



# The current state applications of ethyl carbonate with ionic liquid in sustainable biodiesel production: A review

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## ABSTRACT

Driven by the high energy demand and environmental concerns, biodiesel as a substitute for fossil fuels is recognized as promising renewable and clean energy. Biodiesel has gained interest around the world over the last few years because it could be used to reduce most regulated exhaust emissions. Herein, we discuss the application of catalytic transesterification by using ionic liquids (ILs) catalyst with alcohol and waste oil for the clean synthesis of biodiesel in order to reduce the emission of NO<sub>x</sub> and CO. However, the running cost of this process is still higher than that of the conventional chemical transesterification. Non-edible sources such as waste oil, non-edible vegetable oil, and waste animal oil are commonly used to produce biodiesel due to their low cost and no dependency on the food chain. This review provides an overview of the recent progresses in improving the biodiesel production process by using ILs and determining the activation energy and the properties of the finished product. In addition, the future direction in biodiesel production via ILs catalysis in the transesterification has been discussed.

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## 1. Introduction

Novel technologies are being developed to overcome the disadvantages associated with the biodiesel production processes. The demand for energy is gradually increasing in every sector (e.g., transportation, agriculture, and domestic), and this issue would consequently lead to fuel shortage owing to the gradual decline in fossil fuel reserves [1]. Biofuels are obtainable from renewable sources like plants, crops, and agricultural and forestry by-products, offering sustainability, energy security, and environmental compatibility [2]. Sustainability is an overarching concept connecting nations, economies, and national communities through developmental considerations in the environmental, economic, and societal realms. Indeed, many national agencies of People's Republic of China (Environmental Protection Agency, National Natural Science Foundation of China Agency, the Science and Technology Foundation of University Agency, etc.) have specific policies of sustainability.

Biodiesel is a mono-alkyl ester of long-chain fatty acids produced by the transesterification of vegetable oils, animal fats [3], and waste cooking oil [4]. Globally, numerous non-edible vegetable oil plants are naturally available such as *Jatropha curcas*, *Maduca indica*, and *Pongamia pinnata*, represent second-generation biodiesel feedstocks [5,6]. It has been reported that approximately 70–95% of biodiesel cost is attributed to raw feedstock cost [7]. Most of these crops are grown in Southeast Asia and have been successfully introduced in humid tropical regions of the world and parts of China [8]. Several researches have been recently published regarding biodiesel production from different sources shown in Table 1.

Methanol has been widely used in the transesterification of triglycerides. However, it is toxic and thus, non-toxic reagent is required for the transesterification process [9,10]. Diethyl carbonate (DEC) is a promising high oxygen-containing and biodegradable candidate, which can be produced by using ethanol and dimethyl carbonate (DMC) has been used as an acyl acceptor [11].

New generation polymer-based ILs for the transesterification of DEC has become the target of interest for many researchers studying biodiesel production because of their advantages and environmentally friendly nature [12]. DEC has been used in different capacities in the biodiesel production process (Fig. 1). Certain ILs that are regarded as “green” solvents have received

worldwide attention in various fields, including catalysis [13], according to previous researches, the functions of ILs vary considerably depending on their structural properties that may lead to improved reaction activity for reactants with large molecular size and surface areas, thermal, chemical stability, reusability, and water tolerance activity [14]. In recent years, the emerging concept of green chemistry using eco-friendly materials and ILs advanced catalysts for chemical transformations has gained immense attention; catalyst has significant negative effect towards environment [15]. Currently, homogeneous base catalysts, e.g. KOH and NaOH are generally being utilized in industry for biodiesel production [16]. Difficult catalyst separation and consequently high cost for product purification are the major drawbacks of homogeneous base catalysis systems [17], homogeneous acid catalysts are difficult to recycle and need to high temperatures, and give rise to serious environmental problems [18].

They have been used in supercritical or non-supercritical transesterification [19], enzymatic transesterification [20], and glycerol carbonate transesterification [21–23]. However, DMC-based catalytic transesterification is reported to be a time-consuming process and requires high amount of catalysts owing to the polarity difference between the reactant and catalyst [24]. In addition, engine tests indicated that 5 wt % DEC in diesel fuel could reduce almost 50% particulate emissions [25].

This review aims to provide a detailed account of the ways in which DEC and non-edible oil with ILs as catalyst has been used in the transesterification of biodiesel, review focuses on the non-edible oil sources, the kinetics of the reaction; and the properties of products and by-product application were evaluated, and future suggestions have been provided. The current knowledge on ILs catalysis, reusability, and deactivation as well as the influence of activation energy on the transesterification process are reviewed herein. We propose the major advantages associated with the usage of DEC with non-edible oil with ILs, such as environmental friendliness; however, as transesterification performed using DEC and ILs is not cost-effective, efforts are underway to reduce the cost.

## 2. Methodology

Articles for dialkyl carbonates such as DEC, DMC, ILs, feedstock, enzyme catalysts, and other catalysts were collected by searching through Scientific databases such as Science Direct, Springer, Baidu

**Table 1**  
Summary of transesterification reaction involving various alcohol.

| Oil                       | Solvents   | Catalyst and amount   | Temperature (°C) | Solvent:Oil (mol/mol) | Time (h) | Yields (%) | Refs  |
|---------------------------|--|---|------------------|-----------------------|----------|------------|-------|
| Palm oil                  | DEC/DMC  | 15 wt % KOH   | 100              | 14:1                  | 20       | 90.8       | [11]  |
| <i>Pistacia chinensis</i> | DEC  | 300 wt % PEI  | 120              | 5:1                   | 6        | 93         | [14]  |
| <i>Jatropha curcas</i>    | DMC  | 9 wt % KOH  | 80               | 10:1                  | 8        | 94         | [26]  |
| <i>Pongamia pinnata</i>   | DMC  | 9 wt % KOH  | 80               | 10:1                  | 8        | 96         | [23]  |
| Waste cooking oil         | Triethylammoniumhydrogensulfate [Et <sub>3</sub> NHSO <sub>4</sub> ] | 5.2 wt % KOH  | 170              | 15:1                  | 3        | 96.9       | [70]  |
| Canola oil                | DMC  | 2 wt % Crystallized CH <sub>3</sub> ONa   | 65               | 3:1                   | 1        | 96         | [39]  |
| <i>Jatropha curcas</i>    | DMC  | 7 wt % CaO–La <sub>2</sub> O <sub>3</sub> –Al <sub>2</sub> O <sub>3</sub>                 | 150              | 15:1                  | 3        | 90         | [56]  |
| Canola oil                | DMC  | 1.5 wt % Triazabicyclodecene (TBD)  | 70               | 3:1                   | 2        | 97.99      | [100] |
| <i>Jatropha curcas</i>    | DMC  | 260 wt % [IMHPS][C <sub>18</sub> ], PIL   | 80               | 5:1                   | 6        | 90         | [113] |
| Waste cooking oil         | DMC  | 2.5 wt % [HO.S (CH <sub>2</sub> ) <sub>6</sub> –NEt <sub>3</sub> ][Cl–FeCl <sub>3</sub> ] | 120              | 5:1                   | 4        | 95         | [47]  |
| Free fatty acids          | MeOH   | 10 wt % [DDPA][Tos]   | 60               | 1.5:1                 | 3        | 92.5       | [48]  |
| Vegetable oil             | DMC  | 5.2 wt % Biochar–pseudo-catalytic   | 380              | 36:1                  | 2        | 95.4       | [57]  |
| Rapeseed oil              | DMC  | 25 wt % [PrSO <sub>3</sub> HMIM][HSO <sub>4</sub> ]                                       | 110              | 5:1                   | 5        | 95.77      | [82]  |
| Soybean oil               | MeOH   | 6 wt % 1,1,3,3-trimethyl-2-octyl-guanidine hydroxide (IL <sub>2</sub> )                   | 55               | 15:1                  | 4        | 97         | [152] |
| Sunflower oil             | MeOH   | 0.43 wt % NaOH  | 40               | 4.5:1                 | 2.5      | 96.5       | [153] |
| <i>Jatropha curcas</i>    | MeOH   | 2 wt % Bi <sub>2</sub> O <sub>3</sub> –La <sub>2</sub> O <sub>3</sub>                     | 150              | 15:1                  | 4        | 93         | [154] |



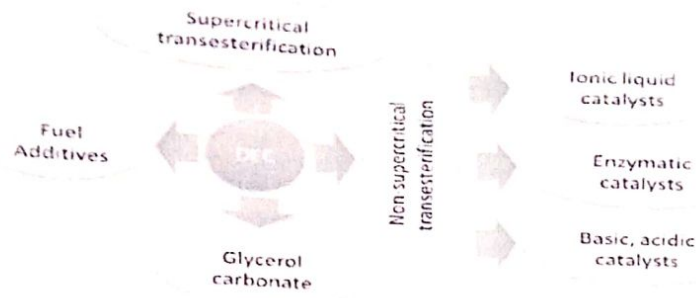


Fig. 1. Various application of DEC in the biodiesel production.

websites and Scopus. The main keywords used in the search for identifying the knowledge gap related to the selected topic included diethyl carbonate, biodiesel, dialkyl carbonate with ILs, dialkyl carbonate with enzyme catalysts, kinetic study, and properties of biodiesel published in peer reviewed journal in the year of study (2000–2021).

### 3. Effective and eco-environmental production of biodiesel by using ILs with DEC

The presence of a catalyst is an important during transesterification because it enhances the reaction rate and yield [26]. Methanol is especially used because of lower cost and its physical and chemical advantages. Dennis [27], reported that methanol can rapidly reacts with triglycerides, and most of the catalyst is easily dissolved in it. The good performance of DEC could be attributed to the lower hydrophobicity ( $\log P = 1.21$ ) and mutual solubility with triglycerides [15]. DEC has two times the oxygen content compared with other solvents and is an attractive eco-friendly alternative to other solvent. Also, engine tests indicated 5 wt % DEC in diesel fuel could reduce approximately 50% emissions [11]. Studies in which dialkyl carbonate has been used in the transesterification reaction are listed in Table 1.

The reaction between triglycerides and short-chain dialkyl carbonates could produce a mixture of fatty acid esters and fatty acid glycerol carbonate esters (FAGCs), and FAGCs continue to react with acyl acceptors in the same way to produce other molar fatty acid esters (FAEEs) and glycerol dicarbonate (GDC), which could be hydrolyzed into an eco-friendly chemical named glycerol carbonate (GC) (Fig. 2).

In a previous study, the thermal stability of fatty acid methyl esters (FAMES) and the biodiesel prepared from various plants oil was investigated in supercritical methanol over a range temperatures and pressures between 270 °C/17 MPa and 380 °C/56 MPa [28]. Since most plants oil contain high amount of poly-unsaturated fatty acids, they tend to be vulnerable to thermal degradation at higher than 300 °C [29,30]. The second and third generation of biodiesel is produced from non-edible crops (i.e. vegetable and algal oil) and waste oil (i.e. waste animal oil and waste cooking oil) [7]. *Jatropha*, *Simarouba*, *Neem*, *Rubber*, and *Karanja* as a non-edible vegetable oil has been considered as a commercially viable alternative to edible oil for biodiesel production because of its physicochemical characteristics [31,32].

Multi-functionalized ILs have been found to be the best choice [33], owing to their solvation properties [34] and acidity/basicity of ILs can be tuned for specific applications by suitably choosing the cation/anion or its substitution pattern [35–37] as shown in Fig. 3. Transesterification is a cost-effective and an efficient process for producing biodiesel; it has been used for reducing the production

cost by using IL with dialkyl carbonates. IL catalysts have shown to higher catalytic activity than the acidic [38], basic, and enzymatic catalysts, although very few studies have reported the use of IL catalysts with DEC [39–41].

Similarly, Liang et al. [33] synthesized acidic-based solid IL polymers by coupling acidic IL oligomers with divinylbenzene. The synthesized IL was used as a catalyst for the transesterification of triglycerides in one-spot reaction, with a total biodiesel yield of 99%. The high acidity of the synthesized IL was attributed to its high hydrophobic surface area, acidity, and stability. The distance between the sulfonic acid groups in these ILs, which are the active sites for the transesterification reaction, can also influence the conversion. Furthermore, the large sized triglyceride molecules cannot access the acidic sites due to steric hindrance, thereby increasing the activation energy. Recently, Liu et al. [42] investigated that the mesoporosity of polymer ILs is thought to facilitate reagent access to internal active sites, enhancing performance. The successful use of non-edible oil as a feedstock with the polymer ILs offers a compelling way to bring down the total cost of biodiesel.

The catalytic activity of [PAMAM<sub>3256</sub> C<sub>12</sub>] PIL was better than that of [MHPS] [C<sub>18</sub>]<sub>y</sub> PIL during the transesterification of *P. chinensis* oil (PCO) with DEC [14]. The reaction conditions for this process were optimized to yield 93% PCO-derived ethyl esters. The authors also compared the yield when synthesized PILs were used during a single transesterification reaction performed using DEC. The mild reaction conditions (1:5 M ratio of PCO:DEC), 300 wt % PIL loading, 120 °C, 400 rpm, and 6 h reaction time and the recyclability of [PAMAM<sub>3256</sub> C<sub>12</sub>] allow sustainable synthesis of fatty acid esters in an eco-friendly and cost-effective manner. The activation energy for the first-order transesterification reaction was 4.862–14.885 kJ mol<sup>-1</sup>, and providing an alternative route for the production of sustainable fuels. The authors also reported the production of biodiesel directly from the seeds of *P. chinensis* Bunge and *J. curcus* L. by using DEC. Jeon et al. [43] revealed some ILs that are efficient for the production of biodiesel from different feedstocks and acid-functionalized IL catalysts that have high activity for acid-catalyzed reactions.

The catalytic activity of IL catalysts and other catalysts such as Al–Zn-MCM-41-50 was compared during the transesterification of DMC with DEC. The reaction was performed at 125, 150, 175, and 200 °C with feed ratio of 1:1. Al–Zn-MCM-41-50 was found to be less active than IL catalysts for biodiesel production [44]. Yanfei et al. [45] also reported the methanolysis of soybean oil by using four ILs based on *N, N, N*-triethyl-*N*-propanesulfonic acid ammonium cation by using response surface methodology (RSM) based on the central composite rotatable design. The order of catalytic activity for the anions in the ILs was as follows: [H<sub>2</sub>SO<sub>4</sub>] > [p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>] > [H<sub>2</sub>PO<sub>4</sub>] > [CF<sub>3</sub>COO]. The highest yield was achieved with [(CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>N(CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>H][HSO<sub>4</sub>] ILs than with acidic catalysts.



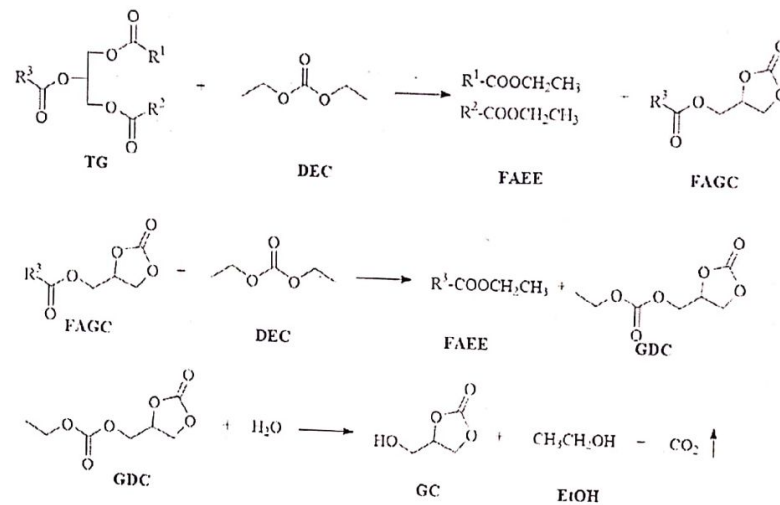


Fig. 2. Production of ethyl esters by using transesterification of triglyceride and DEC.

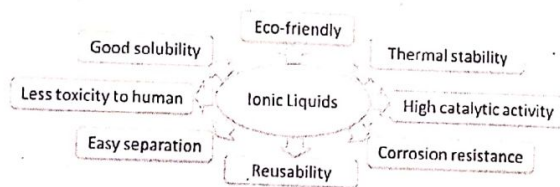


Fig. 3. Applications of ionic liquid catalyst.

He et al. [46] synthesized and characterized a long-chain Brønsted acid IL, 3-(*N,N*-dimethyldodecylammonium) propane-sulfonic acid toluenesulfonate ([DDPA][Tos]) for synthesizing biodiesel from free fatty acids (FFAs). A good yield (92.5–96.5%) of biodiesel product was obtained under the following optimum conditions: molar ratio of alcohols to FFAs of 1.5:1, mole fraction of IL at 10%, reaction temperature of 60 °C, and reaction time of 3 h. The long-chain Brønsted acidic IL showed good catalysis and could be recycled up to nine times. Moreover, Liu et al. [47] investigated the IL [HO<sub>2</sub>S-(CH<sub>2</sub>)<sub>3</sub>-NEt<sub>3</sub>]Cl-FeCl<sub>3</sub> containing both Brønsted and Lewis acidic sites for the synthesis of biodiesel from waste cooking oil. Because of the dual functionality of the IL, the yield of biodiesel was more than 95% at 120 °C for 4 h. Man et al. [48] used triethylammoniumhydrogensulfate (Et<sub>3</sub>NHSO<sub>4</sub>) as the pretreatment solvent, followed by KOH for the transesterification of crude palm oil. The biodiesel yield was 82.1% when only 5.2 wt % (with respect to reaction mixture) of Et<sub>3</sub>NHSO<sub>4</sub> was used at 170 °C for 3 h. The end product obtained after KOH treatment was 96.9%.

Different base catalysts were analyzed for their biodiesel production potential by using dialkyl carbonate in the presence of CH<sub>3</sub>OK, KOH, NaOH, CH<sub>3</sub>ONa, and K<sub>2</sub>CO<sub>3</sub> [49]. KOH and CH<sub>3</sub>OK were found to be the most reactive catalysts for DMC-mediated transesterification reaction, affording yields of 92.0% and 93.8%, respectively. Despite being strong bases, CH<sub>3</sub>OK, KOH, NaOH, CH<sub>3</sub>ONa, and K<sub>2</sub>CO<sub>3</sub> could only afford low yield of FAMES, which might be partly attributed to their lower solubility in dialkyl carbonate. However, the use of acid/base catalysts often leads to decay and emulsification problems and difficult purification and regeneration [3,6,7]. Exposure to these chemicals should be avoided during biodiesel production [50–53]. In general, for industrial applications, considerable efforts have been made to design acidic ILs

to replace homogeneous and heterogeneous acids in various chemical reactions [54].

Chlorometallate-based ILs have also been used as immobilizers for metal compounds such as zinc and tin complexes, which are the active catalyst precursors for the transesterification of soybean oil. DaSilveira et al. [40] immobilized the complex [Sn(3-hydroxy-2-methyl-4-pyrone)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] in 1-*n*-butyl-3-methylimidazolium tetrachloroindate ([BMI][InCl<sub>4</sub>]). Zinc and Tin complexes have been shown to be more active than traditional catalysts in comparable acidic or basic conditions [55]. Furthermore, the disadvantage of using these complexes is that recovery is difficult and these catalysts cannot be reused as they are dissolved in the reaction medium.

The mixed-oxide catalyst with a molar ratio of 6:2:1 (Ca–La–Al) showed high catalytic activity for FAME synthesis (more than 90% of FAME was obtained). The catalyst also exhibited high stability and could be reused for up to five cycles with less than 5% yield reduction per cycle [56]. However, the disadvantage of using this mixed-oxide catalyst is the difficult to reaction oxidation.

Jechan et al. [57] introduced a sustainable approach to synthesize biodiesel from vegetable oil and DMC via pseudo-catalytic transesterification on a maize residue biochar. The biodiesel yield reached up to 95.4% under the optimal operational conditions (380 °C and molar ratio of DMC to olive oil of 36:1). The biodiesel yield reached up to 95.4% under the optimal operational conditions (380 °C and molar ratio of DMC to olive oil of 36:1).

Li et al. [58] reported biodiesel production by using alkyl carbonate and methanol with enzyme as a catalyst; the result supported the use of alkyl carbonate for minimizing biodiesel production cost, as has been reported by some studies. The highest biodiesel yields of 92% and 94% were achieved under optimum conditions such as enzyme dosage of IUAI-ROL/g PCO, dialkyl carbonate/methanol to oil molar ratio of 5:1, water content 20% by weight of oil, reaction temperature of 37 °C, and reaction time of 60 h. However, one of the common drawbacks associated with the use of enzymes for biodiesel synthesis is their weak operational stability, because of the rapid deactivation of the biocatalyst that impairs their exploitation at the industrial scale [59–61]. Recently, ILs have emerged as exceptionally non-aqueous green reaction media because of their unique solvent properties [62]. The use of ILs as reaction media for lipase-catalyzed biodiesel synthesis has also been reported [63].

The efficiency for the transesterification of triglycerides was





study showed ultrasound-assisted intensification of biodiesel synthesis from waste cooking oil by using methyl acetate and immobilized lipase obtained from *Thermomyces lanuginosus* (Lipozyme TLIM) as a catalyst. The system conditions for the ultrasound-assisted approach were oil-to-methyl acetate molar ratio of 1:9, enzyme loading of 3% (w/v), and reaction time of 3 h, and the biodiesel yield obtained under these conditions was 96.1% [64,65]. However, enzyme catalysts are more expensive, have limited regeneration and reuse potential, and require a long operating time [66]. Zulficar et al. [67] studied the enzymatic transesterification of *J. curcas* seed oil (JCSO), 6:1 of methanol: oil ratio and 0.5% water content, 10% nano-biocatalyst (Lipase-PDA-TiO<sub>2</sub> NPs) concentration at 37 °C for 30 h achieved biodiesel yield was 92%.

The reaction yields from enzyme-catalyzed transesterification are yet unfavorable compared to those obtained from IL-catalyzed reactions, and thus render the process impractical and uneconomical [68]. More active and stable catalysts can be produced by combining enzymes with imidazolium ILs [69] because ILs can protect the lipase from deactivation induced by methanol. When [BMIM]NTf<sub>2</sub> was used in combination with lipase for biodiesel production, the biodiesel yield was 96.3% from soybean oil [70,71]. Taken together, the results of these studies suggest that:

- ILs provide an ideal medium for the separation of biodiesel and removal of the glycerol carbonate by-product. However, long-term/or continuous biodiesel production systems based on ILs are lacking, and the accumulation of glycerol carbonate and recovery of ILs are likely to pose future challenges. Reusability is a very important aspect of ILs catalyst that can affect the cost and energy of the process by continuously recycling the catalyst. In addition, the environmental fate and any potential toxicity issues for most ILs are still largely unknown, only a few preliminary reports on their toxicological properties are available.
- DEC had higher efficiency of biodiesel production than methanol with enzyme catalyst. However, excess methanol leads to the inactivation of the enzyme, resulting in low enzymatic activity.
- The reaction yields from enzyme-catalyzed transesterification are yet unfavorable compared to those from IL-catalyzed reactions. Although further studies on the behavior of ILs structure should be carried out, the combination of biocatalysts and this clean separation methodology enhances the possibility of developing green industrial processes.

#### 4. Cost effective co-product production by using DEC with various kinds of catalysts

GC is a potential substitute for several important expensive petroleum-derivative compounds used as surfactants, lubricants, and electrolytes, and components of CO<sub>2</sub> separation membrane and for polymer synthesis. Considering the efficiency, convenience, and ease of operation, transesterification of triglycerides with DEC and ILs is considered as the most prospective and simplest method for GC synthesis, unlike the reaction of triglycerides with DMC, and EC. To the best of our knowledge, the performance of IL catalysts has rarely been investigated with regard to the synthesis of GC in the presence of short-long chain alcohol (Table 2).

Folasegun et al. [72] investigated the GC production mechanism and showed that the utilization of dialkyl carbonates (such as DMC, DEC, and EC) in biodiesel production is an efficient way of producing GC as a by-product. TGs react with dialkyl carbonates to produce methyl carbonate diglycerides (MCDGs) and FAMES, and

then MCDGs further react to produce dialkyl carbonate mono-glycerides (DMCMGs) and FAMES. Finally, DMCMGs rapidly undergo rearrangement to form a cyclic compound that further reacts with dialkyl carbonates to produce GC. Thus, the reaction between triglycerides and short-chain dialkyl carbonates produces FAGCs and GC (Fig. 2) [72].

When immobilized IL was used in the transesterification of glycerol with EC, 86% glycerol conversion was noted in 5 min accompanied with the generation of ethylene glycol with greater than 75% selectivity [73]. Most studies suggested that GC synthesis was efficient between 70 °C and 90 °C [73–75] when chemical catalysts were used and at 60 °C when biocatalysts with DMC were used [76–78]. GC is a green substitute for important petro-derivative compounds as ethylene carbonate or propylene carbonate [79]. The reactions involving hydrotalcite with DMC [80], and IL with DMC [81] require higher temperature of 100–120 °C.

Recently, Fan et al. [82] investigated the use of IL as a green solvent and catalyst. A new approach for producing glycerol-free biodiesel was developed using DMC catalyzed by sulfonated imidazolium ionic liquid (SIL). The highest yield of FAMES with the SIL catalyst 1-propylsulfonate-3-methyl imidazolium hydrogen sulfate ([PrSO<sub>3</sub>HMIM][HSO<sub>4</sub>]) was 95.77% under the optimum conditions.

A copolymer of acidic IL oligomers and divinylbenzene (PIL) has also been used as a catalyst for the simultaneous (trans)esterification of FFA-containing triglyceride mixtures (waste cooking oil), possessing a high acid density of 4.4 mmol g<sup>-1</sup>, high pore volume and surface area of 323 m<sup>2</sup> g<sup>-1</sup>, and mean pore diameter of 35 nm [83]. The PIL copolymer was more active than the acidic IL alone, allowing 99% conversion of oleic acid with MeOH at only 1 wt % catalyst loading. PIL also achieved 99% yield in rapeseed transesterification with MeOH under the same reaction conditions and could convert high FFA content in waste cooking oil to biodiesel with 99% yield. The spent catalyst showed no structural changes or loss of acidic sulfur, and hence could be efficiently recycled with almost no loss in performance [84]. Hence, the development of a highly efficient and stable IL catalyst is important and desired for glycerol transesterification.

Homogeneous catalysts such as K<sub>2</sub>CO<sub>3</sub>; KOH; 1, 5, 7-triazabicyclo [4.4.0] dec-5-ene; and 1-n-butyl-3-methylimidazolium-carboxylate have high catalytic activities for GC production, but they are not preferable as they cannot be separated and reused easily [74,85,86]. Some heterogeneous catalysts [87], KNO<sub>3</sub>/CaO [88], potassium fluoride-modified hydroxyapatite [89], LiNO<sub>3</sub>/Mg<sub>4</sub>AlO<sub>5</sub> [90], CaFeAl mixed oxide [91], and Mg/Al/Zr mixed oxides [92,93] have also been used for the transesterification process. However, most of these catalysts have drawbacks such as rapid deactivation, long reaction time, additional solvent requirement, and high reactant molar ratio. Pan et al. [81] used NaOH under different reaction conditions (70 °C for 2 h at a DMC/glycerol molar ratio and obtained 77% glycerol conversion and 23% GC selectivity.

Recently, GC production was formed when glycerol was reacted with DMC, DEC, and DBC in the presence of *Candida antarctica* lipase B (Novozym 435), by using tert-butanol as a solvent, 100% glycerol conversion was achieved after 12 h [94]. Conversion rates increased with alkyl chain length, with DMC, DEC, and DBC yielding 65%, 69%, and 79% conversion after 6 h, respectively. Similar result was reported by Lee et al. [95], who investigated whether Novozym 435 biocatalyst and silica gel could be reused by conducting repeated batch operation. GC was successfully synthesized with more than 90% conversion from DMC and glycerol with a molar ratio of 10 via Novozym 435-catalyzed transesterification at 70 °C for 48 h. This reaction uses with DEC and can produce high conversion rates in a short time.

Taken together, the findings of these studies suggest that:



Reaction conditions and performance of various catalysts and dialkyl carbonate in glycerol carbonate.

| Feedstocks                | Catalyst   | Solvent:Oil (mol/mol) | Reaction time (h) | Temperature (°C) | GC yield (%) | Refs  |
|---------------------------|--|-----------------------|-------------------|------------------|--------------|-------|
| Glycerol                  | <b>Acid/base catalysts</b>                                     |                       |                   |                  |              |       |
| Glycerol                  | NaOH   | 5:1 (DMC:Oil)         | 1.5               |                  |              |       |
| Glycerol                  | H <sub>2</sub> SO <sub>4</sub>                                 | 5:1 (DMC:Oil)         | 1.5               | 75               | 98           | [135] |
| Glycerol                  | MgO  | 2:1 (EC:Oil)          | 5                 | 75               | 80           | [136] |
| Glycerol                  | CaO  | 2:1 (DMC:Oil)         | 0.2               | 50               | 78           | [137] |
| Glycerol                  | Metal oxides-hydrotalcite                                      | 4:1 (DMC:Oil)         | 2                 | 60               | 93.5         | [138] |
| Glycerol                  | k-Zeolite  | 3:1 (DMC:Oil)         | 1.5               | 75               | 77           | [81]  |
| Glycerol                  | Mg/Zr/Sr   | 3:1 (DMC:Oil)         | 1.5               | 90               | 95           | [138] |
| Glycerol                  | LiNO <sub>3</sub> /Mg <sub>4</sub> AlO <sub>5.5</sub>          | 3:1 (DMC:Oil)         | 1.5               | 80               | 56           | [139] |
| Glycerol                  | K <sub>2</sub> CO <sub>3</sub>                                 | 3:1 (DEC:Oil)         | 48                | 73               | 96.24        | [140] |
| Glycerol                  | Al/Mg hydrotalcite   | 2:1 (EC:Oil)          | 5                 | 50               | 95           | [141] |
| <i>Jatropha curcas</i>    | <b>Ionic liquids catalysts</b>                                 |                       |                   |                  |              |       |
| Glycerol                  | [IMHPS]x[C18]y   | 5:1 (DMC:Oil)         | 6                 | 80               | 82           | [137] |
| Glycerol                  | 1,3-Dichlorodistannoxanes                                      | 5:1 (DEC:Oil)         | 2                 | 100              | 74           | [142] |
| Glycerol                  | IL (BMIM <sub>2</sub> -CO <sub>2</sub> )                       | 3:2:1 (DMC:Oil)       | 1.33              | 74               | 99.1         | [143] |
| Glycerol                  | IL ([Mof <sub>1,4</sub> ][N(CN) <sub>2</sub> ])                | 3:1 (DMC:Oil)         | 13                | 120              | 93           | [88]  |
| Glycerol                  | IL ([TMA][OH])   | 3:1 (DMC:Oil)         | 1.5               | 80               | 95           | [144] |
| Bio-glycerol residual oil | <b>Enzyme catalysts</b>  |                       |                   |                  |              |       |
| Bio-glycerol residual oil | Enzyme biocatalyst   | 10:1 (DMC:Oil)        | 6                 | 60               | 90           | [145] |
| Bio-glycerol residual oil | Enzyme biocatalyst   | 10:1 (DEC:Oil)        | 6                 | 60               | 95           | [146] |
| Soybean oil               | Enzyme biocatalyst   | 10:1 (DBC:Oil)        | 6                 | 60               | 92           | [147] |
| Glycerol                  | Novozym 435  | 6:1(Tert-butanol:Oil) | 5                 | 60               | 92           | [148] |
| <i>P. chinensis</i> oil   | Guanidine IL   | 1:0.025 (DMC:Oil)     | 1.5               | 80               | 92           | [149] |
| Rapeseed oil              | [PEI <sub>10000</sub> C <sub>12</sub> ] PIL                    | 5:1 (DEC:Oil)         | 6                 | 120              | 95.5         | [142] |
| Palm oil                  | Sulfonated imidazolium IL                                      | 5:1 (DMC:Oil)         | 5                 | 110              | 95           | [14]  |
| Glycerol                  | Immobilized-lipase   | 10:1 (DMC:Oil)        | 5                 | 55               | 70           | [82]  |
| Glycerol                  | Ca(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> | 2.5:1 (DMC:Oil)       | 3                 | 60               | 80           | [145] |
|                           |  |                       |                   |                  | 95           | [146] |

• The use of IL during transesterification yields better results than when other homogenous, heterogeneous, and enzyme catalysts are used. Recently, more attention has been paid to ILs as green solvents due to their low volatility, vapor pressure, flammability, and environmental advantages.

• Heterogeneous catalysts are not suitable for GC production owing to drawbacks such as deactivation, long reaction time, additional solvent requirement, and high reactant ratio. Furthermore, homogeneous catalysts are not preferable as they cannot be separated and reused easily.

### 5. Kinetic study and activation energy of biodiesel production by using DEC with ILs

The kinetic study of transesterification with the methylating agent, dialkyl carbonate has not been widely investigated. Therefore, in this review, IL reaction system consisting of triglycerides and dialkyl carbonate for the production of biodiesel is described. Catalysis is among the most active research fields as it attempts to reduce the quantity of materials and activation energies required and can accomplish many of the objectives of biodiesel. Catalytic reactions have additional positive implications, such as catalyst recovery from the final reaction mixture to increase reusability throughout several recycles [96].

Few studies have investigated the kinetics of triglycerides during dialkyl carbonate reactions, and the first-order transesterification of triglycerides was found to be the best kinetics mechanism. The kinetics of triglycerides were determined when Rathore et al. [23] estimated activation energy (E<sub>a</sub>) was of the order of 38.0 ± 2 and 35.5 ± 2 kJ mol<sup>-1</sup> for DMC, and 40.4 ± 2 and 38.2 ± 2 kJ mol<sup>-1</sup> for DEC, for the conversion of *J. curcas* and *P. pinnata* oil, respectively. Notably, the activation energy for supercritical DMC was slightly lower than that for supercritical DEC. The summary of the kinetics investigated is shown in Table 3.

The reported activation energy for non-catalytic supercritical transesterification varied with different reaction conditions and

natures of oil [97]. Non-catalytic transesterification necessitates high activation energy (117 kJ mol<sup>-1</sup>, 128 kJ mol<sup>-1</sup>, or 29 kJ mol<sup>-1</sup>), whereas non-catalytic supercritical transesterification requires less activation energy (9–65 kJ mol<sup>-1</sup>) owing to the change in the polarity of the reactant under supercritical condition. Pan et al. [98] specified the efficient activation energy (83.56 kJ mol<sup>-1</sup>). Under mild reaction conditions, one-pot conversion of non-edible *Firmiana platanifolia* L. oil into biodiesel was possible by using inexpensive, scalable imidazolium salt-based solid Brønsted acid-Lewis acid bifunctional catalyst ([DSI][FeCl<sub>4</sub>]). The [DSI][FeCl<sub>4</sub>] catalyst exhibited excellent catalytic performance, and kinetic studies showed that the catalytic process followed the first-order kinetics. Long-chain PILs have recently been used as a new generation of ionic solvents, considering that several long-chain PILs have an amphiphilic nature and thus represent a new class of cationic surfactants with peculiar properties [99].

Recently, catalysts obtained from *Thevetia peruviana* sources have been used in the transesterification with DMC. Panchal et al. [100] investigated the kinetic transesterification of *T. peruviana* oil with DMC (molar ratio, 1:4) and prepared a CH<sub>3</sub>OK alkali catalyst; the activation energy for the conversion of TG to MG ranged from 10.752 to 32.817 kJ mol<sup>-1</sup>. The transesterification of *T. peruviana* oil to DMC-esters (DMC-TP-BioDs) proceeds via the first-order mechanism. The use of CH<sub>3</sub>OK catalyst for transesterification oxidation obtained this disadvantage of CH<sub>3</sub>OK catalyst.

Islam et al. [101] determined the activation energy for the second-order reaction between DMC and canola oil when triazabicyclodecene was used as a catalyst. They found that the activation energy was significantly reduced and the progress of the reaction was expedited using the basic triazabicyclodecene catalyst and DMC. A kinetic model based on the triazabicyclodecene-catalyzed transesterification reaction of canola oil was developed using an oil/DMC molar ratio of 1:3, catalyst concentration of 1.5 wt % based on oil weight, and temperatures of 50, 60, and 70 °C. The activation energy of the second-order reaction was 36.4 kJ mol<sup>-1</sup>, and the rate constants were 1.09 × 10<sup>2</sup>, 1.65 × 10<sup>2</sup>, and 2.39 × 10<sup>2</sup> kJ mol<sup>-1</sup> min<sup>-1</sup> at 50, 60, and 70 °C, respectively. The





**Table 3**  
Summary of kinetic study using DEC and DMC.

| Feedstock                                    | Catalyst type  | Solvent:Oil (mol/mol)   | Activation energy (kJ mol <sup>-1</sup> ) | Yield (%) | Refs  |
|--|--|-------------------------|---|-----------|-------|
| <b>Supercritical transesterification</b>     |  |                         |   |           |       |
| <i>Jatropha curcas</i> oil                   | –  | 40:1 (DMC:Oil)          | 35.5 to 38.0                              | 92        | [123] |
| <i>Pongamia pinnata</i> oil                  | –  | 40:1 (DEC:Oil)          | 38.2 to 40.4                              | 94        | [124] |
| <i>Schizochytrium limacinum</i>              | –  | 10:1 (MeOH:Oil)         | 54  | 86        | [102] |
| <i>Schizochytrium limacinum</i>              | –  | 10:1 (DMC:Oil)          | 56.6                                      | 83        | [102] |
| <b>Non-supercritical transesterification</b> |  |                         |   |           |       |
| <b>Alkaline</b>                              |  |                         |   |           |       |
| Glycerol                                     | CH <sub>3</sub> OK   | 3:1.5 (EC:Oil)          | 58.7                                      | –         | [124] |
| <i>Thevetia peruviana</i> oil                | CH <sub>3</sub> OK   | 4:1 (DMC:Oil)           | 10.752 to 32.817                          | 97.5      | [125] |
| Waste frying oil                             | CaO  | 5:1 (MeOH:Oil)          | 78.8                                      | –         | [126] |
| Canola oil                                   | C <sub>7</sub> H <sub>13</sub> N <sub>3</sub>              | 3:1 (DMC:Oil)           | 36.4                                      | 84        | [127] |
| Palm oil                                     | KOH  | 6:1 (DMC:Oil)           | 79.1                                      | 98        | [128] |
| Oleic Acid                                   | NbOPO <sub>4</sub>   | 5:1 (DMC:Oil)           | 62.17                                     | 97.99     | [101] |
| <b>Acidic</b>                                |  |                         |   |           |       |
| Yellow grease                                | CH <sub>3</sub> SO <sub>3</sub> H                          | 5:1 (DMC:Oil)           | 1.99                                      | 94        | [129] |
| <b>Ionic liquid</b>                          |  |                         |   |           |       |
| Oleic Acid                                   | MMFP-IL  | 12:1 (MeOH:Oil)         | 35.3                                      | 95        | [134] |
| <i>Psidium chinensis</i> oil                 | [PEI <sub>1000</sub> C <sub>12</sub> ]                     | 5:1 (DEC:Oil)           | 4.862 to 14.885                           | 93        | [12]  |
| Tung nut oil                                 | Acidic PILs  | 1.5:1 (MeOH:Oil)        | 12.81                                     | 91        | [132] |
| <i>Jatropha curcas</i> oil                   | [IMHFPs] <sub>x</sub> [C <sub>15</sub> ] <sub>y</sub> PILs | 5:1 (DMC:Oil)           | 15.382                                    | 94        | [131] |
| <b>Enzyme</b>                                |  |                         |   |           |       |
| Palm oil                                     | Lipozyme TL IM   | 3:1 (Oleyl alcohol:Oil) | 16.85                                     | 79.54     | [153] |
| Palm oil                                     | lipase Novozyme 435  | 4:1 (DMC:Oil)           | 26  | 90        | [103] |
| Waste cooking oil                            | Lipase 435   | 6:1 (DMC:Oil)           | 18.96                                     | –         | [104] |

Where, - is not measured

activation energy for the transesterification of oil with methanol as the base catalysts was in the range of 33.6–84 kJ mol<sup>-1</sup>. The activation energy obtained (36.4 kJ mol<sup>-1</sup>) with the basic triazabicyclodecene catalyst and DMC as the acyl acceptor was in agreement with the reported range.

Recently, Alessio et al. [102] evaluated whether commercial niobium phosphate can be used as a heterogeneous catalyst in biodiesel production from oleic acid and low-cost raw materials by using DMC as the acyl receptor. He discussed pseudo-homogeneous first-order reaction in forward and backward directions for the esterification of oleic acid. The activation energy ( $E_a$ ) and pre-exponential factor ( $k_0$ ) were estimated to be 62.17 kJ mol<sup>-1</sup> and  $1.816 \times 10^{-6}$  for the forward direction, and 77.75 kJ mol<sup>-1</sup> and  $1.816 \times 10^{-6}$  for the reverse direction, respectively. The activation energy obtained for the conversion of TG to DECMG ranged from 4.862 to 14.885 kJ mol<sup>-1</sup>.

Rathnam and Madras [104], investigated the kinetics of biodiesel production from *Schizochytrium limacinum* microalgae by using three methylating agents, that is, methanol, DMC, and methyl acetate. The reactions were conducted at 518–643 K at 20 MPa and methylating agent to *S. limacinum* microalgae ratio of 10:1. The reaction time was varied between 10 and 80 min. The rate constant ( $k$ ) obtained using pseudo first-order kinetics followed an order of  $k_{\text{methanol}} > k_{\text{dimethyl carbonate}} > k_{\text{methyl acetate}}$ , whereas the activation energy ( $E$ ) for the three systems followed a trend of  $E_{\text{methyl acetate}} > E_{\text{dimethyl carbonate}} > E_{\text{methanol}}$ . The authors reported that the activation energy was the highest at 62.7 kJ/mol for the methyl acetate system, followed by that for DMC (56.6 kJ mol<sup>-1</sup>) and methanol systems (54.0 kJ mol<sup>-1</sup>) [103].

Sun et al. [104] reported the kinetics of the transesterification of palm oil and DMC for biodiesel production during the catalysis of immobilized lipase Novozym 435. The relationship between the initial reaction rate and temperature was determined, and the activation energy was obtained, based on the Arrhenius law. The value of  $E_a$  was 26.0 kJ mol<sup>-1</sup>. The effect of palm oil concentration was investigated over the range of 30–700 mmol/L by maintaining the catalyst amount (5–75 mg/mL). The optimal temperature was 55 °C, indicating that the transesterification kinetics of palm oil and

DMC was in agreement with the ordered bi-bi mechanism [104].

The use of waste cooking oil and DMC as the reactants and lipase-435 enzyme as the catalyst reduced the cost of the reaction run for 4 h, with activation energy of FAME production of about 18.96 kJ mol<sup>-1</sup> [105]. Similarly, Rejasse et al. [106], performed an energy and thermodynamic study by using enzymatic biodiesel synthesis from palm oil and showed that the activation energy of monoglyceride to FAME formation was between 17.78 and 23.35 kJ mol<sup>-1</sup>.

Esteban et al. [107] investigated the transesterification of glycerol with DMC and EC and CH<sub>3</sub>OK used as a catalyst. The kinetic study was performed under mild operation conditions: temperature (50–70 °C by using DMC; 40–60 °C by using EC), molar excess of organic carbonate to glycerol (1.5–3), and low catalyst loads (1000–2500 ppm for DMC; 50–150 ppm for EC). During the reaction with DMC, the model contemplates an irreversible reaction with activation energy of  $28.4 \pm 1.5$  kJ mol<sup>-1</sup> and deactivation constant of  $0.03 \pm 0.01$  min<sup>-1</sup>. When EC is used, the activation energy was  $83.0 \pm 1.6$  kJ mol<sup>-1</sup> and  $58.7 \pm 11.4$  kJ mol<sup>-1</sup> for the direct and reverse reactions, respectively, and the deactivation constant was  $0.11 \pm 0.02$  min<sup>-1</sup>.

Comparisons of the produced activation energies employing homogeneous and heterogeneous catalyst methods have been reported. Many researchers have used homogeneous alkali catalysts such as sodium hydroxide and potassium hydroxide to develop processes for the activation energies. Owing to the low cost; these catalysts are the most commercialized [108]. Deshmane and Ade-wuyi [109], and Birla et al. [110] reported catalytic transesterification; homogeneous catalytic reaction necessitates less activation energy, 26–83 kJ mol<sup>-1</sup>, unlike >79 kJ mol<sup>-1</sup> required for the heterogeneous catalytic reaction. Berrios et al. [111] also obtained activation energy values of 50.7 and 44.5 kJ mol<sup>-1</sup> for forward reaction and 31.01 and 42.76 kJ mol<sup>-1</sup> for the reverse reaction catalyzed by 5% and 10% sulfuric acid, respectively. The activation energy values for transesterification reaction are generally higher than those of esterification reactions (54.6–79.1 kJ mol<sup>-1</sup>). Li et al. [112] determined the effective activation energy for biodiesel production from *Camptotheca acuminata* seed oil catalyzed by novel





Bronsted-Lewis acidic IL [BSO<sub>3</sub>HMIM]HSO<sub>4</sub>-Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> catalyst. A high conversion yield (95.7%) and activation energy of 37.68 kJ mol<sup>-1</sup> were obtained in 60 min under relatively low temperature of 60 °C. The Bronsted-Lewis acidic IL [BSO<sub>3</sub>HMIM]HSO<sub>4</sub>-Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> catalyst exhibited excellent catalytic performance compared to homogeneous and heterogeneous catalysts. Acidic ILs are the new type of catalysts with high-density active sites as liquid acids, but non-volatilization as solid acids. Furthermore, cations and anions of ILs can be designed to bind a series of groups with specific properties, in order to regulate the acidity. Recently, they have been used to replace traditional liquid acids such as sulfuric acid and hydrochloric acid for biomass conversion [113,114].

Pan et al. [115] investigated the activation energy by using the 4 wt % acidic IL-functionalized mesoporous melamine-formaldehyde polymer (MMFP-IL) dosage at 90 °C for 3 hands MeOH to oleic acid mole ratio of 12:1. Kinetic analysis indicated that the reaction obeyed first-order reaction kinetics and activation energy (E<sub>a</sub> = 35.3 kJ mol<sup>-1</sup>) was relatively lower than that reported previously. The outstanding catalytic performances of ILs could be ascribed to their remarkable properties such as strong acidity, high acid sites, and high oxidation stability [116].

The following conclusions can be drawn from the analysis of the different experimental results:

- Synthesized activation energy by using dialkyl carbonate was more effective than that using other solvents such as methanol and butanol.
- The use of IL for the transesterification process produced activation energies that were better than those produced when other homogenous, heterogeneous, and enzyme catalysis were used.
- IL catalysts have more advantages than other catalysts. The activation energy was found to be excellent when dialkyl carbonate and waste oil with ILs was used. Therefore, the transesterification of dialkyl carbonate and waste oil with ILs can provide a sustainable alternative fuel in the future.

### 6. Environmental considerations of biodiesel produced from dialkyl carbonate by using ILs

Transesterification of oil with short-chain alcohols seems a simple and fascinating way to produce biodiesel with good viscosity. The usage of short-chain alcohols may also have some advantages such as higher reaction activity [117]. The effect of long-chain alcohols and triglycerides has been investigated [118,119]. The physical properties of biodiesel are shown in Table 4.

The major disadvantages of biodiesel are higher viscosity, lower energy content, higher NO<sub>x</sub> emissions, lower engine speed and power, injector coking, engine compatibility, higher price, and higher engine wear [120]. These problems have been addressed by using biodiesel especially that prepared from dialkyl carbonate with ILs, such as that with no sulfur and NO<sub>x</sub> emissions [14]. The alarming rate of increase in atmospheric CO<sub>2</sub> level can be relieved, to a certain extent, by using biodiesel usage, thereby mitigating the effects of global warming. Biodiesel usage could help reduce CO<sub>2</sub> emissions into the atmosphere over its life cycle [121]. Takase et al. [31] undertook theoretical and experimental studies to investigate the performance and exhaust characteristics of Neem, Jatropha and Karanja biodiesels, study indicated that CO, NO<sub>x</sub>, HC and smoke emission could reduce to 18%, 3%, 18% and 12% respectively for Neem biodiesel when compared to fossil diesel. Similarly, a study on comparison of life-cycle greenhouse gas (GHG) emissions showed a 55% reduction relative to conventional jet fuel, with emission of 40 kg CO<sub>2</sub> eq/GJ of fuel produced from Jatropha [122].

Kinematic viscosity has an important impact on fuel injection and combustion. It is an index expressing the stickiness of a fuel. Kinematic viscosity needs to be regulated within a safety range of 3.5–5 mm<sup>2</sup>/s and 1.9–6 mm<sup>2</sup>/s according to the EN14214 and ASTM6752 regulation, respectively. Recently, Panchal et al. [14] reported that biodiesel production catalyzed by novel [PEH<sub>1000</sub>C<sub>12</sub>] PIL with DEC proved was an efficient and environmentally friendly technology. Biodiesel produced from *P. chinensis* oil with DEC has greater kinematic viscosity of 4.1 mm<sup>2</sup>/s, specific gravity of 0.86 g/cm<sup>3</sup>, and acid value of 0.31 mgKOH/g, which meets the ASTM standard. Similarly, Panchal et al. [123] investigated the production of biodiesel from yellow grease with DMC and methanesulfonic acid (CH<sub>3</sub>SO<sub>3</sub>H) as a catalyst. The properties of biodiesel, such as kinematic viscosity, were found to be 1.56 mm<sup>2</sup>/s, and specific gravity was found to be 0.87 g/cm<sup>3</sup>. Panadare et al. [108] compared the use of ILs and enzyme catalysts, and obtained moderate kinematic viscosity of 3.85 mm<sup>2</sup>/s, under parameter conditions such as waste cooking oil and DMC as reactants and Lipase-435 enzyme as the catalyst.

Another study by Biodiesel Emission [124] showed that the level of polycyclic aromatic hydrocarbons (PAHs), which have been identified as potential cancer-causing compounds, also decreased by 80% in biodiesel emission. In addition, expanded biodiesel use would enormously contribute to environmental protection, energy saving and economic development.

In general, methyl esters have higher flash point (FP) than diesel, which is usually around 100 to 120 °C, whereas conventional FP for diesel fuel is only 55 to 66 °C, admirable biodegradability and lubricity, and higher combustion efficiency compared to the corresponding properties of petro-diesel [125]. The biodiesel was characterized by the physical properties of the produced methyl esters, such as the FP of fried soybean oil methyl esters was found to be 100 °C, density was 0.86 g/cm<sup>3</sup>, cloud point (CP) was 5 °C, pour point (PP) was -5 °C, and kinematic viscosity was 3.93 mm<sup>2</sup>/s. Thus, methyl esters are safe for transport, handling, and storage purpose [126]. This high FP of biodiesel is attributed to the presence of a predominantly unsaturated acid chain length of C18:1 and C18:2 in the vegetable oil [127].

Few researchers have used DEC for biodiesel production and have found zero sulfur and reduced emission of CO<sub>2</sub>. Biodiesel has higher cetane number than diesel fuel because of its long-chain fatty acids with 2–3 double bonds; it is without aromatics and contains 10–11% oxygen by weight. Biodiesel produced using DEC has more oxygen content than others produced using solvents such as methanol [13]. These characteristics of biodiesel reduce the emission of CO<sub>2</sub>, HC, and particulate exhaust gases compared to those emitted by diesel fuel. Conventional fuel contains more sulfur and thus damages the atmosphere by releasing SO<sub>2</sub>. However, biodiesel synthesized using DEC has almost zero sulfur content [4].

Biodiesel has many promising characteristics, including reduced exhaust emission [128]. The economic advantages of biodiesel are that it reduces greenhouse gas emission, helps reduce a country's reliance on crude oil imports, and supports agriculture by providing new labor and market opportunities for domestic crops. The corrosion behavior of Co (salophen) catalyst and DEC to a stainless steel reactor and the corrosion rate to stainless steel by using Co catalyst was shown to be below 0.005 mm/a [15].

The acidic value suggests that conversion is better by using DMC with ILs than by using DMC with CH<sub>3</sub>ONa. Gardy et al. [104] also reported the synthesis of a novel magnetic SO<sub>2</sub>/Fe-Al-TiO<sub>2</sub> solid acid catalyst for biodiesel production via the transesterification of waste cooking oil. The physical characteristics of biodiesel conformed to ASTM and EU standards, with a cloud point of -11.3 °C. Decomposition or combustion of synthetic biodiesel occurred at >144 °C and was complete at 226 °C. Transesterification conditions



**Table 4**  
Fuel properties produced using DEC, DMC, and DEC/DMC compared with ASTM 6751-02 and EN14112.

| Feedstocks                      | Catalyst                                       | Solvent:Oil (mol/mol) | Kinematic viscosity (mm <sup>2</sup> /s) | Specific gravity (g/m <sup>3</sup> ) | Acid value (mgKOH/g) | Flash point (°C) | Cloud point (°C) | Pour point (°C) | Refs  |
|---------------------------------|--|-----------------------|--|--------------------------------------|----------------------|------------------|------------------|-----------------|-------|
| <b>Supercritical method</b>     |  |                       |  |                                      |                      |                  |                  |                 |       |
| Rapeseed oil                    | –  |                       |  |                                      |                      |                  |                  |                 |       |
| Soybean oil                     | –  | 41:1(DMC:Oil)         | 4.3                                      |                                      |                      |                  |                  |                 |       |
| <b>Non-Supercritical method</b> |  |                       |  |                                      |                      |                  |                  |                 |       |
| <b>Alkaline</b>                 |  |                       |  |                                      |                      |                  |                  |                 |       |
| Palm oil                        | KOH  | 2:1(DMC:Oil)          | 4.5                                      |                                      | 0.14                 | –                | –                | –               | [18]  |
| Palm oil                        | KOH  | 14:1(DEC/DMC:Oil)     | 4.6                                      | 0.87                                 | 0.5                  | –                | –                | –               | [19]  |
| <i>Pongamia pinnata</i> oil     | KOH  | 3:1 (DMC:Oil)         | 5.2                                      | 0.88                                 | 0.064                | –                | –                | –               | [114] |
| Soybean oil                     | CH <sub>3</sub> OK                             | 9:1 (DMC:Oil)         | 4.4                                      | 0.89                                 | 0.28                 | –                | –                | –               | [116] |
| Waste cooking oil               | Calcined Mg/Al HT                              | 4:2 (MeOH/EtOH:Oil)   | 3.7                                      | 0.896                                | 0.5                  | 122              | 5                | 3               | [151] |
| <i>Thevetia peruviana</i> oil   | CH <sub>3</sub> OK                             | 4:1 (DMC:Oil)         | 3.99                                     | 0.84                                 | 0.05                 | –                | –                | –               | [72]  |
| <b>Acidic</b>                   |  |                       |  |                                      |                      |                  |                  |                 |       |
| Fried soybean oil               | KBr  | 4:1 (DMC:Oil)         | 3.93                                     | 0.87                                 | 0.2                  | 135              | 9                | –3              | [150] |
| Yellow grease                   | CH <sub>3</sub> SO <sub>3</sub> H              | 5:1 (DMC:Oil)         | 1.56                                     | 0.86                                 | 0.26                 | 148              | 4                | 1               | [10]  |
| <i>Schizochytrium limacinum</i> | CH <sub>3</sub> SO <sub>3</sub> H              | 4:1 (DMC:Oil)         | 3.87                                     | 0.87                                 | 0.5                  | 100              | 6                | –5              | [121] |
| <i>Schizochytrium limacinum</i> | CH <sub>3</sub> ONa-treated algae              | 4:1 (DMC:Oil)         | 3.69                                     | 0.856                                | 0.3                  | 115              | 1                | –2              | [152] |
| <i>Schizochytrium limacinum</i> | CH <sub>3</sub> SO <sub>3</sub> H              | 4:1 (DMC:Oil)         | 3.87                                     | 0.82                                 | 0.4                  | 130              | 7                | –2              | [154] |
| <b>Ionic liquid</b>             |  |                       |  |                                      |                      |                  |                  |                 |       |
| <i>Pistacia chinensis</i>       | [PEI <sub>1000</sub> C <sub>18</sub> ] PILs    | 5:1(DEC:Oil)          | 4.1                                      | 0.86                                 | 0.31                 | 103              | 1                | –1              | [12]  |
| <i>Jatropha curcas</i>          | [IMHPS] [C <sub>18</sub> ] <sub>y</sub> PIL    | 5:1(DMC:Oil)          | 4.12                                     | 0.851                                | 0.312                | 110              | 2                | –4              | [131] |
| Yellow grease                   | Superhydrophobic porous poly-PIL               | 21.9:1(MeOH:Oil)      | 4.1                                      | 0.87                                 | 0.16                 | –                | –                | –               | [157] |
| <i>Schizochytrium limacinum</i> | [BSMBIM] [CF <sub>3</sub> SO <sub>2</sub> ] IL | 12:1(MeOH:Oil)        | 4.94                                     | 0.88                                 | 0.45                 | 161              | –                | –               | [158] |
| Soybean seed oil                | p-toluene sulfonate [DDPA] [Tos]               | 2:1 (MeOH:Oil)        | 4.12                                     | 0.86                                 | 0.31                 | 148              | 4                | 1               | [124] |
| Tung nut seed oil               | Acidic-PILs                                    | 1.5:1 (MeOH:Oil)      | 4  | 0.85                                 | 0.3                  | 150              | –2               | –4              | [152] |
| <i>Jatropha curcas</i>          | [IMHPS] [C <sub>18</sub> ] <sub>y</sub>        | 5:1 (DMC:Oil)         | 3.9                                      | 0.851                                | 0.31                 | 110              | 2                | –4              | [131] |
| <b>Enzymatic</b>                |  |                       |  |                                      |                      |                  |                  |                 |       |
| Waste cooking oil               | Lipase-435                                     | 6:1 (DMC:Oil)         | 3.85                                     | 0.882                                | 0.41                 | –                | –                | –               | [104] |
| Soapstocks oil                  | 5% Novozym 435                                 | 3:1 (DEC:Oil)         | 4.2                                      | 0.87                                 | 0.5                  | –                | –                | –               | [15]  |

Where, – is not measure.

were as follows: methanol: WCO molar ratio of 10:1, and 2.5 h of reaction time at 90 °C by using 3 wt % of the SO<sub>4</sub>/Fe–Al–TiO<sub>2</sub> catalyst.

Two important parameters for low-temperature applications of a fuel are CP and PP. The CP is the temperature at which wax first becomes visible when the fuel is cooled. The PP is the temperature at which the amount of wax from a solution is sufficient to gel the fuel; thus, it is the lowest temperature at which the fuel can flow. Biodiesel has higher CP and PP than conventional diesel.

Taken together, the results of these studies suggest that:

- CO, CO<sub>2</sub>, NO<sub>x</sub>, and sulfur emissions decrease with the use of dialkyl carbonate and waste oil with ILs. CO emission decreases by about 4–55.76% depending on different conditions.
- Biodiesel synthesized using DEC with waste oil and ILs has reduced emission of hydrocarbon and almost zero sulfur content.
- Biodiesel synthesized using DEC has more oxygen content than that synthesized using other solvents.
- Considering all factors, IL catalysts has more advantages than other catalysts. ILs and DEC with waste oil are environmentally friendly and promising acid processes for biodiesel synthesis. Biodiesel fuel properties vary depending on the

solvent and catalyst and the biodiesel conversion process. Most reviewed biodiesel fuels have excellent kinematic viscosity; they are manufactured using dialkyl carbonate and waste oil with ILs. However, the viscosity, density, FP, CP, and PP ranges of biodiesels are close to those of diesel fuel. Therefore, transesterification of dialkyl carbonate and waste oil with ILs can ensure sustainable alternative fuel in the future.

## 7. Future direction of biodiesel production

The issues of environmental and energy security are fundamental challenges of the 21st century. Dependence on conventional fossil fuels is leading to global warming and possible major disruptions in social structures [37]. Therefore, World are trying to find environmentally begin alternative to harmful chemical. In view of that, DEC has become the target of interest for many researchers studying biodiesel production because of their advantages and environmentally friendly nature. Advancements in green synthesis methods will be key to the future success of ILs chemistry and its suitability to environmental fields. Facile control over the basic properties ILs (e.g., pore size, high surface area, and functional groups) can expand their environmental applicability in various





respectively. This review suggests that non-edible oil or waste oil and DEC with IL catalyst is a promising process that can sustain biodiesel growth. However, the future of the non-edible biodiesel will also depend upon the establishment of low-cost and competent biodiesel production technologies. Using waste oil as raw material to produce biodiesel can not only solve the debate between fuel and food, but also solve some problems in waste oil disposal.

As the cost of biodiesel production is a major concern nowadays, the recyclability of IL catalysts used in the biodiesel process should be taken into account. Recycling of ILs reduces the cost of biodiesel production. To date, they are currently unused in industrial applications; expensive, and in a negative aspect for their treatment after usage prior to disposal [159]. The high thermal stability and non-volatility properties of ILs have somehow suggested potential problems with persistence to the environment. Hence, there are some key challenges to be addressed in future research. (1) Future needs to research activities are in progress to identify cost effective such as feedstock and biodiesel process. (2) The next generation of ILs should be made cheaper, stability, recyclable, and eco-friendly. (3) This can be achieved by preventing ILs from leaching off the carriers and loss of activity caused by the alcohol and stirring force. With the impending commercial availability of the economically feasible future generation biodiesel, this fuel should remain as a substitute to fossil fuel that can potentially satisfy mid-term energy needs to form part of the total solution to worldwide energy and environmental woes.

### 8. Conclusions

With swelling population and industrial development, the demand for energy will see multifold increases in the future. IL-catalyzed production of biodiesel has attracted remarkable attention recently, owing to the merits such as mild reaction conditions, environmental friendliness, and reusability. The feedstock type is one of the most important parameters in biodiesel production which covers the production cost. Similarly, studies have shown that the greenhouse gases emission ratio of waste oil biodiesel is better than natural oil and other biodiesel; making it more sustainable energy source. This technique shows remarkable potential for industrial-scale production of biodiesel. Various approaches have been developed for ILs; nevertheless, only a few of them seem to be economically feasible. Most of the commercial ILs are prepared using polymeric materials, because this process is simple, and the carrier development is a cost-effective process. However, the stability of ILs needs to be enhanced.

IL catalysts have been shown to produce high yields and mild reaction conditions comparable with those when homogeneous, heterogeneous, and enzyme catalysis is used; moreover, IL catalysts can be easily separated from the reacting mixtures for recycling. In addition, the formed biodiesel product is expected to be superior in quality in terms of lubricity, oxidation stability, density, kinematic viscosity, cetane number, and acid value.

Among the cited ILs with DEC, we consider that salts with Bronsted acidity or basicity are especially interesting because, in addition to a low risk of environmental contamination, they allow high conversion yields of vegetable oils and animal fats to biodiesel in a short time with mild reaction conditions. In addition, Bronsted acidic ILs can be used in the conversion of both FFAs and triglycerides to biodiesel without the need of pretreatment of the oil for moisture removal. This feature facilitates biodiesel production and reduces process costs, making them promising candidates in the production of biodiesel.

### Declaration of competing interest

This manuscript has not been published or presented elsewhere in part or in entirety and is not under consideration by another journal. We have read and understood your journal's policies, and we believe that neither the manuscript nor the study violates any of these. There are no conflicts of interest to declare.

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**PRINCIPAL**

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