# Recent advances in biodiesel production from agricultural products and microalgae using ionic liquids: Opportunities and challenges

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## ABSTRACT

Biodiesel is considered as a potential substitute for petroleum-based diesel fuel owing to its comparable prop-erties to diesel. Biodiesel is generally produced from renewable sources such as agricultural products and microalgae in the presence of a suitable catalyst. Recently ionic liquid (IL) catalyzed synthesis of biodiesel has become a promising pathway to an eco-friendly production route for biodiesel. This review focuses on the use of ILs both as solvents as well as catalysts for sustainable biodiesel production from agricultural feedstocks and microalgae with high free fatty acid content. Reactions catalyzed by ILs are known to render high reactivity under the mild condition and high selectivity of ester product with simple separation steps. The article first discusses the state of the art of biodiesel production using ILs along with the physicochemical properties of the produced biodiesel. Then, current IL technologies were elucidated in terms of the categories such as acidic and basic ILs. The use of more advanced ILs such as supported ionic liquids and ionic liquid-enzyme catalysts on different biodiesel feedstocks were also discussed. Furthermore, the role of IL catalyst in intensified biodiesel production methods such as microwave and ultrasound technologies were also discussed. Finally, the prospects and challenges of IL catalyzed biodiesel production are discussed in this article. The review shows that ILs with brønsted acidity or basicity not only pose a low risk to the environment but also result in high biodiesel yields with mild reaction conditions in a short time. Brønsted acidic ILs can convert free fatty acids as well as tri-glycerides to biodiesel without the need for pretreatment, which facilitates in reducing the production cost of biodiesel. From the review, it can be concluded that ILs present great potential as catalysts for biodiesel production.

## 1. Introduction

Increased worldwide energy consumption, heightened dependency on fossil-based fuels, and environmental concerns have triggered the need for developing new energy systems [1,2]. It has been reported that the use of fossil fuels is the primary reason for significant environmental issues, such as air pollution and global warming. The United Nations has, therefore, set SDG-7 to ensure that everyone has access to afford-able, secure, and renewable energy by 2030 to lower the adverse impact of fossil fuel utilization. A viable renewable fuel should be technologi-cally feasible, readily available, environmentally sustainable, and techno-economically competitive [3]. As such, renewable energy sour-ces such as biofuels have been recognized as a potential replacement for conventional petroleum fuel [4–6]. Among the different types of bio-fuels, liquid biofuel such as biodiesel is the most prominent in the transportation sector as alternatives to diesel fuel [7]. The use of bio-diesel could reduce the emission of exhaust greenhouse gases, unburned hydrocarbons, particulate matters, poly-aromatics, and sulfur from the engines [8]. A wide range of edible and non-edible oil sources including

palm oil, jatropha oil, mustard oil, beauty leaf oil, microalgae oil, rubber seed oil, mahua oil, animal fats, waste cooking oil, etc. can be used for biodiesel production [9–12].

Commercial biodiesels are produced via the transesterification reaction, conducted in the presence of an acidic or basic catalyst depending on free fatty acid (FFA) content of the feedstock [13]. In this regard, the development of an environmentally benign catalyst is highly sought-after for a more sustainable way of biodiesel synthesis. ILs were initially introduced as alternative green reaction media due to their unique physicochemical properties such as non-volatility, non-flammability, thermal stability, and controlled miscibility [14]. At present, these are extensively used in controlling the reaction as catalysts. Synthesis of biodiesel using ILs as a catalyst is a promising pathway to an eco-friendly production [15,16]. ILs refers to a Newtonian liquid composed of ionic species, i.e., organic cations and organic or inorganic anions [17]. Other properties that are favorable over both conventional homogeneous and heterogeneous catalysts include excellent dissolving capacity, immiscibility with organic solvents, high chemical stability,

and recyclability [17,18]. Moreover, ILs can be engineered as "task-specific ILs (TSILs)" or "Designer Solvents," owing to the ability to finely change and calibrate the structural functionalities on the cationic or anionic part to increase the desired effect on the selected choice [19]. The application of ILs is presented in Fig. 1.

The coupling of ILs with co-catalyst, such as metal ions, complexes, clusters of ligands, could further facilitate their catalytic activity of reaction process [20]. Hence, ILs have a multitude of advantages compared to other catalysts (e.g., metal salt, zeolites, enzyme, solid acid catalysts, etc.). Essential elements of using IL catalytic system, for instance, techno-economic and environmental aspects, can be easily addressed as they can be easily applied to a continuous process with minimal wastewater production [21,22]. From an industrial standpoint, a suitable catalyst should have high reactivity and selectivity with ease of separation and reusability highly desired. Applying ILs reduce not only the number of reactions and purification procedures but also improves the economic feasibility of the process [23].

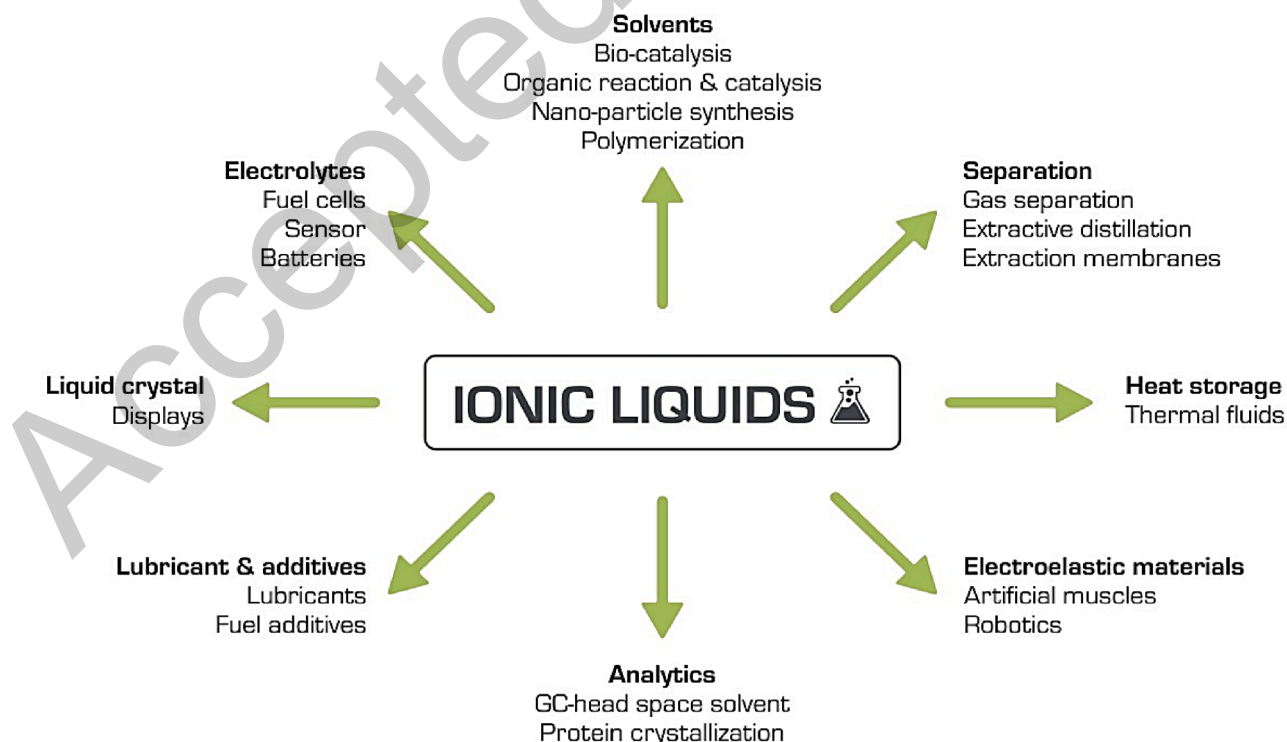To date, many research has been carried out on IL-catalyzed



**Fig. 1.** The application of ILs in several areas.

biodiesel production. The previous reviews on this subject are mostly pivoted on the properties and general/specific application of ILs [24–28]. A recent review on this topic authored by Asim et al. [29] directed their study mostly on lignocellulosic biomass processing. However, reviews on biodiesel production using ILs are still scarce [30]. A critical review of various IL categories and recent breakthroughs on using ILs with intensification techniques is still missing. This review aims to fulfill the knowledge gap by analyzing the various IL categories extensively together with the use of IL-catalyzed reaction in biodiesel synthesis. Different feedstocks obtained from agricultural products and wastes, as well as microalgae species, are discussed along with their significant properties of the respective biodiesels. The theoretical background, catalytic characteristics, chemical insights, and reaction operating conditions of the ILs are discussed with the performance profile of catalytic activity in biodiesel synthesis. The use of acidic or basic ILs and their reaction parameters are reviewed, while more advanced and novel ILs such as supported ILs and IL enzyme catalyst are also studied. Furthermore, intensification techniques such as microwave and ultrasound-assisted methods used in conjunction with ILs catalysis techniques are presented. Finally, the prospects and challenges of using ILs-catalyzed processes for evaluating the sustainability of the synthesis process are discussed.

## 2. Biodiesel from agricultural waste and microalgae

As mentioned previously, biodiesel is regarded as a potential alternative fuel for compression ignition engines with up to 20% (v/v) blend of biodiesel, which does not require any modification in the diesel engine [31,32]. A wide range of feedstocks, including vegetable oils, animal fats, waste cooking oils, microalgae oils, and microbial oils have been utilized for biodiesel synthesis [33,34]. Most commercial biodiesel being produced in the world today is made from edible oils, resulting in 'food vs fuel' controversy which questions the use of edible oils for energy use rather than food production [35,36]. The use of oils extracted from agricultural wastes (crop residues, wood residues, etc.) for biodiesel production could reduce the feedstock price and avoid direct competition with the food crop industry [34]. These biodiesels are often referred to second-generation biodiesels. The waste-to-energy concept is an attractive thermochemical pathway that is suitable for mass production and is compatible with the current infrastructure of the energy and chemical industry [37,38].

In recent years, third-generation biodiesels are studied extensively, which are derived from microalgae [39,40]. Microalgae lipid oils can be efficiently extracted before they can be converted into biodiesel [41]. They have minimal competition with land crops as they do not compete for land availability [42]. Microalgae oil properties are also inherently similar to other vegetable oils. Microalgae, as a biodiesel feedstock is gaining popularity due to the rapid growth rates and high oil contents inherent within the biomass [43]. Microalgae are capable of producing 19,000 to 57,000 L oil/acre within a year, which is significantly higher than any current biodiesel feedstock [44]. Direct extraction and conversion of algal oil to biodiesel via one-pot procedure is also an exciting option as this single-step process could reduce the overall environmental impact and cost. However, the integration of this technique is still at a developing stage, owing to the economic unfeasibility for industrial applications, and thus deserve further research exploration [45]. The

**Table 1**
Properties of the biodiesel from the various feedstocks.

| Property | Production method | Acid value (mg KOH/g) | Viscosity at 40 °C (mm²/s) | Density at 15 °C (kg/m³) | Heating value (MJ/kg) | Flash point (°C) | Cloud point (°C) | Pour point (°C) | Oxidation stability (h) | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| ASTM D6751 | – | ≤0.5 | 1.9 to 6.0 | – | – | 100–170 | – | – | ≥3 | [48] |
| EN 14,214 | – | ≤0.5 | 3.5 to 5.0 | 860 to 900 | – | ≥120 | – | – | ≥8 | [48] |
| Palm oil | Alkali-catalyzed transesterification | – | 4.91 | 875 | 39.90 | 152 | 13 | 12 | 7.2 | [55] |
| Rubber seed oil | Acid and alkaline transesterification | 0.18 | 5.96 | 881 | 41.07 | 140 | – | – | – | [56] |
| *Jatropha curcas* | Alkali-catalyzed transesterification | 0.2 | 4.268 | 878.8 | 40.899 | 176.5 | 3 | 2 | 8.41 | [57] |
| Rice bran | Alkali-catalyzed transesterification | 0.34 | 5.365 | 886.9 | 39.957 | 174.5 | 0 | −3 | 3.58 | [58] |
| Castor oil | Homogenous alkaline transesterification | 0.63 | 15.4 | 946.1 | 38.34 | 194 | −18 | −30 | – | [59] |
| Soybean oil | IL transesterification | – | 4.08 | 884 | 39.8 | 141 | 2 | −2 | – | [60] |
| Flaxseed oil | Alkali-catalyzed transesterification | 2.24 | 2.97 | 876 | 40.46 | 171 | −4 | −9 | – | [61] |
| *Calophyllum inophyllum* | Alkali-catalyzed transesterification | 0.34 | 5.6872 | 877 | 39.389 | 141.5 | 8 | 8 | 3.58 | [62] |
| Cascabela ovata oil | Alkali-catalyzed transesterification | 0.49 | 4.98 | 866.8 | – | 168 | 3 | – | – | [63] |
| Poon oil *(Sterculia foetida)* | Alkali-catalyzed transesterification | – | 6.0 | 875 | 40.211 | 162 | – | 1.0 | – | [64] |
| Beef tallow | Ultrasonic irradiation | – | 4.66 | 830.5 | – | 146 | – | – | – | [65] |
| Dairy waste scum | CaO transesterification | – | 4.16 | 830 | – | 130 | 10 | 17 | – | [66] |
| Waste frying palm oil | Alkali-catalyzed transesterification | – | 4.401 | 875 | 38.73 | 70.6 | – | – | – | [67] |
| Wastewater scum | Acid and alkaline transesterification | 1.43 | 4.941 | – | – | 176 | 13 | – | 0.1 | [68] |
| *Chlorella* sp. | Alkali-catalyzed transesterification | 0.37 | 4.73 | 883.6 | 37.06 | 179 | – | – | 6.76 | [69] |
| *Chlorella protothecoides* | Alkali-catalyzed transesterification | 0.29 | 4.43 | 882 | – | – | – | – | 4.52 | [70] |
| *Nannochloropsis* sp. | Alkali-catalyzed transesterification | – | 4.19 | 869 | 40.72 | 144 | 7 | −6 | – | [71] |
| *Scenedesmus incrassatulus* | Enzymatic transesterification | – | 3.78 | 803 | 41 | – | 9 | 3 | 19 | [72] |
| *Spirulina platensis* | Alkali-catalyzed transesterification | 0.75 | 12.4 | 863.7 | 45.63 | 189 | −3 | −9 | – | [73] |

properties of the biodiesel should also adhere to the ASTM D6751 or EN 14214 standards as a form of quality control. Table 1 depicts the various biodiesel feedstocks, along with the properties of the corresponding biodiesel.

The choice of feedstock is generally not solely based on the amount of lipid available in the feedstock but also the fatty acid composition (FFA) of those feedstocks as these control the properties of produced biodiesels [46,47]. The transesterification or alcoholysis of triglycerides (TG) with short-chain alcohol in the presence of a catalyst is commonly used for biodiesel production [48,49]. The process has been commonly adopted as it is capable of achieving high yields at relatively low costs.

Common factors influencing the transesterification efficiency include the reaction temperature, methanol to oil ratio, reaction time, catalyst type and concentration, FFA content and water content of the oil [50]. Non-catalytic transesterification processes can also yield high biodiesel conversion but are often conducted under extreme temperature (200 to 400 °C) and pressure (10 to 25 MPa) conditions, which reduce the economic feasibility of the process [51]. Therefore, a catalyst is often used to convert the biodiesel under milder conditions. The selection of an efficient catalyst with optimum concentration is one of the most significant factors to achieve high biodiesel conversion at a shorter re-action time [52]. Commercially, homogeneous catalysts such as
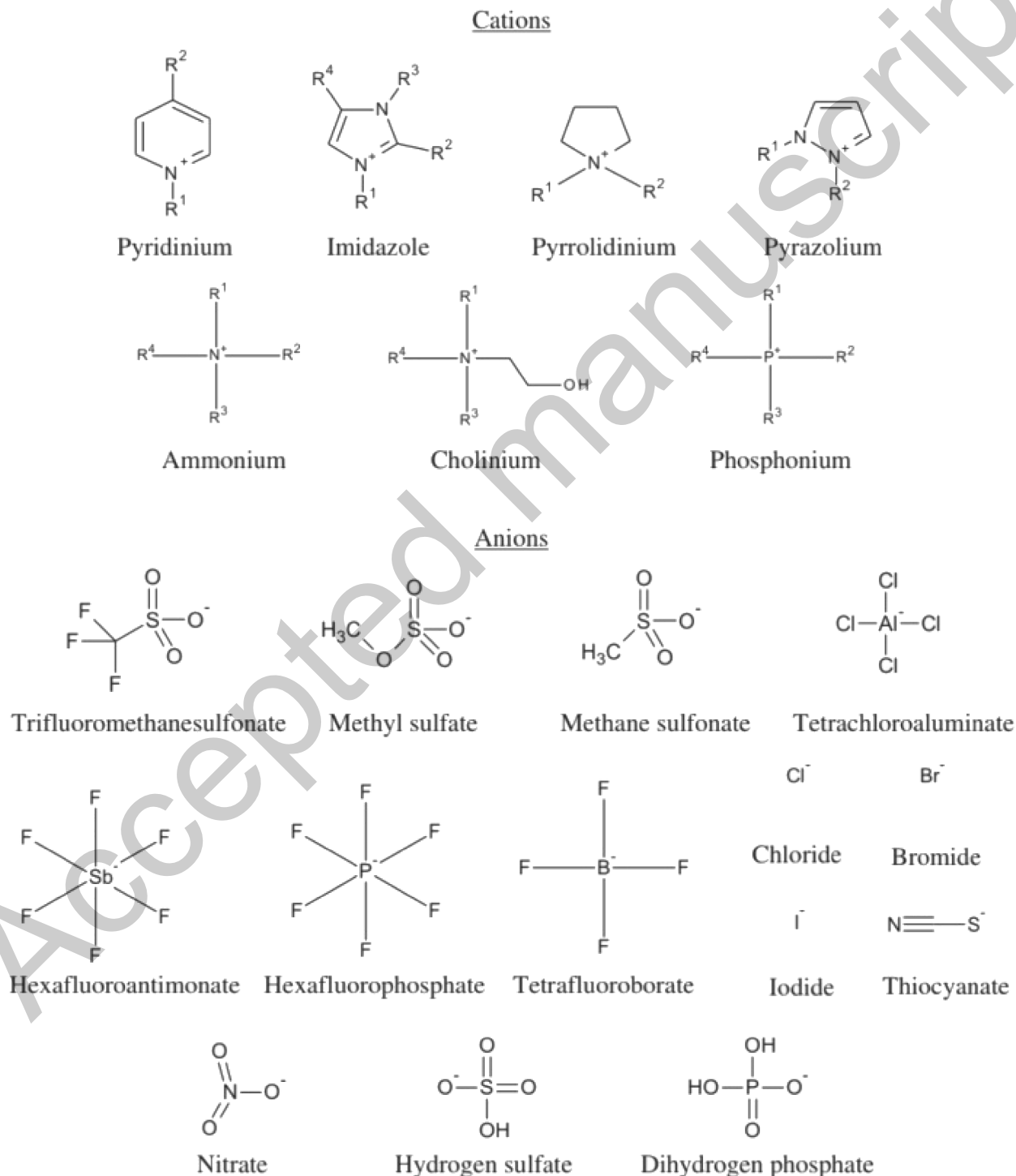


**Fig. 2.** Commonly used cations and anions in ionic liquids [41] (Image used with permission).

potassium hydroxide, sodium hydroxide, or sulfuric acid have been used for the transesterification reaction. Although commercial catalysts are relatively cheap and abundantly available, their hazardous and non- green characteristics make it unsustainable to the environment [23]. These catalysts also generate large amounts of wastewater during post- processing steps and cannot be recycled, making it an energy-intensive process [53]. Besides, the catalyst is partially miscible in biodiesel resulting in problems of product separation from the reactant mixture [54]. The drive for utilizing greener and environmentally benign pro-cesses have pushed researchers to study the use of ILs as an alternative catalyst.

## 2.1. ILs as a catalyst in biodiesel synthesis

its melting temperature of below 100 °C and are primarily made of ions (both cations and anions) and short-lived ion pairs [41]. These ILs have changed the 'like dissolves like' rule as they can dissolve both polar and non-polar species [74]. The cations and anions of ILs can independently affect the IL's physicochemical properties (viscosity, melting point, density, conductivity, refractive index, etc.) as well as introduce features for any given application (controlling solute solubility, hydrophobicity vs. hydrophilicity, chirality, adding functional groups for catalysis/reactivity purposes, etc.). Typical IL cations and anions are shown in Fig. 2. Based on the properties, ILs can be divided into two groups (a) acidic (acidic ionic liquids, AILs) and (b) basic (basic ionic liquids, BILs), [41]. Their properties can be modified by altering the combination of cations and anions. Some cations base are attached with alkyl substituents such as the addition of functional groups to provide an acidic nature such as sulfonic acid [–SO₃H] and carboxylic acid [–COOH] [20].

In contrast, the anions are weakly basic organic or inorganic compounds which constitute a diffused or protected negative charge [75].

### 2.1.1. Acidic ionic liquids (AILs)

AILs can be split into three major categories: (i) Lewis acidic ionic liquids (LAILs), (ii) Brønsted acidic ionic liquids (BAILs), and (iii) Brønsted-Lewis acidic ionic liquids (BLAILs) [22]. LAILs accept lone pair electrons from a Lewis base due to its Lewis acid site. BAILs possess one or multiple Brønsted acid sites to move a proton to a Brønsted base, depending on the number of acidic sites in the ILs. BLAILs have both Brønsted and Lewis acidic sites, which exhibit a stronger acidity due to the effect of both acidic sites working simultaneously to promote the catalytic activity.

In the case of high FFA content feedstocks, two-step processes involving pretreatment of feedstock oil using esterification, followed by alkaline-catalyzed transesterification of the product, are often conducted. A literature summary on these processes via ILs is given in Table 2. Elsheikh *et al.* [76] pre-screened BAILs with different alkyl groups such as 1-butylimidazolium hydrogen sulfate ([BIM][HSO₄]), 1-butyl-3-methyl-imidazolium hydrogen sulfate ([BMIM][HSO₄]), and 1-methylimidazolium hydrogen sulfate ([MIM][HSO₄]), where the catalytic activity were in accordance to the acidity of the BAILs, as follows: [BMIM][HSO₄] > [BIM][HSO₄] > [MIM][HSO₄]. They used triethylammonium hydrogen sulfate ([Et₃N][HSO₄]) for the esterification of crude palm oil prior to transesterification using KOH. A similar method was adopted by Man *et al.* [77]. In a later study, Elsheikh *et al.* [78] used BAILs with multi-acid sites, 1-butyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate ([BSPIM][HSO₄]) for the same feedstock, where 95.7% conversion was achieved due to the double Brønsted acidic sites from both cations and anions. In a longer alkyl chain of [-SO₃H]

**Table 2**
Summary of AILs catalyzed esterification followed by alkali-catalyzed transesterification of oils.

| Feedstock | IL type | ILs | Optimal reaction conditions | | Conversion (C)/ Yield (Y) % | Recyclability | Ref |
|---|---|---|---|---|---|---|---|
| | | | First step | Second step | | | |
| Crude palm oil (3.49 wt% FFA) Esterified oil (0.3 wt% FFA) | BAILs (sole acid site) | [BMIM][HSO₄] | 958=-0IL: 4.5 wt% Temperature: 160 °C Time: 2 h Molar ratio of methanol:oil: 12:1 | KOH: 1 wt% Temperature: 60 °C Time: 0.83 h Molar ratio of methanol:oil: 6:1 | 91.2 (C) 98.4 (Y) | – | [76] |
| Waste c-ooking oil Esterified oil (1.0 mg KOH/g oil) | BAILs (sole acid site) | [BMIM][HSO₄] | IL: 5 wt% Temperature: 160 °C Time: 1 h Molar ratio of methanol:oil: 15:1 | KOH: 1 wt% Temperature: 60 °C Time: 1 h Molar ratio of methanol:oil: 6:1 | 95.7 (Y) | 6 | [84] |
| Crude palm oil (3.49 wt% FFA) Esterified oil (0.44 wt% FFA) | BAILs (sole acid site) | [Et₃N][HSO₄] | IL: 45.2 wt% Temperature: 170 °C Time: 3 h Molar ratio to methanol:oil: 15:1 | KOH: 1 wt% Temperature: 60 °C Time: 0.83 h Molar ratio of methanol:oil: 6:1 | 82.1 (C) 97.3 (Y) | – | [77] |
| Crude palm oil (6.98 mg KOH/g oil) Esterified oil (0.12 wt% FFA) | BAILs (multi-acid sites) | [BSPIM][HSO₄] | IL: 4 wt% Temperature: 150 °C Time: 2 h Molar ratio of methanol:oil: 12:1 | KOH: 1 wt% Temperature: 60 °C Time: 0.8 h Molar ratio of methanol:oil: 6:1 | 95.7 (C) 97.8 (Y) | | [85] |
| *Citrullus colocynthis* oil (6.36 mg KOH/g) Esterified oil (0.23 wt% FFA) | BAILs (multi-acid sites) | [MSBIM][HSO₄] | IL: 3.8 wt% Temperature: 130 °C Time: 2 h Molar ratio of methanol:oil: 12:1 | KOH: 1 wt% Temperature: 60 °C Time: 0.8 h Molar ratio of methanol:oil: 6:1 | 96.7 (C) 98.8 (Y) | 8 times (close to FFA conversion) | [79] |
| Waste cooking oil Esterified oil (1.0 mg KOH/g oil) | BAILs (multi-acid sites) | [BSMBIM][CF₃SO₃] | IL: 4 wt% Temperature: 120 °C Time: 4 h Molar ratio of methanol:oil: 12:1 | KOH: 1 wt% Temperature: 60 °C Time: 1 h Molar ratio of methanol:oil: 6:1 | 78.1 (C) 94.5 (Y) | 7 times with high yield production8[th] time (70.5%) | [86] |
| *Jatropha curcas* oil (8.15 wt% FFA) Esterified oil (0.49 mg KOH/g oil) | BAILs (sole acid site) | [BSMIM][Cl] | IL: 10 wt% Temperature: 70 °C Time: 6 h Molar ratio of methanol:oil: 12:1 | KOH: 4.5 wt% Temperature: 64 °C Time: 0.33 h Molar ratio of methanol:oil: 6:1 | 93.9 (C) 98.6 (Y) | 4 | [82] |

functionalized group based BAILs, 1-methyl-3-(4-sulfobutyl)-imidazolium hydrogensulfate ([MSBIM][HSO$_4$]), significant FFAs-esterification was achieved (96.7%), from the crude *Citrullus colocynthis* oil [79]. Furthermore, this [MSBIM][HSO$_4$], being an imdiazolium based IL, performed better than the pyrazolium based BAIL, 1-methyl-2-(4-sulfobutyl)-pyrazolium hydrogen sulfate ([MSBP][HSO$_4$]) [79]. This can be attributed to the combination of the unstable base cation with functionalized [–SO$_3$H] chain, which contributed to a greater Brønsted acidity, that offers a stronger proton donor [80]. Elsheikh and Akhtar [81] observed the two sulfonic chains existing in 1,3-disulfonic acid imidazolium hydrogen sulfate ([DSIM][HSO$_4$]) further enhanced the acidity. It is to be noted that, [Cl] anion based SFILs, 1-(1-butylsulfonic)-3-methylimidazolium chloride ([BSMIM][Cl]), showed good catalytic activity [82], due to the strong hydrogen bond acceptors on [Cl], promoting the catalytic activity by increasing the acid site accessibility [83].

Direct transesterification of various feedstock oil to biodiesel via AIL offers a better conversion process, as illustrated in Table 3. Generally, the stronger the acidity, the better the catalytic efficiency. Khiratkar *et al.* [87] utilized two types of SFILs, with two different cation base, namely, 4-(1-ethyl-1H-benzimidazole-3-yl) butane-1-sulfonate (a benzimidazolium based BAILs (BBAILs)) and 4-(1-ethyl-1H-imidazole-3-yl) butane-1-sulfonate (imidazolium based BAIL (ImBAILs)) for the production of methyl ricinoleate. BBAILs exhibited better catalytic activity compared to that of ImBAILs, owing to a higher Brønsted acidity of BBAILs. Sun *et al.* [88] reported on hydrogen sulfate anion based ILs ([BMIM][HSO$_4$]), acting as an extractant for lipid extraction and acid catalyst for in-situ transesterification in *Nannochloropsis* sp. with biodiesel yield of up to 95.3% in a short time of 30 min. Lee *et al.* [89] utilized 1-butyl-3-methylimidazolium trifluoromethane sulfonate ([BMIM][CF$_3$SO$_3$]) for the single-step lipid extraction and conversion to biodiesel with a moderate yield of 54%.

Apart from that, in multi-acid sites of BAILs, SFILs is among the most utilized ILs reported to date [90–92]. Khiratkar *et al.* [87] applied an additional [-SO$_3$H] based BBAILs with a better catalytic activity of up to 97.7% biodiesel yield [93,94]. In addition, acidic [HSO$_4$]$^-$ anion based ILs have also shown to have better catalytic activity than that of sulfonate [SO$_3$]$^-$ anion based ILs, owing to [HSO$_4$]$^-$ anion having higher acidity strength [95]. A series of alcohol with differing carbon chain lengths (C$_1$-C$_4$) was further investigated, where the increase in alcohol carbon chain length decreased the biodiesel yield [96]. As the size of the alcohol moiety becomes larger (longer carbon chain length), the nucleophilic attack by the hydroxyl group becomes difficult due to the increased distance to the reacting hydroxyl group.

Fan *et al.* [97] evaluated a series of acidic [HSO$_4$]$^-$ anion based SFILs, where the catalytic performance is affected by the presence of various cation functional groups, i.e., pyridine, triethylamine, and N-methyl-imidazole groups. Based on the results, the catalytic activities of these ILs follows the order of pyridine > N-methyl-imidazole > trimethyl-amine. In terms of the alkyl chain length, [BSO$_3$HMIM][HSO$_4$], being a butyl based [-SO$_3$H] (longer carbon chain length), imidazolium cation showed better catalytic activity [90,98]. Besides, Olkiewicz *et al.* [99] investigated a series of alkane sulfonic acid imidazolium and sulfonic acid ammonium-based ILs. Among them, 4-(3-methylimidazolium) butane sulfonic acid trifluoromethane sulfonate ([MIMC$_4$SO$_3$H] [SO$_3$CF$_3$]) and 4-(trihexylammonium) butane sulfonic acid trifluoromethane sulfonate ([N$_{666}$(C$_4$SO$_3$H)][SO$_3$CF$_3$]) gave the highest biodiesel yields from transesterification of sewage sludge lipids. As for the anion based ILs, methanesulfonate [SO$_3$CF$_3$]$^-$ anion revealed the highest catalytic activity as well as FAME yield. The capability of [SO$_3$CF$_3$]$^-$ anion has equivalent efficiency to the methyl sulfonate [CH$_3$SO$_3$]$^-$ anion [100]. Between these [SO$_3$CF$_3$]$^-$ and [CH$_3$SO$_3$]$^-$ anions, [SO$_3$CF$_3$]$^-$ anion showed an almost full turnover efficiency, owing to the strong electron-withdrawing ability of fluorine atom in the [SO$_3$CF$_3$]$^-$ anion. To date, the majority of research has focused on imidazole-based or pyridine-based ILs but with certain drawbacks, such as difficulty in

preparation, higher cost, and harmful effect on the environment [101,102]. Luo *et al.* [92] applied a different type of eco-friendly BAIL, known as caprolactam-based BAILs which achieved significant biodiesel yield (96.9%). This is owing to the cation core of caprolactam assembled by the [-SO$_3$H] group that would contribute to a stronger Brønsted acidity.

Researchers have also reported on the use of Lewis acid-based ILs (LAILs). Guo *et al.* [103] investigated a series of tosylate based ILs, which is of a nearly neutral based ILs, coupling with several Lewis acidic metal chlorides, such as ZnCl$_2$, FeCl$_3$, AlCl$_3$, CuCl$_2$, CoCl$_2$, and MnCl$_2$. Among these, [BMIM][TS]-ZnCl$_2$ performed the best catalytic activity of 92.5% biodiesel yield for the transesterification of jatropha oil, which is increased by 28.8% in comparison to the sole [BMIM][TS] catalytic system. In brief, the performance data of jatropha biodiesel yield were in the following order: Zn$^{2+}$ > Mn$^{2+}$ > Fe$^{2+}$ > Co$^{2+}$ > Al$^{3+}$ > Cu$^{2+}$. The metal ion (e.g., Cu$^{2+}$) contributed to the lowest catalytic activity, which can be attributed to the absence of coordinate bond formation [103]. As such, the trivalent metallic ions forms of Fe$^{3+}$ and Al$^{3+}$ exhibited higher yields of 97% and 86% compared to other bivalent metallic ions of Ni$^{2+}$, Cu$^{2+}$, and Co$^{2+}$, which caused by the relatively stronger acidity in trivalent metallic ions.

Recently, research revealed a combination of mixed acid IL catalytic system (BLAIL) having the simultaneous effect of both Brønsted and Lewis acidic ILs [21,104,105]. Han *et al.* [106] utilized tin-based BLAILs, propane sulfonate-functionalized methylimidazolium-tin chloride ([SO$_3$H-pmim][Cl]-SnCl$_2$). Significant biodiesel yield was obtained (94.9%), which is higher than the sole Lewis acid SnCl$_2$ (56.6%) and Brønsted acid [SO$_3$H-pmim][Cl] (75.3%). In addition, the catalytic activity of [DSI][FeCl$_4$] was higher than 'Amberlyst 15' (62.3%) and Nafion NR50 (24.1%) [107]. Cai *et al.* [108] reported on using [CF$_3$SO$_3$]$^-$ anion based SFILs, [Ps-MTH][CF$_3$SO$_3$] coupled with FeCl$_3$ with high biodiesel yield of 97%. Based on the synergistic effect from both ions ([CF$_3$SO$_3$]$^-$ and Fe$^{3+}$), [CF$_3$SO$_3$]$^-$ acts as a strong organic acid due to the negative induction effect between the -CF$_3$ and -SO$_3$H group which makes the acid easy to ionize a proton. Then, the triglyceride carbonyl group will combine with the proton to form a carbocation intermediate via nucleophilic substitution with methanol, followed by the formation of a diglyceride [109].

### 2.1.2. Basic ILs (BILs)

BILs are ILs of alkaline nature with high thermal stability and low decomposition temperature [27,117]. Other advantages include properties similar to inorganic bases, stability in air and water, high catalytic efficiency ease of separation, and reusability [27]. BILs are used to replace conventional alkali catalysts such as KOH, NaOH, K$_2$CO$_3$, NaHCO$_3$, NaOAc, trimethylamine, and tetrabutylammonium acetate [27]. Nonetheless, the reports on the use of BILs in biodiesel production remains scarce in the published research compared to that of AILs. Theoretically, the more basicity of the IL, the better is the catalytic activity [118]. As shown in Table 4, several types of BILs were used, such as choline based ILs [60,119], amino acid-based ILs [120], guanidine based ILs [121], imidazolium based ILs [103,122,123] and hydroxide based ILs [87,124,125]. Among these, amino acid-based ILs is made up of bioavailable compounds (bio-based ILs), can be seen as a greener solvent as well as catalysts [126]. ILs are made up of amino acid counterparts containing a carboxylic residue and an amine moiety, which can be converted into charged ion species [127]. Based on a series of amino acid-based ILs tested in the study [120], arginine anion based ILs gave significantly higher catalytic performance than histidine anion based ILs. Both [TBA][Arg] and [Ch][Arg] can be catalyzed fully in transesterifying sunflower oil to biodiesel (>99%), whereas [TMA][Arg] showed a lower convertibility compared to [Ch][Arg]. In contrast, in histidine based ILs category, [TBA][His] performed better than [Ch][His] and [TMA][His]. However, only 12.2% biodiesel yield was achieved with [TBA][His].

Double basic ILs, also known as dicationic basic ILs (DBILs) such as

**Table 3**
Summary of AILs in the transesterification of various feedstock oil for biodiesel production.

*(a) BAILs with sole acid site*

| Feedstock | ILs | Optimal reaction conditions | Conversion (C) or Yield (Y) % | Recyclability | Refs. |
|---|---|---|---|---|---|
| Soybean oil | [NMPH][CH$_3$SO$_3$] | IL: 2.8 wt%<br>Temperature: 78 °C<br>Time: 8 h<br>Molar ratio of ethanol:oil: 5.4:1 | 96.5 (C) | 4 | [100] |
| Vegetable oil | [PSMIM] | IL: 1.4 wt%<br>Temperature: 70 °C<br>Time: 14 h<br>Methanol:oil: 5 g:5 g | 77.8 (C) | – | [110] |
| *Nannochloropsis oceanica* | [BMIM][CF$_3$SO$_3$] | IL:biomass: 0.05 g:0.03 g<br>Enzyme: 0.1 g<br>Temperature: 55 °C<br>Time: 14 h<br>Methanol:oil: 14 ml:1 ml | 54.0 (Y) | – | [89] |
| *Triglycerides in Nannochloropsis* sp. | [BMIM][HSO$_4$] | IL:biomass: 0.9:1 w:w<br>Temperature: 200 °C<br>Time: 0.5 h<br>Methanol:biomass: 3:1 w/w | 95.3 (Y) | 4 | [88] |

*(b) BAILs with multi-acid sites*

| Feedstock | ILs | Optimal reaction conditions | Conversion (C) or Yield (Y) | Recyclability | Refs. |
|---|---|---|---|---|---|
| Canola oil<br>Palm oil<br>Soybean oil<br>Sunflower oil | 3,3-(hexane-1,6-diyl) bis(6-sulfo-1-(4-sulfobenzyl)-1H-benzimidazolium) hydrogensulfate [HDSSBD][HSO$_4$](BBAILs) | IL: 3.2 wt%<br>Temperature: 60 °C<br>Time: 5 h<br>Molar ratio of methanol:oil: 9:1 | 95.1 (C)<br>84.5 (C)<br>91.9 (C)<br>93.3 (C) | 8<br>–<br><br> | [94] |
| Soybean oil | [C$_4$SO$_3$Hpy][HSO$_4$]<br>[C$_4$SO$_3$HMIM][HSO$_4$]<br>[C$_3$SO$_3$Hpy][HSO$_4$]<br>[C$_3$SO$_3$HMIM][HSO$_4$]<br>[C$_3$SO$_3$HEt$_3$N][HSO$_4$] | IL: 5 wt%<br>Temperature: 120 °C<br>Time: 8 h<br>Molar ratio of methanol:oil: 8:1 | 94.5 (Y)<br>71.3 (Y)<br>87.7 (Y)<br>66.8 (Y)<br>60.1 (Y) | 6<br>– | [97] |
| Waste oil | [SO$_3$H-Bpy][HSO$_4$] | IL: 1.2 wt%<br>Temperature: 70 °C<br>Time: 16 h<br>Methanol:oil: 2.91 g:5 g | 94.5 (Y) | – | [111] |
| Waste oil | [BSO$_3$HMIM][HSO$_4$] | IL: 10 wt%<br>Temperature: 140 °C<br>Time: 6 h<br>Molar ratio of methanol:oil: 8:1 | 97.0% (Y) | 5 | [98] |
| Vegetable oil | [PSMIM][HSO$_4$] | IL: 1.4 wt%<br>Temperature: 70 °C<br>Time: 4 h<br>Methanol:oil: 5 g:5 g | 79.7 (C) | – | [110] |
| Rapeseed oil | [BSO$_3$HMIM][HSO$_4$] | IL: 2 wt%<br>Temperature: 130 °C<br>Time: 3 h<br>Molar ratio of methanol:oil: 12:1 | 85.0 (Y) | – | [90] |
| Bitter apple oil | [SBP][HSO$_4$] | IL: 5.2 wt%<br>Temperature: 170 °C<br>Time: 6 h<br>Molar ratio of methanol:oil: 15:1 | 89.5 (Y) | 7 | [78] |
| *Firmiana platanifolia* L.f. (FPLF) oil | [DSI][Cl] | IL: 5 wt%<br>Temperature: 120 °C<br>Time: 8 h<br>Molar ratio of methanol:oil: 15:1 | 86.0 (Y) | – | [107] |
| Sewage sludge lipids | [MIMC$_4$SO$_3$H][SO$_3$CF$_3$] | IL: 7 wt%<br>Temperature: 120 °C<br>Time: 5 h<br>Molar ratio of methanol:oil: 10:1 | 90.0 (Y) | 1 | [99] |
| Palm oil | [Taz-prSO$_3$H][HSO$_4$]<br>[Taz-prSO$_3$H][Tos]<br>[Taz-prSO$_3$H][CH$_3$SO$_3$]<br>[Taz-prSO$_3$H][CF$_3$SO$_3$] | IL: 3 wt%<br>Temperature: 120 °C<br>Time: 2.5 h<br>Molar ratio of methanol:oil: 18:1 | 91.7 (Y)<br>95.9 (Y)<br>98.9 (Y)<br>99.7 (Y) | – | [91] |
| Coconut oil | [CyN$_{1,1}$PrSO$_3$H][Tos] | IL: 4 wt%<br>Temperature: 110 °C<br>Time: 2 h<br>Molar ratio of methanol:oil: 15:1 | 98.7 (Y) | 7 | [112] |
|  | [PhCH$_2$N$_{1,1}$PrSO$_3$H][Tos]<br>[PhCH$_2$N$_{1,1}$PrSO$_3$H][HSO$_4$]<br>[CyN$_{1,1}$PrSO$_3$H][HSO$_4$]<br>[Ps-MIM][Tos]<br>[Ps-MIM][HSO$_4$] | IL: 3 wt%<br>Temperature: 100 °C<br>Time: 2 h<br>Molar ratio of methanol:oil: 9:1 | 77.2 (Y)<br>68.6 (Y)<br>73.2 (Y)<br>86.0 (Y)<br>62.9 (Y) | – | |

**Table 3** (*continued*)

*(b) BAILs with multi-acid sites*

| Feedstock | ILs | Optimal reaction conditions | Conversion (C) or Yield (Y) | Recyclability | Refs. |
|---|---|---|---|---|---|
| Palm oil | [CyN$_{1,1}$PrSO$_3$H][p-TSA] | IL: 3 wt%<br>Temperature: 120 °C<br>Time: 2.5 h<br>Molar ratio of methanol:oil: 24:1 | 98.4 (Y) | 7 | [113] |
| | [PhCH$_2$N$_{1,1}$PrSO$_3$H][p-TSA] | IL: 3 wt% | 65.2 (Y) | – | |
| | [PhCH$_2$N$_{1,1}$PrSO$_3$H][HSO$_4$] | Temperature: 110 °C | 59.3 (Y) | | |
| | [CyN$_{1,1}$PrSO$_3$H][HSO$_4$] | Time: 1.5 h | 81.5 (Y) | | |
| | [Ps-MIM][p-TSA] | Molar ratio of methanol:oil: 15:1 | 81.9 (Y) | | |
| | [Ps-MIM][HSO$_4$] | | 60.3 (Y) | | |
| | [SPP][HSO$_4$] | | 80.0 (Y) | | |
| | [MBSP][HSO$_4$] | | 62.0 (Y) | | |
| | [MPSP][HSO$_4$] | | 47.0 (Y) | | |
| Tung oil | [Ps-N-Ch(Me)$_2$][p-TSA] | IL: 5 wt%<br>Temperature: 120 °C<br>Time: 2 h<br>Molar ratio of methanol:oil: 21:1 | 98.9 (Y) | 5 | [114] |
| | [Ps-N-Ch(Me)$_2$][HSO$_4$] | IL: 3 wt% | 73.6 (Y) | – | |
| | [Ps-MIM][p-TSA] | Temperature: 110 °C | 76.6 (Y) | | |
| | [Ps-MIM][HSO$_4$] | Time: 1.5 h<br>Molar ratio of methanol:oil: 15:1 | 56.5 (Y) | | |

*(c) Lewis acidic ILs (LAILs)*

| Feedstock | ILs | Optimal reaction conditions | Conversion (C) or Yield (Y) | Recyclability | Ref |
|---|---|---|---|---|---|
| Vegetable oil | [BMIM][FeCl$_4$] | IL: 10 wt% | 97.0 (Y) | – | [115] |
| | [BMIM][AlCl$_4$] | Temperature: 55 °C | 86.0 (Y) | | |
| | [BMIM][CuCl$_4$] | Time: 8 h | 66.0 (Y) | | |
| | [BMIM][NiCl$_4$] | Molar ratio of methanol:oil: 9:1 | 60.0 (Y) | | |
| | [BMIM][CoCl$_4$] | | 18.0 (Y) | | |
| Waste oil | [Et$_3$NH]Cl-AlCl$_3$ | IL: 1.2 wt%<br>Temperature: 70 °C<br>Time: 24 h<br>Methanol:oil: 2.91 g:5 g | 78.8 (Y) | – | [116] |

*(d) Brønsted-Lewis acidic ILs (BLAILs)*

| Feedstock | ILs | Optimal reaction conditions | Conversion (C) or Yield (Y) | Recyclability | Refs. |
|---|---|---|---|---|---|
| *Firmiana platanifolia* L.f. (FPLF) oil | [DSI][FeCl$_4$] | IL: 6 wt%<br>Temperature: 123 °C<br>Time: 11 h<br>Molar ratio of methanol:oil: 24:1 | 98.7 (Y) | 4 | [107] |
| Soybean oil | [SO$_3$H-pMIM]Cl-SnCl$_2$ | IL: 8 wt%<br>Temperature: 150 °C<br>Time: 24 h<br>Molar ratio of methanol:oil: 30:1 | 94.9 (Y) | 3 | [106] |
| Soapberry oil | [Ps-MTH][CF$_3$SO$_3$]-FeCl$_3$ | IL: 3.1 mmol<br>Temperature: 127 °C<br>Time: 8 h<br>Molar ratio of methanol:oil: 28:1 | 97.0 (Y) | 5 | [108] |

1,2-bis (3-methylimidazolium-1-yl) ethylene imidazolide, gave excellent biodiesel yield of >99% as reported by Fan *et al.* [122]. From the study, the biodiesel yield decreased following the trend: 1,2-bis(3-methylimidazolium-1-yl) ethylene imidazolide > 1,4-bis (3-methylimidazolium-1-yl) butylene imidazolide > 1,6-bis (3-methylimidazolium-1-yl) hexylene imidazolide which can be attributed to the increase in the number of carbon atoms alkyl chain connected with cations. The long-chain carbon resulted in mass transfer difficulty in the reaction media owing to both steric and inductive effect [128]. The lengthening alkyl chain of the ILs increased the electron-releasing ability of the acid, resulted in the inductive effect. Moreover, an inductive effect also reduces the electrophilicity of the carbonyl carbon, leading to an energy-hindered rate-limiting nucleophilic attack by the alcohol [128]. In terms of the steric hindrance, it increases with molecular size, whereby induces electronic repulsion between non-bonded atoms of reacting molecules [129]. The repulsive hindrance reduces electron density in the intermolecular region and thus weakens the bonding interactions [130]. Aside from that, different branch chain of alcohols also affected the transesterification catalytic activity, owing to

the different dissociation degrees (pKa value) of the four alcohols (methanol, ethanol, 1-butanol, and 2-propanol) in the oil phase. As such, the use of 1-butanol and 2-propanol gave very low turnover efficiency with only 14.2% and 4.0% biodiesel yield, respectively, while, with the use of ethanol manage to achieve 93.6% biodiesel yield. Besides, with sole basic site imidazolium based ILs, namely, 1-butyl-3-methylimidazolium imidazolide ([BMIM][Im]) exhibited high catalytic activity with biodiesel yield up to 95% at mild reaction conditions from the transesterification of soybean, rapeseed and sunflower oil [123]. However, in another study of using 1-butyl-3-methylimidazolium tosylate ([BMIM][TS]) in the transesterification of jatropha oil only gave 63.7% of biodiesel yield [103]. The strong Lewis basicity of the imidazolium anion contributes to a better catalytic activity than the tosylate anion, the former exhibiting higher thermal stability as well [131].

Apart from that, hydroxide based ILs have similar basicity to imidazolium based ILs (e.g. [BMIM][Im]) but stronger basicity than acetate-based ILs (e.g. [BMIM][OAc]) [132]. Liang *et al.* [125] investigated a series of five hydroxide based ILs namely bis-(3-methyl-1-imidazole)-ethylene dihydroxide (IMC$_2$OH), bis-(3-methyl-1-

**Table 4**

Summary of BILs in the transesterification of various feedstock oil for biodiesel production.

| Feedstock | Type of ILs | ILs | Optimal reaction conditions | Conversion (C) or Yield (Y) % | Recyclability | Reference |
|---|---|---|---|---|---|---|
| Sunflower oil | Amino acid | [Ch][Arg] | IL: 28.84 mmol | 99.8 (Y) | – | [120] |
| | | [TBA][Arg] | Temperature: 80 °C | 99.7 (Y) | | |
| | | [TMA][Arg] | Time: 1 h | 98.1 (Y) | | |
| | | [Ch][His] | Molar ratio of methanol: | 0.07 (Y) | | |
| | | [TBA][His] | oil: 9:1 | 12.2 (Y) | | |
| | | [TMA][His] | | 3.5 (Y) | | |
| | | [Ch][Ala] | IL: 4 wt% | 6.3 (Y) | | |
| | | [Ch][Ser] | Temperature: 50 °C | 1.7 (Y) | | |
| | | [Ch][Leu] | Time: 21 h | 2.8 (Y) | | |
| | | [Ch][Phe] | Molar ratio of methanol: | 0.1 (Y) | | |
| | | [Ch][His] | oil: 9:1 | 6.8 (Y) | | |
| | | [Ch][Met] | | 0.9 (Y) | | |
| | | [Ch][Gly] | | 1.9 (Y) | | |
| Soybean oil | Dicationic imidazolide | 1, 2-bis (3-methylimidazolium-1-yl) ethylene imidazolide | IL: 4 wt% Temperature: 60 °C | 99.6 (Y) | 5 | [122] |
| | | 1, 4-bid (3-methylimidazolium-1-yl) butylene imidazolide | Time: 2.5 h | 92.5 (Y) | – | |
| | | 1, 6-bis (3-methylimidazolium-1-yl) hexylene imidazolide | Molar ratio of methanol: oil: 15:1 | 90.2 (Y) | | |
| | | 1, 2-bis (3-methylimidazolium-1-yl) ethylene imidazolide | IL: 4 wt% Temperature: 60 °C Time: 2.5 h Molar ratio of ethanol: oil: 15:1 | 93.6 (Y) | | |
| | | 1, 4-bid (3-methylimidazolium-1-yl) butylene imidazolide | IL: 4 wt% Temperature: 60 °C Time: 2.5 h Molar ratio of butanol: oil: 15:1 | 14.2 (Y) | | |
| | | 1, 6-bis (3-methylimidazolium-1-yl) hexylene imidazolide | IL: 4 wt% Temperature: 60 °C Time: 2.5 h Molar ratio of 2-propanol:oil: 15:1 | 4.0 (Y) | | |
| Rapeseed oil Soybean oil Sunflower oil | Imidazolide | [Bmim][Im] | IL: 6 wt% Temperature: 60 °C Time: 1 h Molar ratio of methanol: oil: 6:1 | 95.0 (Y) | 6 | [123] |
| Cottonseed oil | Hydroxide | IMC$_2$OH | IL: 0.4 wt% | 98.6 (Y) | 7 (96.2%) | [125] |
| | | IMC$_3$OH | Temperature: 55 °C | 98.5 (Y) | | |
| | | IMC$_4$OH | Time: 4 h | 97.5 (Y) | | |
| | | IMC$_5$OH | Molar ratio of methanol: | 96.5 (Y) | | |
| | | IMC$_6$OH | oil: 12:1 | 94.3 (Y) | | |
| Castor oil | Hydroxide | [BTBD][OH] | IL: 0.9 wt% | 96.0 (Y) | Many times | [124] |
| | | [BMIM][OH] | Temperature: 40 °C | 88.0 (Y) | | |
| | | [TBA][OH] | Time: 1 h | 65.0 (Y) | | |
| | | | Molar ratio of methanol: oil: 6:1 | | | |
| Castor oil | Hydroxide | 3-benzyl-1-(4(sec-butyl)benzyl)-1H-benzimidazole-3-iumhydroxide (PIL(OH − )) | IL: 5 wt% Temperature: 70 °C Time: 24 h Molar ratio of methanol: oil: 12:1 | 59.0 (Y) | – | [87] |
| | | 3-(2,3-dihydroxypropyl)1-methyl-1H-imidazole-3-ium hydroxide (DFImIL-OH − ) | IL: 5 mol% Temperature: 70 °C Time: 24 h Molar ratio of methanol: oil: 12:1 | 68.0 (Y) | 3 | |
| Soybean oil | Choline | [Ch][OH] | IL: 4 wt% | 95.0 (Y) | 4 | [60] |
| | | [Ch][OMe] | Temperature: 60 °C | 88.3 (Y) | | |
| | | [Ch][Im] | Time: 2.5 h | 76.9 (Y) | | |
| | | | Molar ratio of methanol: oil: 9:1 | | | |
| *Jatropha curcas* oil | Choline | [Ch][OH] | IL: 4 wt% Temperature: 60 °C Time: 4 h Molar ratio of methanol: oil: 9:1 | 95.0 (Y) | 4 (87%) | [119] |
| Soybean oil | Guanidine | 1,1,3,3-trimethyl-2- octyl-guanidine hydroxide | IL: 6 wt% Temperature: 55 °C Time: 4 h Molar ratio of methanol: oil: 15:1 | 97.2 (Y) | – | [121] |

imidazole)-propylene dihydroxide (IMC$_3$OH), bis-(3-methyl-1-imidazole)-butylene dihydroxide (IMC$_4$OH), bis-(3-methyl-1-imidazole)-pentylene dihydroxide (IMC$_5$OH), and bis-(3-methyl-1-imidazole)-hexylene dihydroxide (IMC$_6$OH) with different carbon atoms in the alkyl chain of the cations of ILs. The carbon chain length in the cations significantly affected the catalytic activity, where the biodiesel yields decreased gradually with the rise of the carbon atoms in alkyl chain cations of ILs. This scenario was due to both inductive and steric effects [128], which has been discussed previously. It is to be noted that, all the hydroxide based ILs exhibited excellent performance in the cottonseed oil transesterification, where the biodiesel yield exceeds 94%. Specifically, IMC$_2$OH and IMC$_3$OH performed excellently with>98% yield of biodiesel, which is close to the chemical equilibrium conversion. IMC$_2$OH, having the shortest carbon chain lengths in the cations of ILs, achieved not only the highest biodiesel yield but also exhibited the highest stability which can be reused up to 7 times with the minor loss of activity of 2.4% only. Fang et al. [124] introduced a novel hydroxide based IL, 1-butyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene hydroxide ([BTBD][OH]), which achieved an excellent biodiesel yield of 96%. They showed that for imidazolium based IL ([BMIM][OH]), an yield of 88% biodiesel was obtained. However, low biodiesel yield (65%) was obtained by using [TBA][OH] owing to the lack of basicity of the [TBA] cation and thus low turnover catalytic activity efficiency. Nonetheless, in a recent work conducted by Khiratkar et al. [87], 3-(2,3-dihydroxypropyl)1-methyl-1H-imidazole-3-ium hydroxide (DFImIL-OH$^-$) and poly(3-benzyl-1-(4-(sec-butyl)benzyl)-1H-benzimidazole-3-iumhydroxide) [PIL(OH$^-$)] were used as catalysts for biodiesel synthesis from castor oil. (DFImIL-OH$^-$) and PIL(OH$^-$) resulted in biodiesel yields of 68% and 59%, respectively. The low yield of biodiesel might be due to the complexity of the benzyl substituent in [PIL(OH$^-$)] and the longer chain of carbon atom in (DFImIL-OH$^-$), which reduced the basicity of the ILs for the catalytic efficiency. Zhang et al. [121] investigated the effect of 1,1,3,3-trimethyl-2-octyl-guanidine hydroxide with high electronegativity as well as basicity and found that it displays an excellent biodiesel yield of 97.2%. Specifically, the electronegativity is related to ionization energy, where the electron attraction gets weaker along with a decrease of electronegativity, followed by an increase in the OH$^-$ ionization ability. Moreover, the ILs exhibited a stronger conductivity, and thus accelerated the ion movement to increase the rate of transesterification for the biodiesel synthesis. In addition, the excellent amphipathicity of this IL has also made it better at mass transfer with the reactants to enhance the catalytic activity.

It has been reported in the literature that, choline hydroxide IL (ChOH) results in high biodiesel yield of 95% for transesterification of soybean oil [60]. The reusability test showed that ChOH exhibited a little drop or no drop in catalytic activity after four successive use, making it a highly potential environmental friendly catalyst to replace the traditional basic catalysts [60,119]. Fan et al. [60] compared the catalytic activity of different choline based ILs and found that ChOH exhibited better catalytic activity than other choline based ILs, i.e., choline methoxide ([Ch][OMe]) and choline imidazolium ([Ch][Im]). This result further suggested that hydroxide anion of the ILs gave excellent catalytic activity owing to stronger basicity which favors the transesterification reaction.

In summary, the catalytic activity of BILs for the transesterification was highly favored in methanol medium, owing to the dependence on the capability of activating the methoxyl group by the active species of BILs, especially OH$^-$ anion species of ILs.

# 3. Advanced IL-catalyzed transesterification process

Apart from being used as a single homogeneous catalyst, a combination of IL and other solid materials (e.g., magnetic nanoparticles, molecular sieves, and polystyrene), which act as a support to AILs/BILs, can further enhance the catalytic activity in biodiesel synthesis. Due to high cost, difficulty in product separation, problems in catalyst recovery

and large quantity requirements, ILs are generally immobilized onto the surface of solid materials to prepare supported ILs [133]. This provides catalytic activity from both catalytic counterparts as well as further promote the catalytic performance [134].

## 3.1. Supported ILs

The development of novel and promising immobilization carriers for ILs is necessary as these could be applied at large scale production facilities [135]. A literature summary of these applications is shown in Table 5. Wu et al. [133] reported on the use of surface-functionalized magnetic nanoparticle and ILs, i.e. by immobilizing multi-acid sites BAILs, 1-(propyl-3-sulfonate) imidazolium hydrogen sulfate [SO$_3$H-(CH$_2$)$_3$-HIM][HSO$_4$] onto the surface of the magnetic support, Fe$_3$O$_4$@SiO$_2$, using 3-chloropropyltrimethoxysilane as the "linker". Similarly, Zhang et al. [136] also studied the effect of the same magnetic support, Fe$_3$O$_4$@SiO$_2$, with BLAILs (FS-B-L-IL). The difference between these two studies is the acidity sites of the AILs. As for the heterogeneous catalyst counterpart, the Fe$_3$O$_4$ particle was inserted in the silica matrix, resembled a core–shell structure with strong magnetic responsiveness. The ILs were immobilized on the surface of nanoparticle via coupling reagent [133]. In a recent study, Zhang et al. [137] studied the development of another magnetically acidic ILs polymers (PILs) with the hydrophobic regulator catalyst (Fnm-PILs) using anion exchange and radical polymerization. PILs are ionic polymers composed of polymeric backbone and an IL species in monomer repeating units, that could perform dual functions of IL and polymers synergistically. The synergistic effects from both counterparts contributed to less viscosity of IL, improved the acid active sites of the catalyst [138]. Overall, the developed magnetic catalyst was easily synthesized and exhibited higher stability [139]. It is to be noted that, this kind of supported BAILs can be easily separated from reaction products without centrifugation or filtration, owing to the magnetic forces that could help in the separation process [133,136,137]. They also show excellent recyclability performance of > 4 cycles. As such, using magnetic supported ILs can selectively capture target objects from the complex samples, magnetically control the onset and termination reactions and ensure straightforward recycling of magnetic carriers [140].

Aside from the magnetic PILs, Feng et al. [134] developed a PIL, P (VB-VS)HSO$_4$, where the IL was immobilized on the 1-vinyl imidazole-based crosslinked copolymer microsphere, without the magnetic property. The developed IL functionalized on crosslinked copolymer microsphere had abundant meso-macropores, high surface areas, strong mechanical strength, and superior thermal stability. These PILs microspheres also showed better catalytic performance (>95%) compared to the magnetically acidic PILs (89.2–92.4%) [137]. This was attributed to the size of the PIL particle that promotes the catalytic activity and also favors the convenience of the operation process [134]. This also facilitates the recovery process for up to 5 consecutive cycles. Other type of PILs, such as, the copolymerization of BAILs oligomers of 1-(3-sulfopropyl)-4-vinyl pyridinium hydrogen sulfate ([SO$_3$H(CH$_2$)$_3$VPy] [HSO$_4$]), 1-(3-sulfopropyl)-3-vinyl imidazolium hydrogen sulfate ([SO$_3$H(CH$_2$)$_3$VIm][HSO$_4$]) and 1-(3-sulfopropyl) triethylammonium hydrogen sulfate ([SO$_3$H(CH$_2$)$_3$Et$_3$NH][HSO$_4$]) with divinylbenzene (DVB) or poly divinylbenzene (PDVB) [110,111,116,141,142]. These PILs exhibited excellent catalytic activity in the biodiesel production from waste and vegetable oil transesterification reaction. All these PILs have a high hydrophobic surface area to improve the mass transfer efficiency and thus avoid the leaching effect of the acid active site of the catalyst. Moreover, this supported BAILs also reduced the synthesis cost owing to the prevention of using expensive coupling reagents [141].

Supported BAIL catalyst involving immobilization of functional moieties with IL-like structures onto a porous high surface area support material has also been reported [143,144]. This supported ionic liquid catalyst possesses the advantages of having high acidity, activity, and stability. For instance, a benzimidazolium based [-SO$_3$H] functionalized

**Table 5**
Summary of a combination of ILs and other catalysts, supported or used as supporting material.

| Feedstock | Type of ILs | ILs | Optimal reaction conditions | Conversion (C) or Yield (Y) | Recyclability | Refs. |
|---|---|---|---|---|---|---|
| Soybean oil | Supported dual BAILs | [SO$_3$H-(CH$_2$)$_3$-HIM][HSO$_4$] onto the surface of Fe$_3$O$_4$@ SiO$_2$ | IL: 10.8 wt%<br>Temperature: 110 °C<br>Time: 4 h<br>Molar ratio of methanol: oil: 6:1 | 92.9 (C) | 4 | [133] |
| *Koelreuteria integrifoliola* oil | Supported BLAILs | Brønsted-Lewis acid bifunctional BLAILs-Fe$_3$O$_4$@SiO$_2$ | IL: 10 wt%<br>Temperature: 160 °C<br>Time: 10 h<br>Molar ratio of methanol: oil: 40:1 | 93.7 (Y) | 5 | [136] |
| *Euphorbia lathyris L.* oil<br>*Xanthium sibiricum Patr.* oil<br>*Jatropha curcas L.* oil<br>*Datura stramonium L.* oil<br>*Firmianaplatanifolia L.f.* oil<br>*Koelreuteriaintegrifoliola* oil | Supported BAILs | [FnmS-SH]<br>[CF$_3$SO$_3$]<br>(Fnm-PILs) | IL: 5 wt%<br>Temperature: 120 °C<br>Time: 6 hMolar ratio of methanol:oil: 18:1 | 91.7 (Y)<br>89.2 (Y)<br>92.5 (Y)<br>91.6 (Y)<br>90.8 (Y)<br>93.4 (Y) | 5<br>–<br><br><br><br> | [137] |
| Soapberry oil | Supported BAILs | P(VB-VS)HSO$_4$<br>(PILs) | IL: 8.7 wt%<br>Temperature: 150 °C<br>Time: 8 h<br>Molar ratio of methanol: oil: 29:1 | 95.2 (Y) | 6<br>– | [134] |
| Coconut oil<br>Palm oil<br>Tung oil | | | IL: 8.7 wt%<br>Temperature: 120 °C<br>Time: 3 h<br>Molar ratio of methanol: oil: 20:1 | 95.5 (Y)<br>95.8 (Y)<br>95.2 (Y) | | |
| Waste cooking oil | Supported BAILs | [SO$_3$H(CH$_2$)$_3$VIm][HSO$_4$] and DVB<br>(PILs) | IL: 1.0 wt%<br>Temperature: 70 °C<br>Time: 12 h<br>Molar ratio of methanol: oil: 16:1 | 99.0 (Y) | 6 | [142] |
| Waste cooking oil | Supported BAILs | [SO$_3$H(CH$_2$)$_3$VIm][HSO$_4$] with PDVB<br>(PILs) | IL: 1.0 wt%<br>Temperature: 70 °C<br>Time: 10 h<br>Molar ratio of methanol: oil: 15:1 | 99.0 (Y) | 6 | [116] |
| Waste cooking oil | Supported BAILs | [SO$_3$H(CH$_2$)$_3$Et$_3$NH][HSO$_4$] and DVB<br>(PILs) | IL: 1.0 wt%<br>Temperature: 70 °C<br>Time: 12 h<br>Molar ratio of methanol: oil: 15:1 | 99.1 (Y) | 6 | [141] |
| Vegetable oil | Supported BAILs | [SO$_3$H(CH$_2$)$_3$VIm][HSO$_4$] and DVB<br>(PILs) | IL: 1.4 wt%<br>Temperature: 70 °C<br>Time: 4 h<br>Methanol:oil: 1 g:1 g | 94.2 (C) | 10 | [110] |
| Waste cooking oil | Supported BAILs | ILs on DVB and VPy<br>(PILs) | IL: 0.8 wt%<br>Temperature: 70 °C<br>Time: 8 h<br>Methanol:oil: 2.91 g:5 g | 99.1 (Y) | 6 | [111] |
| Castor oil | Supported BAILs | Benzimidazolium based sulfonic acid functionalized solid support (SILC) | IL: 3.0 wt%<br>Temperature: 70 °C<br>Time: 6 h<br>Molar ratio of methanol: oil: 12:1 | 94.9 (Y) | 5 | [144] |
| Jatropha oil<br>Neem oil | | | IL: 3.0 wt%<br>Temperature: 70 °C<br>Time: 7 h<br>Molar ratio of methanol: oil: 12:1 | 95.7 (Y)<br>94.4 (Y) | | |
| Soybean oil | Supported BILs | SBA-15-pr-ILOH | IL: 7.0 wt%<br>Temperature: 65 °C<br>Time: 8 h<br>Molar ratio of methanol: oil: 20:1 | 95.4 (C) | 4 | [146] |
| *Firmiana platanifolia L.f.* oil | Supported BILs | Fe$_3$O$_4$@SiO$_2$@SBA-15(FnmS-PILs) | IL: 4.0 wt%<br>Temperature: 85 °C<br>Time: 5 h<br>Molar ratio of methanol: oil: 9:1 | 92.8 (Y) | 5 | [148] |
| Soybean oil | Supported BILs | [C$_8$VIm][Br] monomer and [BVD] cross-linker | IL: 9.15 wt%<br>Temperature: 65 °C<br>Time: 9.3 h | 96.3 (Y) | 5 | [151] |

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**Table 5** (*continued*)

| Feedstock | Type of ILs | ILs | Optimal reaction conditions | Conversion (C) or Yield (Y) | Recyclability | Refs. |
|---|---|---|---|---|---|---|
| *Xanthium sibiricum Patr* oil | Supported BILs | [β- CD-6-C$_3$Im]$^+$[OH]$^-$ <br> [β-CD-2-C$_3$Im]$^+$[OH]$^-$ | Molar ratio of methanol: oil: 21.9:1 <br> IL: 8.0 wt% <br> Temperature: 65 °C <br> Time: 12 h | 91.4 (Y) <br> 34.5 (Y) | – | [152] |
| Waste cooking oil | Supported BILs | [Bmin]OH/Mg-Al-La | Molar ratio of methanol: oil: 40:1 <br> IL: 3.0 wt% <br> Temperature: 65 °C <br> Time: 6 h | 98.7 (Y) | 6 | [153] |
| Wet Oleaginous Yeast *Rhodosporidium diobovatum* biomass | BAILs and KOH | [C$_2$MIM][EtSO$_4$] and KOH | Molar ratio of methanol: oil: 12:1 <br> IL:biomass: 2:1 g:g <br> Temperature: 65 °C <br> Time: 2.5 h <br> Methanol:oil: 16.9 g:1 g | 97.1 (C) | – | [155] |

IL on solid supports (silica) was applied for the transesterification of non-edible oils, including jatropha, castor, and neem oil, yielding about 95% biodiesel with high acid value [144]. Besides, the immobilization of IL onto the metal–organic frameworks has recently been reported. For instance, Fan *et al.* [145] evaluated the immobilization of an SFIL ([Psim][HSO$_4$]) onto the hybrid mesoporous material (SO$_4^{2-}$/ZrO$_2$-SiO$_2$(Et)) via a one-step condensation technique combined with hydrothermal treatment. The hybrid organic-ionic nature of these hybrid materials with the IL further enhances the intramolecular interactions. Moreover, owing to the co-existence of both Brønsted and Lewis acid active sites from both counterparts of the supported BAILs, better catalytic activity was observed (98.9%) along with the abilities of water and acid resistance [145]. They maintained acceptable yields after 5 consecutive runs.

On the other hand, fewer studies were carried out in supported BILs. For instance, the encapsulation of IL onto a mesoporous silica matrix. Xie *et al.* [146] investigated SBA-15 silica-supported BILs (SBA-15-pr-ILOH), via encapsulation of 4-butyl-1,2,4-triazolium hydroxide onto SBA-15 silica using 3-chloropropyltriethoxysilane as a coupling reagent. Sammah and Ghiaci [147] reported on immobilizing an oligomeric ILs onto a SiO$_2$ mesoporous matrix. These developed, supported BILs showed excellent catalytic activities and reusability for the transesterification reaction. Besides, providing supports with the high surface area along with readily separable magnetic property contributed to the implementation of a more efficient, convenient, and cost-effective magnetic PIL. Zhang *et al.* [148] reported on the immobilization of magnetic mesoporous carrier (Fe$_3$O$_4$@SiO$_2$@SBA-15), FnmS-PILs, which was synthesized through the anion exchange methods and facile radical polymerization. In another recent study, an amino-functionalized BILs (ABIL-Im) was immobilized on the functionalized Fe$_3$O$_4$@HKUST-1 materials, resulting in a solid hybrid base catalyst [149]. In comparison, the magnetic PILs displayed a biodiesel yield of approximately 92% [148,149], which is slightly less than the supported BAILs involving the encapsulation of ILs onto a mesoporous silica matrix (95–96%) [146,147], although not by a great extent. Core-shell structured nanocomposites with a mesoporous silica shell and Fe$_3$O$_4$ core were applied, due to their unique properties, for instance, low toxicity, magnetic response, and versatile derivation of the silica shell [150]. Moreover, Jiang *et al.* [151] implemented a superhydrophobic porous PILs ([C$_8$VIm][Br] and [BVD]) solid base catalyst, without the magnetic property, for soybean biodiesel production. However, for the same reaction conditions and feedstock adopted, heterogeneous CaO catalyst showed higher catalytic activity than the superhydrophobic porous PILs solid basic catalyst, owing to the weaker basic strength of this PIL [151]. Overall, except for requiring longer reaction time (9.3 h) [151] than the other magnetic PILs (3–5 h) [148,149], the use of this superhydrophobic porous PILs solid basic catalyst could significantly simplify the product separation process for methanol and catalyst recycling, as well as avoid

metal ion contamination [151]. Aside from that, Chang *et al.* [152] reported on a supramolecular BIL, [CD-6-C$_3$Im][OH], which was synthesized from mono-(6-imidazolyl-6-deoxy)-β-CD, with lower biodiesel yield of 91.4%. On the contrary, Sun *et al.* [153] reported an excellent catalytic activity with a yield of up to 98.7%, the highest among the supported BIL studies, as shown in Table 5. In this study, an imidazolium based ILs, [Bmin][OH], was immobilized onto the oxide surface to obtain IL/Mg-Al-La catalyst [153]. Pure Mg-Al-La catalyst exhibited low catalytic activity in the transesterification of high acid value waste cooking oil. Meanwhile, IL immobilized on Mg-Al-La catalyst enhanced the basic strength and basicity of supports, where the basicity increased from 1.04 to 2.48 mmol/g after immobilization [153]. As such, the catalytic activity of the immobilized IL/Mg-Al-La catalyst in the transesterification was improved. The modification of La$^{3+}$ cation in the oxide framework has enhanced the Schottky effect as the main reason to increase the basicity of Mg-Al-La support [154]. Based on the findings mentioned above, the supported BAILs/LAILs both deserve even more attention in a greener biodiesel production process.

### 3.2. IL lipase co-catalysts

Lipase-catalyzed reaction has also emerged as an alternative bio-catalyzed technique to the conventional synthesis. Lipases can be found in animals, plants and microorganism and help in the metabolism of oils and fats. Some early lipases were isolated from prokaryotic microorganisms such as *Pseudomonas aeruginosa*, *Serratia marcescens*, and *Pseudomonas fluorescens* species, but do not have a protocol for commercial production due to the sequence complexity and molecular variety till date [156]. The lipase acts as a digestive enzyme to facilitate the transfer of lipids and deposition of fat that is used as an energy reservoir [157]. In biodiesel conversion, lipases are hydrolases that act on the carboxyl ester bonds in triglycerides to yield fatty acids and glycerol at the lipid-water interface [158]. This is due to the active centre of most lipases being covered by an amphiphilic polypeptide loop, which assumes an open conformation when in contact with hydrophobic substrates such as oil droplets [156]. During open conformation, the catalytic activity is increased and is highly selective towards oils and fats.

The enzymatic lipase-catalyzed activity has shown higher stability, selectivity, and improved activity for the biodiesel synthesis [135]. Besides, the use of lipase as biocatalyst could enhance the catalytic activity but are often unstable in the presence of short-chain alcohols (methanol) due to enzyme inactivation [159]. In addition, economic concerns usually limit the application of enzymes for large scale biodiesel production due to high material cost. The use of IL in a lipase-catalyzed reaction as a co-catalyst (Fig. 3) offers a significant contribution as it could avoid the mass transfer limitations faced by the organic solvents [135]. The instability of lipases under high temperature, pressure

conditions and with certain solvents also limits its usage. Moreover, the issues on environmental contamination, hazards, and toxicity derived from the organic solvents were also concerns [160]. To address these problems, the ILs were predicted to be a promising substitute for the inorganic solvents, owing to its eco-friendly properties that could lead to greener industrial processes [126].

Recently, various types of IL has been investigated in different kinds of lipase-catalyzed transesterification, as depicted in Table 6. Lipases from different sources exhibited different substrate specificity and catalytic activity. For the selection of IL, the anions contributed to a more significant effect on the biodiesel yield than their cation counterparts [161]. As illustrated in Table 6, hydrophobic ILs with $[NTf_2]^-$ anion has shown better biodiesel yield compared to that of $[BF_4]^-$ and $[PF_6]^-$ anions based ILs, as a co-catalyst with different lipase. Hydrophobic ILs was immobilized with the enzyme as it preserves the essential water associated with the protein molecule, thus allowing high enzyme activity along with an increase of the substrate solubility and solvent viscosity, which favors the biodiesel production [162].

Diego et al. [163] screened a series of hydrophobic ILs using immobilized lipase for the efficient production of biodiesel. A total of fifteen ILs composed of $[BF_4]$, $[PF_6]$ or $[NTf_2]$ anions attached with a different alkyl chain length of the methyl imidazolium cations ($[C_{10}MIM]$, $[C_{12}MIM]$, $[C_{14}MIM]$, $[C_{16}MIM]$ and $[C_{18}MIM]$) were assayed in conjunction with Candida Antarctica lipase B (CAL) and Pseudomonas fluorescens lipase AK. Among this combination of ILs and enzymes, the highest catalytic activity was achieved with the use of $[C_{16}MIM][NTf_2]$ immobilized with CAL with 245.13 U g$^{-1}$ IME. Based on the results, an increase in the alkyl chain length of the imidazolium cation further improved the catalytic activity. The maximum synthetic efficiency was observed for $[C_{16}MIM]$ cation based ILs, after which it decreased. Theoretically, the increase of alkyl chain lengths of the substituent of the imidazolium ring would increase the hydrophobicity, maintaining the essential water layer around the protein molecule and resulting in the reduction in direct protein–ion interactions [164]. In a similar manner, Ríos et al. [165] assessed 10 different ILs immobilized with CAL for the biodiesel production, where the result revealed as follow: [EMIM][TFO] < [BMIM][TFO] and [BMIM][Tf₂N] < [BdMIM][Tf₂N] < [OMIM][Tf₂N]. These results can be explained by the increase in cation hydrophobicity and decrease in anion nucleophilicity, both effects enhancing the enzyme activity. These results were following the previous result on screening the nature of ILs and effects on lipases that catalyze butyl propionate ester synthesis [166]. Besides, Liu et al. [161] studied the effect of cation and anion structures using a range of nineteen different ILs. Among them, [OmPy][BF₄]-Burkholderia cepacia lipase (BCL) exhibited the best ILs-BCL catalyst with a biodiesel yield of 82.2% but was lower than those $[PF_6]^-$ and $[NTf_2]^-$ anion based ILs [163,167]. Based on the result trend, the increase of ILs-BCL activity was in the following order: $[PF_6]^-$ > $[NTf_2]^-$ > $[TfO]^-$ > $[BF_4]^-$ > $[CH_3SO_3]^-$ ~ $[Cl]^-$. This was due to the ILs with anions containing $[BF_4]^-$, $[Cl]^-$, $[OH]^-$, $[TfO]^-$ and $[CH_3SO_3]^-$ have higher nucleophilic properties compared to that of $[PF_6]^-$ and $[NTf_2]^-$. The high nucleophilic properties could diminish the catalytic performance [168].

Excellent catalytic activities were also obtained by using another catalytic system composed of $[PF_6]^-$ anions based ILs ($[BMIM][PF_6]$) immobilized with Penicillium expansum lipase (PEL) and Rhizopus chinensis lipase (RCL), with excellent biodiesel yields of 93.5% and 96.6%, respectively, from Millettia pinnata seed oil [169]. This is to be noted that, these ILs enzyme can be recycled up to 5 times with moderate loss in the conversion efficiency. Similarly, $[BMIM][PF_6]$ immobilized on PEL has also been successfully applied in biodiesel production from corn oil [167]. The $[BMIM][PF_6]$-PEL catalyzed conversion was slightly higher than $[BMIM][PF_6]$-CAL catalyzed conversion. Later, Su et al. [170] conducted a $[PF_6]^-$ anions based ILs with mono-alkyl chain cation, $[HMIM][PF_6]$, immobilized on Candida rugosa lipase (CRL) from Chinese tallow kernel oil. $[HMIM][PF_6]$, being the mono-alkyl group, could simplify the downstream processing and boost the biodiesel conversion up to 95.4%. Similar observation to that of other works [90,98], where mono-alkyl carbon cation based ILs gave better catalytic activity compared to that of the longer alkyl carbon chain length. This is mainly due to both inductive and steric effects, which has been discussed previously (Section 2). In a recent study, Fan et al. [171] investigated dialkyl-based ILs, $[C_1C_3OHPyr][NTf_2]$, immobilized with CRL with slightly less biodiesel yield of 82.4%. This could be due to the hydroxyl group holding the $H_2O$-mimicking property, and hydrogen-bonding functionality are weaker compared to the longer alkyl chain length based ILs. Moreover, the enzyme (CRL) could also be the reason that is leading to a less flexible and active conformation. Aside from the hydrophobic ILs, significantly lower biodiesel yields were achieved using zwitter-type ILs, (Oct-PrSO₃) immobilized with CAL from sunflower oil [172]. This was presumably due to the reduced miscibility of longer alkyl chain length of zwitter-type ILs (Oct-PrSO₃), which led to mass transfer limitations between the substrates and the catalysts (Souza
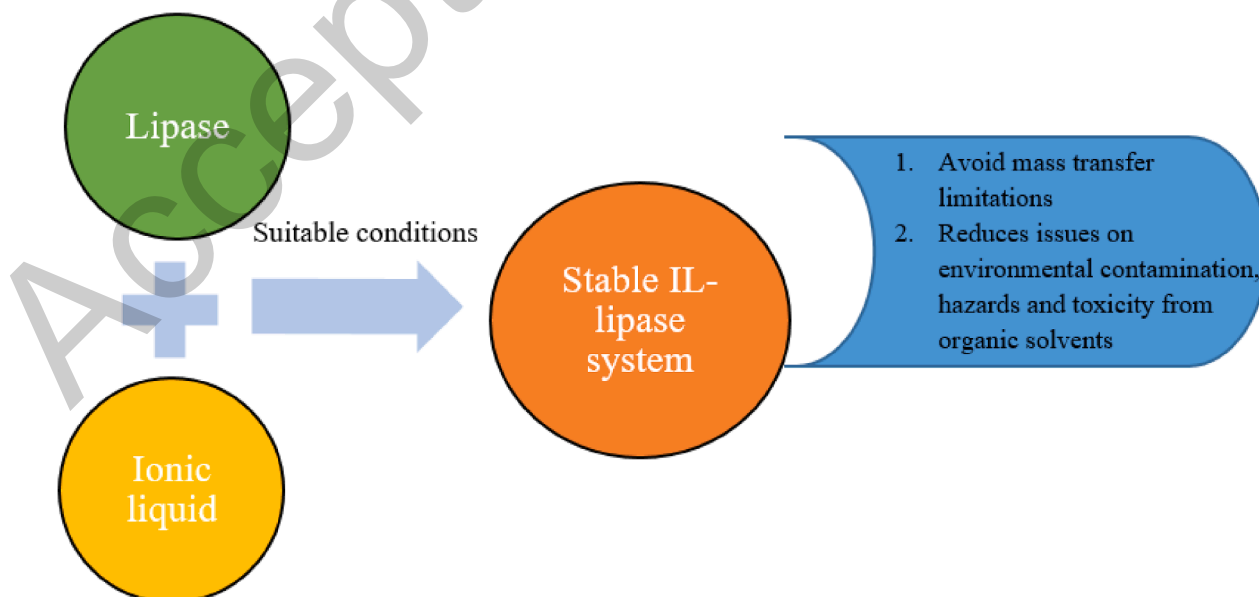


**Fig. 3.** ILs enzyme-catalyzed reaction.

**Table 6**
Summary of a combination of ILs and enzyme.

| Feedstock | IL | Enzyme | Optimal reaction conditions | Conversion (C) or Yield (Y) | Recyclability | Refs. |
|---|---|---|---|---|---|---|
| Olive oil<br>Sunflower oil<br>Palm oil<br>Waste cooking oil<br>Triolein | $[C_{16}MIM][NTf_2]$ | *CAL* B and Pseudomonas fluorescens lipase AK | IL: 800 µl<br>Temperature: 60 °C<br>Time: 24 h<br>Molar ratio of methanol:oil: 6:1<br>Enzyme: 10 wt% | 93.4 (Y)<br>92.8 (Y)<br>94.1 (Y)<br>96.9 (Y)<br>99.4 (Y) | – | [163] |
| Sunflower oil | $[OMIM][NTf_2]$ | *Candida antarctica* lipase B | IL: 800 ml<br>Temperature: 40 °C<br>Time: 24 h<br>Molar ratio of methanol:oil: 12:1<br>Enzyme: 75 mg | 60.0 (C) | – | [165] |
| Soybean oil | $[OmPy][BF_4]$ | *BCL* PS | IL: 2.4 ml<br>Temperature: 40 °C<br>Time: 12 h<br>Molar ratio of methanol:oil: 100:2.43 Enzyme: 4.0 wt% | 82.2 (Y) | – | [161] |
| *Millettia pinnata* seed oil | $[BMIM][PF_6]$ | *Penicillium expansum* lipase | IL: 2.0 ml<br>Temperature: 40 °C<br>Time: 48 h<br>Molar ratio of methanol:oil: 6:1<br>Enzyme: 20 wt% | 93.5 (Y) | 5 | [169] |
| Corn oil | $[BMIM][PF_6]$ | *Penicillium expansum* lipase | IL: 1.5 ml<br>Temperature: 40 °C<br>Time: 24 h<br>Molar ratio of methanol:oil: 2:1<br>Enzyme: 200 mg | 86.0 (Y) | – | [167] |
| Chinese tallow kernel oil | $[HMIM][PF_6]$ | *Candida rugosa* lipase | IL:oil: 1:1 mg:g<br>Temperature: 40 °C<br>Time: 24 h<br>Molar ratio of methanol:oil: 4:1<br>Enzyme: 20 wt% | 95.4 (Y) | – | [170] |
| Soybean oil | $[C_1C_3OHPyr][NTf_2]$ | *Candida rugosa* lipase | IL: 1.0 g<br>Temperature: 25 °C<br>Time: 2 h<br>Molar ratio of methanol:oil: 2.5:1<br>Enzyme: 30 mg | 82.4 (Y) | – | [171] |
| *Chlorella pyrenoidosa* oil | $[BMIM][PF_6]$ | *Penicillium expansum* lipase<br>*CAL* | IL: 1 ml<br>Temperature: 40 °C<br>Time: 48 h<br>Molar ratio of methanol:oil: 3:1<br>Enzyme: 0.1 g | 90.7 (Y)<br>86.2 (Y) | – | [173] |
| *Chlorella vulgaris* or *Chlorella protothecoides* | $[C_{16}mim][NTf_2]$ and $[Bmim][Cl]$ (95:5 (w/w)) | *CAL* B | IL:microalgae: 1.0 g:0.5 g<br>Temperature: 60 °C<br>Time: 2 h<br>Molar ratio of methanol:oil: 6:1<br>Enzyme: 18 wt% | 100.0 (Y) | 5 | [174] |

*et al.*, 2015). Besides, in microalgae-based biodiesel production, Bauer *et al.* [172] reported *Chlorella zofingiensis* whole-cell in water resulted in 74.8% of lipid extraction, 27.7% of biotransformation products and up to 16.2% biodiesel by using a zwitter-type ILs (Oct-PrSO₃) and CAL. In another work, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) offered a promising solvent in coupling with the enzymatic transformation, providing a high conversion yield of biodiesel up to 90.7% [173]. In recent work, Lozano *et al.* [174] implemented a novel method for the algae oil extraction and the subsequent conversion to biodiesel of up to 100% yield via a binary mixture of ILs enzyme catalytic system, i.e., hydrophobic [C₁₆MIM][NTf₂] (Sponge-Like ILs, SLILs) and hydrophilic [BMIM][Cl] ILs, coupling with Novozym 435. Hydrophobic IL, bearing with [NTf₂] anion, could offer an excellent reaction medium for biodiesel synthesis, while the hydrophilic [BMIM][Cl] could dissolute the cellulosic biomass materials. Furthermore, [C₁₆MIM] [NTf₂] provided a clean separation of the biodiesel product, as well as the recovery and reuse of the binary mixture of ILs enzyme catalytic system.

In summary, ILs containing [PF₆]⁻ and [NTf₂]⁻ anions showed better biodiesel conversion efficiency than those of [BF₄]⁻, [OH]⁻, [Cl]⁻, [CH₃SO₃]⁻ and [TfO]⁻ anions. Among them, [PF₆]⁻ and [BF₄]⁻ anions are reactive and prone to release harmful and corrosive hydrogen fluoride gas [175]. In this regard, [NTf₂]⁻ is by far the most potential

anion with a more chemically stable property than the [PF₆]⁻ and [BF₄]⁻ anions [176]. Besides, alcohols with longer carbon chain length signify higher molecular mass; thus, higher density and greater mass transfer limitations were observed [177]. As such, methanol has shown to have the highest catalytic activity among all the different carbon chain lengths of alcohol (methanol, ethanol, n-propanol, and n-butanol), as conducted by Diego *et al.* [163]. Overall, an ideal IL-enzymatic catalytic system should have: (i) good enzyme compatibility to ensure the enzyme's active structure and functionality are aligned with the suitable hydrophobic IL, (ii) a high substrate solubility to increase the availability of the substrate concentration for the enzyme, and (iii) a low viscosity to maximize the mass transfer for the easier accessibility of the substrate to the enzyme.

## 4. Intensification techniques for biodiesel production

Microwave and ultrasound-assisted IL-catalyzed reactions are the emergent technologies in replacing the conventional method for biomass conversion to biodiesel [178]. These technologies can dramatically reduce reaction times, improve catalytic activities, enhance the selectivity as well as the yield [179,180]. The use of microwave and ultrasound-assisted IL catalytic system for biodiesel production is still at a developing stage, as depicted in Table 7.

**Table 7**
Summary of microwave and ultrasound-assisted ILs-catalyzed reaction for biodiesel synthesis.

| Feedstock | Type of reactor | Type of ILs | Catalyst | Optimal reaction conditions | Conversion (C) or Yield (Y) % | Recyclability | Ref. |
|---|---|---|---|---|---|---|---|
| Waste cooking oil | Microwave synthesis reactor | BILs | [MorMeA][Br] | IL: 1 wt% NaOH: 0.75 wt% Temperature: 70 °C Time: 6 min Molar ratio of methanol:oil: 9:1 | 98.1 (Y) | 7 | [183] |
| Jatropha oil | Microwave synthesis reactor | BILs | [MorMeA][Br] | IL: 1 wt% NaOH: 0.75 wt% Temperature: 70 °C Time: 6 min Molar ratio of methanol:oil: 9:1 | 98.5 (Y) | 7 | [184] |
| Palm oil | Long neck flask (Microwave irradiation) | BAILs (multi-acid sites) | [HSO$_3$-BMIM][HSO$_4$] | IL: 9.17 wt% Temperature: 108 °C Time: 6.4 h Molar ratio of methanol:oil: 11:1 | 98.9 (Y) | 6 | [185] |
| | Long neck flask (Conventional heating) | | | IL: 9.17 wt% Temperature: 108 °C Time: 8 h Molar ratio of methanol:oil: 11:1 | 92.9 (Y) | | |
| *Camptotheca acuminata* seed oil | Digital microwave-assisted reactor | Supported BAILs | [BSO$_3$HMIM] HSO$_4$–Fe$_2$(SO$_4$)$_3$] | IL: 4 wt% Temperature: 60 °C Time: 1 h Molar ratio of methanol:oil: 5:1 | 95.7 (Y) | 9 | [186] |
| Castor oil | Ultrasonication horn (22 kHz, 500 W) | BBAIL | benzimidazolium based Brønsted acid IL | IL: 9 mol% Temperature: 50 °C Time: 1.5 h Molar ratio of methanol:oil: 10:1 | 96.0 (Y) | 3 | [194] |

Microwave heating offers energy efficiency and accelerates mixture heating time, where the samples are directly heated through the interaction between microwave energy and molecular dipole moments of the starting materials [181]. The intense and quick heating via microwave irradiation enhances mass transfer rates and promotes cell wall breaking which is facilitated through localized high temperature and pressure gradients [182]. Furthermore, ILs possess a strong capacity for absorbing microwave energy, thereby enhancing the efficiency of ILs-catalyzed reactions [118]. The setup of the ILs-catalyzed microwave-assisted reaction is shown in Fig. 4.

In BILs, Lin *et al.* [183] reported a combination of 1 wt% 4-allyl-4-methylmorpholin-4-ium bromine ([MorMeA][Br]) and 0.75 wt% NaOH produced a high biodiesel yield of 98.1% from the transesterification of waste cooking oil, using a microwave heating system. An improved biodiesel yield of + 3.2% was observed by using mixed catalysts compared to that of NaOH catalyst. The results indicated [MorMeA][Br] enhanced the biodiesel yields along with reduced NaOH use by 0.25 wt%. In the same catalytic system, Lin *et al.* [184] further applied this combination of catalysts for the transesterification of jatropha oil with 98.5% yield of biodiesel. It is to be noted that both studies showed a very short reaction time for this microwave heating system in achieving excellent biodiesel yield. Moreover, morpholinium-based ILs were low cost, thermally stable, and recyclable [184].

BAILs with sole and multi-acid sites, as well as mixed acids (BLAILs) have been applied in conjunction with microwave heating system. Ding *et al.* [185] utilized a BAIL with multi-acid sites, 4-(3-methyl-1-imidazolio)-1-butanesulfonic acid hydrogen sulfate ([HSO$_3$-BMIM][HSO$_4$]) for the transesterification of palm oil along with microwave system. The microwave heating system improves the catalytic activity by boosting the yield by another 6.7% compared to that of conventional heating methods [185]. Nonetheless, in [HSO$_3$-BMIM][HSO$_4$] catalytic system, higher reaction temperature, and longer timeframe are required to reach the optimum catalytic activity. Furthermore, Li *et al.* [186] applied

BLAILs, [BSO$_3$HMIM][HSO$_4$] with various metal sulfates, where the Lewis acid Fe$_2$(SO$_4$)$_3$ contributed to a superior catalytic activity. Among the coupling of different metal sulfates with [BSO$_3$HMIM][HSO$_4$] studied, the biodiesel yield decreased as follows: Fe$_2$(SO$_4$)$_3$ > CuSO$_4$ > ZnSO$_4$ > MgSO$_4$ > CaSO$_4$. The results corresponded with the order of ability to accept electron of metal cation as follows: Fe$^{3+}$ > Cu$^{2+}$ > Zn$^{2+}$ > Mg$^{2+}$ > Ca$^{2+}$. As for the BAILs counterpart, it enhanced the ionization of metal sulfates, based on the synergetic effect of both acidity sites (Brønsted and Lewis acids, Fe$^{3+}$). The success in using this coupling catalyst was also in agreement with other conventional heating studies reported previously [99,100,115].

For BAILs with the sole acid site, Wahidin *et al.* [181] reported that 1-ethyl-3-methylimmidazolium methyl sulfate ([EMIM][MeSO$_4$]) showed the best cell disruption (99.7%) and biodiesel yield (36.8%) from wet *Nannochloropsis* sp. biomass in a direct transesterification using microwave heating system. The use of microwave heating increases the disruption of microalgae cells and thus enabling the release of lipids into the reactant mixture. Methanol acted both as an extraction solvent of lipids as well as a reactant for esters transesterification. The synergistic effect produced by the combination of IL-methanol solvent and microwave heating increased the yield to 42.22% at optimised reaction conditions. Use of the microwave results in a large reduction in activation energy which is caused by the interaction of microwaves at the molecular level in the reaction mixture resulting in dipolar rotation and ionic conduction (dipolar polarization) [187,188]. This scenario increases the local temperature around the OH group, exceeding the activation energy required for the transesterification reaction to take place [189,190].

Apart from that, ultrasonication is also an alternative technique to increase the rate of biodiesel production [191]. The increased collisions between the reactants accelerate the reactions due to the vibration and turbulence arising from the ultrasonic cavitation effect [192,193]. The setup of the ultrasound-assisted ILs-catalyzed reaction via the ultrasonic probe is shown in Fig. 5. This technique was recently applied in
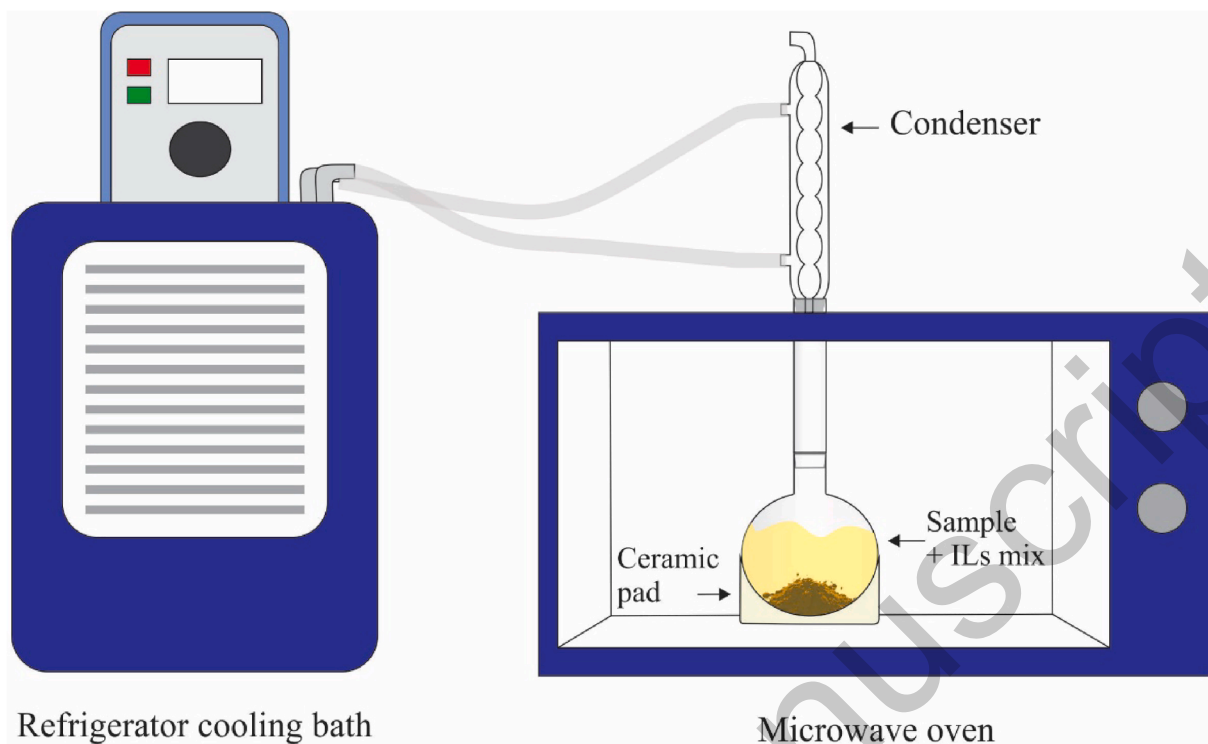
**Fig. 4.** Microwave-assisted ILs-catalyzed reactions.

benzimidazolium based BAILs, on the transesterification of castor oil [194]. It was found that ultrasonication was able to achieve biodiesel synthesis in less time and was about ten times faster than the process without ultrasonication. It should be noted that the ultrasonic treatment can also be conducted with an ultrasonic bath, where the setup is similar, however, the probe is replaced by a water bath that will be sonicated surrounding the sample and aqueous ILs mix. Although there is a significant difference in reaction time with ultrasonication, this technology is challenging when applied in an industrial scale operation due to the increased power and energy requirement [194].

Given the emergence of both microwave and ultrasound-assisted biodiesel production, several future investigations to include a



**Fig. 5.** Ultrasound-assisted ILs-catalyzed reaction via the ultrasonic probe.

continuous microwave and ultrasonic reactor systems with the use of ILs catalysts for techno-economic feasibility studies and pilot-scale tests are essential.

## 5. Prospects and challenges

ILs are attracting a great amount of interest recently, illustrated by their multidisciplinary applications, including chemistry, materials science, environmental science, and chemical engineering [195]. The chemical variety of ILs has grown tremendously, owing to the functional group or the supporting material that can be covalently tethered to the cation or anion (or both), thus offering the prospect of task-specific IL (TSIL) [22]. TSILs are the latest trend of ILs, which have been continuously utilized in the area of organic synthesis [196]. Hence, the important feature of ILs is regarded as their ionic species design ability, where these ions can be fine-tuned through sidechain lengths on the cation as well as a choice of different types of cation based ILs, i.e., imidazolium, ammonium, choline, pyridinium, etc. Meanwhile, the choice of the anion is usually based on the acid/base property. Additionally, some interesting features of IL include dual hydrophobicity-hydrophilicity ends, solute solubility efficiency, and the presence of an additional functional group (e.g. [-SO$_3$H]) in cation. All these generally favors the catalytic activity [197]. In the present review, the most utilized ILs reported for the biodiesel production is sulfonic acid functionalized ILs (SFILs) [106,112,113], choline based ILs [60,119], hydroxide based ILs [87,124,125], polyionic liquids (PILs) [137,151,198], and hydrophobic ILs enzyme [145,170,199]. To be precise, biodiesel production using ILs-catalyzed conversion can be improved by using ILs with (i) either acid or basic catalysts, (ii) strong molecular interactions between cation and anion, (iii) providing supports or combined with enzymatic catalyst, (iv) mixed acids catalysts (BLAILs), or (v) their combinations. In general, acidic type ILs (AILs) are more used than the basic type (BILs). In both AILs and BILs, the stronger the acidity/basicity of the ILs, the better the catalytic activity in esterification/transesterification. BAILs with multi-acid sites and BLAILs exhibited a better catalytic activity compared to the BAILs with the sole acid site. Providing support to LAILs/BAILs is also another possible technique to enhance the catalytic activity for the biodiesel yield since the pore structure of the support is an important factor for the catalytic activity [200].

Furthermore, the use of an enzyme, especially lipases along with ILs contribute several benefits, including a high conversion rate, high selectivity, and enzyme recyclability enhancement [160]. Intensification techniques such as microwave irradiation and ultrasound are the alternatives to the conventional heating system that could accelerate the reactions for better efficiency in biodiesel production [201]. As such, IL-catalyzed transesterification using microwave and ultrasound techniques have successfully enhanced the mixing of reactants while reducing the reaction time compared to that of conventional reaction [202].

The utilization of IL in biodiesel synthesis has proven to be a good choice as it eliminates the limitations of traditional homogeneous catalysts such as difficulty in recovery and corrosiveness, as well the limitations of heterogeneous catalysts such as instability and leaching of acidity groups during reaction [22]. Since IL acts as dual solvent-catalysts, it forms a biphasic solution upon completion of the reaction [203]. This two-layered solution is created with the organic phase (upper layer), separated from the aqueous phase (bottom layer) [204]. This allows for biodiesel to be separated the ILs residues and substrate retaining at the lower layer [205]. Meanwhile, it also favors the forward shift of the reaction [206]. In addition, the extraction processes, which include liquid–liquid extraction, solid–liquid extraction, solid-phase extraction, and induced-precipitation techniques, are also favored when using IL. The use of ILs could exhibit higher biodiesel extraction yields and simple purification in comparison to those of conventional solvents and materials, as reported in a review on ILs-mediated

extraction and separation processes for organic products [207]. In this regard, the development of ILs is the most recent breakthrough as the potential alternative innovation, which has begun to yield some industrial potential in recent years [208].

Recent developments have seen ILs applied in supercritical conditions for biodiesel production. The target of using this supercritical technology is to address certain difficulties faced in the conventional heating method, such as the transesterification reaction speed at ordinary temperature and pressure conditions. However, the development of supercritical IL-catalyzed reaction for the biodiesel production is very limited. Caldas *et al.* [209] first investigated the use of supercritical ethanol to produce soybean biodiesel, achieving a 97.6% conversion yield by using BAILs with the sole acid site, 1-methylimidazolium hydrogen sulfate ([HMIM][HSO$_4$]). In another study, Ortiz-Martínez *et al.* [210] investigated the use of two different acidic anion based BAILs, i.e., 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO$_4$]) and choline dihydrogen phosphate ([Chol][H$_2$PO$_4$]), in supercritical methanol for the transesterification of Karanja oil, achieving 61.6% and 95% conversion yield respectively. These results suggest that the catalytic activity is affected by the relative acidity order of the acidic anion [211].

Nonetheless, ILs, like any other catalysts, are not intrinsically green and environmentally friendly, although ILs have been highly regarded as "green reaction media" in the catalytic processes [212]. In particular, the most utilized SFILs, which bear an acidic [-SO$_3$H] functionalized group in the cation of ILs, are of extremely strong acidity and thus corrosive which could cause serious equipment corrosion [213]. Apart from that, in terms of its economic feasibility, the high cost of most ILs is still a big obstacle hindering their industrial applications, which has continuously caused a barrier to commercialization [214]. Furthermore, the complicated synthesis route of most ILs needs to be addressed to reduce solid/liquid waste produced [215,216]. For a feasible operation, ILs recovery has to be as efficient as possible so that the ILs can be used repeatedly [217]. The development of effective methods for ILs recovery is another main obstacle for the large scale biodiesel production process.

Designing a "greener" IL for catalytic processes for the biodiesel production is difficult, and extensive research is required to improve the understanding of the catalytic activity of various IL. As such, to develop a "greener" ILs, acidic [SO$_4$]$^{2-}$ anion based ILs, by combining with different alkyl sulfate groups such as hydrogen sulfate ([HSO$_4$]$^-$), methyl sulfate ([MeSO$_4$]$^-$), and ethyl sulfate ([EtSO$_4$]$^-$), have been reported with no toxic by-product formation making these environmentally friendly [218]. Moreover, these ILs are stable through its reusability and form a biphasic layer with the organic layer, which could ease the organic product extraction [219]. Among them, [HSO$_4$]$^-$ anion based ILs have been highly studied for various esterification reactions [206,220,221]. For instance, in recent works, Tiong *et al.* [105,222] demonstrated the advantages of using [HSO$_4$]$^-$ anion based ILs, indium trichloride-1-methylimidazolium hydrogen sulfate (InCl$_3$-[HMIM][HSO$_4$]), in the absence of an acidic [-SO$_3$H] functionalized group, as an efficient and recyclable catalyst for the production of levulinic acid and ethyl levulinate biofuel. Although the ILs compose of the sole acid site, solely acidic protons on the [HSO$_4$]$^-$ anionic component is sufficient for the activation of the chemical reaction effectively. Moreover, [HSO$_4$]$^-$ anion based ILs also contribute to effective lignin/cellulose fractionation and thus enhance the cellulose digestibility for subsequent conversion, such as into FAMEs (biodiesel) production [223–225]. As such, the pretreatment step, followed by the subsequent catalytic conversions into biodiesel via one-pot is a viable potential approach by using ILs-catalyzed strategy [208]. This approach inevitably decreases the duration, cost, and energy usage of the conversions, which is a technological breakthrough in eliminating wastewater and solid waste generation. Besides, [HSO$_4$]$^-$ anion based ILs can also be produced more economically due to the feedstock required for the synthesis are low cost and ease of synthesis [214]. For example, for synthesizing triethylammonium hydrogen sulfate ([HNEt$_3$][HSO$_4$]) are triethylamine and sulfuric acid.

The costs for both starting materials are < $2 kg$^{-1}$ in tonne quantities. In addition, a simple mixing and stoichiometric reaction are required for the synthesis of this ILs [226]. In this regard, the use of [HSO$_4$]$^-$ anion based ILs as the catalytic reaction media could benefit the research on the rational design of efficient yet cost-savvy ILs in bringing a bright future for the development of biodiesel production. In any case, an entailed-knowledge on the techno-economic impacts on [HSO$_4$]$^-$ anion based ILs at the pilot-scale is yet to be reported, thus deserve further exploration.

Enzymes as biocatalysts in coupling with ILs inevitably provide advantages for the biodiesel production, but the industrial application of this technology remains scarce. This happens due to several hindrances such as (i) the economic impact of reusability of both ILs and enzyme catalysts in repeated operation cycles, (ii) the development of ILs-immobilization techniques where it involved the substitution of expensive commercial supports, as well as (iii) the high cost and instability of enzymes [159].

The microwave and ultrasound-assisted ILs-catalyzed reactions, supercritical ILs for transesterification processes were the most recent development in this field. Microwave and ultrasound techniques enhance mass transfer characteristics leading to a reduction in reaction times and production costs [227]. At the same time, supercritical ILs technology offers several advantages compared to other methods, including direct reaction without pretreatment step of feedstock, short residence time, high reaction rate, and applicability to a wide variety of feedstocks [228]. Nevertheless, supercritical technology involves energy-intensive processes, which could result in high operating costs [229]. In any case, the use of these techniques with the IL-catalyzed reaction is still at the developing stage, and thus deserve further exploration. It is always necessary to improve existing ILs techniques by developing new ILs methodologies with low cost and environmentally benign sustainable catalytic processes. As such, with the speculation of using [HSO$_4$]$^-$ anion based ILs, in combination with microwave and ultrasound-assisted techniques, could be an option to achieve a greener and sustainable biodiesel production route.

## 6. Conclusions

This review discusses various biodiesel feedstocks that can be obtained from agricultural waste and microalgae, along with their corresponding biodiesel properties. Ionic Liquids (ILs) are salt-like materials that are liquid at room temperature and are primarily made of ions (both cations and anions) and short-lived ion pairs. The use of ILs in catalytic systems has been reported extensively. From the review, ILs with brønsted acidity or basicity not only pose a low risk to the environment but also result in high biodiesel yields with mild reaction conditions in a short time. Brønsted acidic ILs can convert free fatty acids as well as triglycerides to biodiesel without the need for pretreatment, which facilitates in reducing the production cost of biodiesel. In addition, a combination of mixed acid IL catalytic system (BLAILs) also exhibited excellent catalytic activity. Supported ILs could increase the surface area between the reactants and catalysts, thus further enhance the biodiesel yield. Hydrophobic ILs are also excellent co-catalysts in conjunction with the enzyme, as they reduce the possibility of enzyme deactivation. Given the emergence of both microwave and ultrasound-assisted biodiesel production, future investigations on improving those processes, techno-economic feasibility studies, and pilot-scale testing of continuous microwave and ultrasonic reactor systems with IL catalysts are essential. Besides, the cost analysis for utilizing ILs and further life cycle analysis for these processes would also be beneficial for the commercial application of these catalysts. The environmental effect and potential toxic effects from the disposal of ILs are also still unknown. As such, the improvement of IL catalytic activity and simultaneously understanding their economic and environmental risks would be essential for the development of this technology. This review on IL-catalyzed biodiesel production will help to bridge the gap between the current and future synthesis technologies.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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