester yield is not significantly reduced after 6 cycles of using [Et<sub>3</sub>NH]Cl-AlCl<sub>3</sub> (x(AlCl<sub>3</sub>)=0.7)) in the methanolysis of soybean oil [36]. MB3B retains its catalytic activity in the esterification of oleic acid with methanol in eight cycles, providing the conversion degree of 85.3% [38]. After the seventh run, MBIL8B provides the ethyl oleate yield of 80.3% [39].

The reusability experiments of [SO<sub>3</sub>H-Plm-CPMS][HSO<sub>4</sub>]/Fe-SBA-15 in the oleic acid esterification with methanol show the conversion to methyl ester of 80.8% after the sixth cycle [30]. [SO<sub>3</sub>H-(CH<sub>2</sub>)<sub>3</sub>-HIM][HSO<sub>4</sub>] immobilized onto the surface of Fe<sub>3</sub>O<sub>4</sub> · SiO<sub>2</sub> is reused in the oleic acid esterification with ethanol in 8 runs, providing the conversion degree of 84.3% [31]. [BsAIM][OTf] immobilized onto MPS-SiO<sub>2</sub> is used several times in the oleic acid esterification, but its reusability is poor since the conversion of oleic acid to methyl oleate is greatly decreased after the third cycle [32]. [BnMIM][HSO<sub>4</sub>] dispersed onto the high surface area silica gel is reusable and gives the ester yield of 81.0% after the fourth cycle [40]. Recyclability testing of OMR-[C<sub>4</sub>HMTA][SO<sub>4</sub>H] in the reaction of raw brown grease oil with methanol gave excellent results: after the fifth cycle, the FFA conversion is > 96.0% [41].

The solid acidic IL polymer, made through the copolymerization of [SO<sub>3</sub>H(CH<sub>2</sub>)<sub>3</sub>VPy][HSO<sub>4</sub>] oligomers and DVB, is used six times in the waste oil methanolysis with the ester yield of 99.0% [33]. Similar solid acidic IL polymers, made through the copolymerization of [SO<sub>3</sub>H(CH<sub>2</sub>)<sub>3</sub>VIm][HSO<sub>4</sub>] oligomers and DVB [42] or PDVB [35], also show good catalytic activity in 6 cycles of the same waste oil methanolysis.

#### 9.2.4. Recycled acidic IL catalysts in the esterification stage of two-step processes

In a two-stage process, [BSPIM][HSO<sub>4</sub>] gives the FFA conversion higher than 95.0% in 7 batches of the crude palm oil esterification step [47]. Also, the catalytic activity of [MSBIM][HSO<sub>4</sub>] decreases insignificantly after being used 8 times in the biodiesel synthesis from crude *C. colocynthis* oil [45]. In addition, [DSIM][HSO<sub>4</sub>] is used 8 times with the FFA conversion degree > 95.0% [46]. [BSMIM][Cl]

is reusable 4 times in the IL-catalyzed esterification step of the two-step process of *J. curcas* oil conversion, showing minor loss in the catalytic activity [48].

#### 9.2.5. Recycled basic IL catalysts in transesterification

After IMC<sub>2</sub>OH is used 7 times in the methanolysis of cottonseed oil, the ester yield is 96.2% [49]. In case of the glycerol trioleate methanolysis, [BMIM][OH] is used 6 times without a significant drop in its catalytic activity [50]. Also, [BMIM][Im] is successfully used 6 times in the methanolysis of different vegetable oils, giving the ester yield around 95.0% with each oil tested [51]. ChOH shows good reusability in the methanolysis of soybean oil, providing the yield of biodiesel of 82.5% in 4 successive cycles [52]. ChOH is also used 4 times in the non-treated *Jatropha* oil methanolysis, giving the ester yield of 89.0% [53].

#### 9.2.6. Recycled ILs as solvents in biocatalyzed transesterification

Recovered hydrophobic ILs [BMIM][PF<sub>6</sub>] and [EMIM][PF<sub>6</sub>] are efficient solvents in the Novozym 435-catalyzed sunflower oil methanolysis, showing no decrease in the enzyme activity in 4 cycles [55]. The [C<sub>18</sub>MIM][NTf<sub>2</sub>]/Novozym system is successfully used 7 times in the triolein methanolysis [64]. [C<sub>16</sub>MIM][NTf<sub>2</sub>] and [C<sub>18</sub>MIM][NTf<sub>2</sub>] are good solvents for the *Candida antarctica* lipase B-catalyzed methanolysis of triolein, since both the ILs and the enzyme can be recycled and reused [67]. The ester yield close to 100% is achieved in 9 cycles of the [C<sub>16</sub>MIM][NTf<sub>2</sub>]-catalyzed reaction. However, in the system with [C<sub>18</sub>MIM][NTf<sub>2</sub>], the ester yield drops after the seventh cycle because the high IL hydrophobicity that lowers the enzyme stability. Novozym 435 is also reused several times in the methanolysis of rapeseed oil without significant drop in activity, while Ammoeng 102 is successfully recovered and reused more than 10 times [69]. After the fifth cycle of using [BMIM][PF<sub>6</sub>] the conversion yield of 78.9% is achieved in the PEL-catalyzed methanolysis of *M. pinnata* seed oil. After the fifth reuse, Novozym 435 shows conversion efficiency of 97.3% [61]. The catalytic system of *P. cepacia* lipase and [BMIM][NTf<sub>2</sub>] is used 4 times in the production of biodiesel from soybean oil without no decrease in catalytic activity and selectivity [62].

#### 9.2.7. Recycled DESs in biodiesel synthesis

The catalytic system consisting of 95.0 vol% of H<sub>2</sub>SO<sub>4</sub> and ChCl: ZnCl<sub>2</sub> (1:2) is used in the palm oil transesterification, then isolates



**Table 11**  
SWOT analysis of using ILs/DESs in biodiesel production.

Strengths	Weaknesses
<p>Brønsted acidic ILs are more efficient and less corrosive than traditional acidic catalysts (mineral acids). Require mild reaction conditions, low energy demand and low waste treatment. Ensure high biodiesel yield and low possibility of the saponification.</p> <p>Reduce the number of processing steps. IL/biocatalyst systems result in higher selectivity, flexibility in choosing different enzymes for different substrates, increased reaction rate, greater enzyme stability and allowing a small amount of water in substrates. More easily removable from the end reaction mixture because of their low miscibility with alkyl esters. Can be recovered and reused (especially hydrophobic ones).</p> <p>Superior to traditional homogeneous catalysts and solvents with respect to the possibility of recovering. Generate less amounts of wastewater. Attractive physical and chemical properties (wide liquid range, high chemical and thermal stabilities, water and acid resistance, negligible vapor pressure, low flammability, high ionic conductivity, high thermal conductivity, wide electro-chemical potential window). Successful in dissolving wide range of organic and inorganic compounds. Efficient in removing glycerol and remaining alkaline catalyst from crude biodiesel. Possess greater extraction efficiency than common extracting solvents for recovering lipids from microalgal biomass.</p> <p>Opportunities Possibility of different uses (catalyst, cosolvent and extracting solvent) in various steps of the biodiesel production process.</p> <p>Possibility of combination with other catalysts or being used supported onto other materials. Possibility of being used with low-cost feedstocks (waste and non-edible oils). Possibility of being used in novel transesterification technologies (microwave and ultrasound irradiation, with supercritical fluids like CO<sub>2</sub>). Possibility of being used as a cosolvent in combination with other (bio)catalysts to improve their stability and catalytic capability. The enzymatic synthesis of biodiesel with ILs and DESs is a greener alternative to chemical methods. Easier biodiesel separation and purification methods. Recyclability and reusability. Ability to dissolve various compounds, controlled miscibility with organic solvents and possibility of being combined with organic solvents for improving the biomass's oil extraction efficiency. Use of DESs instead of ILs wherever possible because of the advantages such as easy preparation, high purity, low cost (cheaper components for preparation - natural organic salts and complexing agents), no reactivity with water, non-toxicity and biodegradability.</p>	<p>High cost of ILs</p> <p>Complex synthesis and expensive starting reactants for some ILs. Considerable initial investments are needed for the registration and the gathering of the full physico-chemical characterization and eco-toxicity data. High viscosity (affecting processing costs). Many enzymatic transesterification reactions with ILs or DESs are heterogeneous systems involving a complicated liquid-liquid interface.</p> <p>Uncertainty regarding their stability under a prolonged use</p> <p>Traditional recovery and purification methods used for recovering are energy and cost demanding. Many ILs are poorly biodegradable.</p> <p>Some ILs are relatively toxic for the environment. Little information of whole life-cycle assessment.</p> <p>Threats The knowledge of the transesterification reaction kinetics is needed for the production process development, design, operation, scale-up, analysis and control. Absence of standardized procedures for comparison of various alternatives.</p> <p>Limitation created by the REACH legislation. Lack of data of specific ILs about safety, health, biodegradability and toxicity.</p>

from the reaction mixture by freezing and centrifugation and finally regenerates with great success [86]. The ester yield decreases by 30.0% after the fifth use of the catalyst. DEAC with PTSA [87] or P-DES [88] shows good recyclability for the biodiesel synthesis from low-quality crude palm oil having high FFA content. After being reused three times for a pre-treatment, ChCl:PTSA (molar ratio 1:3) has no significant loss in its activity (conversion degree 89.0%, yield 95.0%) [89]. The commercial CaO activated with ChCl:glycerol (1:2) ensures the ester yield of 85.0% after the fifth cycle of the methanolysis of rapeseed oil with no addition of the DES [90]. Also, this DES is compatible with Novozym 435 in the soybean oil methanolysis, where the enzyme is used 4 times without no significant activity loss [4].

## 10. Strengths, weaknesses, opportunities and threats of using ILs/DESs in biodiesel production

An analysis of strengths, weaknesses, opportunities and threats, known as a SWOT analysis, was conducted with the goal of

highlighting the potential advantages and disadvantages of employing ILs/DESs in the biodiesel production and of indicating potential directions for improving it. It is worth-mentioning that this strategic planning tool has already been used for overviewing the relative benefits and pitfalls of ILs syntheses and purifications. For instance, performing the SWOT analyses, Deetlefs and Seddon [128] judged that the synthesis and purification of ILs is “green, but not green enough”. Also, García-Verdugo et al. [129] have quite recently applied the SWOT analysis to identify the advantages and disadvantages of using ILs as alternative solvents in continuous flow (bio)catalytic processes. Only, Stark [130] has carried out the SWOT analysis for evaluating the potentiality of using ILs in an integrated biorefinery converting bio-based raw materials into a number of products including biofuels. However, this tool has not yet been applied for comparing good and bad of the IL/DES use in biodiesel production processes. Therefore, Table 11 summarises the results of the SWOT analysis of using ILs/DESs in the biodiesel production as catalysts, cosolvents or extracting solvents. This SWOT analysis is focused on both internal (strengths and

weaknesses) and external (opportunities and threats) factors influencing the use of ILs/DESSs in the biodiesel production.

The strengths of using ILs/DESSs in the biodiesel production are well-recognized. Some ILs, like Brønsted acidic ILs, are more efficient and less corrosive than the traditional acid catalysts (the mineral acids), usually under mild reaction conditions. Generally, the ILs can stabilize the catalysts and, in some cases, enhance their catalytic activity, which can significantly improve the productivity of continuous processes, the development of new greener processes or the design of new types of reactors that integrate reaction and separation [129]. By simplifying the separation and purification methods, the use of ILs/DESSs allows for the reduction of the number of processing steps. The advantage of their low miscibility with alkyl esters can be used for their easier recovering from the final reaction mixture and reusing, which leads to less production costs. Some ILs are efficient as extracting solvents in removing glycerol and remaining alkaline catalyst from crude biodiesel. They possess greater extraction efficiency than common extracting solvents for recovering lipids from microalgal biomass.

Regarding the weaknesses, the high cost of ILs is a key obstacle to be overcome when they are used. In many cases, this drawback can be outweighed by the overall advantages. The use of much cheaper DESs instead of ILs wherever possible is a way to reduce this problem. Further weaknesses include long-term stability influencing recyclability and viscosity affecting mass transfer and energy costs [130]. Being composed of ions only, ILs feature a low vapor pressure, making distillation as an inadequate technique for their recovering or purifying. In addition, distillation of volatile contaminants from ILs and extraction of non-volatile products are commonly used to recycle and reuse ILs, but both techniques are energy and cost demanding. Even when the ILs can be efficiently reused, there is still an uncertainty regarding their stability under a prolonged use [129]. The additional weaknesses are also a poor biodegradability and a relative toxicity for the environment of some ILs, which might be, in some cases, overcome by using the non-toxic and biodegradable DESs as adequate alternatives. Another way is to search for new microorganisms with the potential to biodegrade the ILs. Finally, the whole life-cycle assessment of ILs or DESs has not most frequently been conducted yet [130].

Regarding to the opportunities, there are many possibilities for various uses of ILs/DESSs (as catalysts, cosolvents and extracting solvents) in various biodiesel production steps (for instance, extraction of lipids from biomass, FFAs from oily feedstocks before the reaction, as well as glycerol, unsaturated fatty acid esters and the leftover catalyst from crude biodiesel after the reaction), alone or combined with other catalysts or cosolvents or being immobilized onto supporting materials. The possibilities of their use with low-quality, low-cost feedstocks (waste and non-edible oils) and in novel transesterification technologies (microwave- or ultrasound-assisted, and with supercritical fluids) are also great opportunities for future applications of ILs/DESSs. In addition, their easy separation from the final reaction mixture enhances the opportunity for their reuse. Moreover, the possibility to use the DESs instead of the ILs allows for the development of new greener and economically more efficient biodiesel production processes. However, further studies are needed to get the kinetic data on the transesterification reaction over ILs or DESs that are necessary for the development, design, operation, scale-up, analysis and control of the biodiesel production process. On the other side, the threats for the application of ILs/DESSs in the biodiesel production are related to legal implementation, market development and competition of biodiesel with fossil-based fuels. The implementation of the REACH (registration, evaluation, authorization and restriction of chemicals) legislation in the case of any new industrial-scale application, especially for new ILs/DESSs, requires a large

initial financial investment for the registration and the gathering of the full physico-chemical characterization and eco-toxicity data required for their evaluation [129]. This analysis suggests that ILs will most probably be employed if no process alternative exists or if high dissolution capacity or extraction selectivity is required [130].

## 11. Conclusion

ILs and DESs are used in biodiesel synthesis as catalysts, cosolvents and extracting solvents. These chemicals are environmentally friendly, make the separation of biodiesel from the reaction mixture easy and can successfully be reused. Having catalytic activity comparable to that of conventional catalysts, they have a bright future in biodiesel production. Especially, Brønsted acidic ILs show good catalytic activity without the need of removing excess moisture from oily feedstocks. Also, hydrophobic ILs are excellent solvents for enzyme-catalyzed synthesis of biodiesel since they provide an efficient protection for the enzyme, thus reducing its deactivation. In a matter of catalyst support, ILs increase the surface area between reactants and the catalyst, thus providing an efficient biodiesel synthesis. Being cheap, non-toxic and stable mixtures, DESs are starting to become interesting in both chemical and biocatalytic biodiesel production. The performance of recycled ILs is proven to be excellent, which might contribute to the reduction of the production cost. In addition, the possibility of using non-edible oils and waste cooking oils as low-cost feedstocks can greatly help in providing a more economical biodiesel production.

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