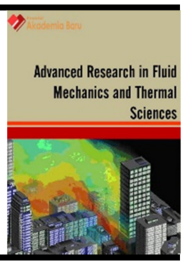
Penerbit Akademia Baru

Journal of Advanced Research in Fluid Mechanics and Thermal Sciences

Journal homepage: www.akademiabaru.com/arfmts.html
ISSN: 2289-7879



A Review on Multiple Functions of Ionic Liquid in Biodiesel Production

Open Access

Atikah Mohamed Sharikh[1], Sarina Sulaiman[1,*], Azlin Suhaida Azmi [1]

[1] Department of Biotechnology Engineering, Kulliyah of Engineering, International Islamic University Malaysia (IIUM), Kuala Lumpur, Malaysia

ARTICLE INFO

Article history:
Received 26 September 2016
Received in revised form 12 December 2017
Accepted 13 December 2017
Available online 14 December 2017

Keywords*:*
Biodiesel, catalyst, solvent, ionic liquid

ABSTRACT

Scarcity of petroleum and constant concern over environmental problems caused by diesel fuels has promoted production of biodiesel from renewable sources. Biodiesel synthesized from transesterification methods in the presence of acid or base catalyst or enzyme requires huge amount of solvent, particularly from alcohol to affirm high production yield. Inevitably, the process results in bulky waste that demands appropriate attention. In attempt to tackle the problem, ionic liquid has been identified to be the most potential substitute for conventional catalyst and solvent required in the biodiesel conversion. Ionic liquid that is widely known as 'green chemical' can be synthesized to meet reaction requirement by careful selection of anion and cations, with correct proportion of each to produce desired mixture. This paper reviews recent applications of ionic liquid in biodiesel production as catalyst, solvent and co-solvent. Since there are few ways in which ionic liquid can be categorized, this paper highlights classification of ionic liquids into two major groups; namely acidic and basic ionic liquid. Discussion on these tswo groups covers their dual- functions in biodiesel production which are as solvent or co-solvent and catalyst as well as the limitation of each group in the biodiesel production.

Copyright © 2017 PENERBIT AKADEMIA BARU - All rights reserved

1. Introduction

Depletion in petroleum based fuel has initiated a great effort to search for fuel replacement to cater world's fuel requirement. Besides, the concern over environmental issues caused by improper waste management and overuse of nature resources lead to exploration of new substances which are greener in nature and less toxic to environment as well as human in general. Attempt in finding renewable sources has driven the development of large-scale non-petroleum based alternative biofuels that constitute liquid such as bioethanol and biodiesel, and gaseous such as biogas and biohydrogen [1].

Chemically, biodiesel or better known as methyl ester is a product of transesterification reaction of triglycerides derived from animal or plant oil [2] in the present of homogeneous or heterogeneous catalyst and organic solvent such as alcohol to produce biodiesel as the main

* *Corresponding author.*
E-mail address: sarina@iium.edu.my (Sarina Sulaiman)

product and glycerol as by-product [3]. To date, acid, base and enzymes have been reported to be the most frequently used and tested catalyst in biodiesel synthesis. But due to some major drawbacks linked to these catalysts, recent trend has shown that research shifts to employing ionic liquid (IL) as green catalyst [4].

Theoretically, 3 moles of alcohol convert 1 mole of triglycerides into 1 mol of methyl ester [2]. Transesterification is a reversible reaction thus excess alcohol is normally supplied into the reaction mixture to shift the equilibrium to product formation [5]. Inevitably, the practice leads to formation large volume of waste. Besides, methanol is volatile thus safety measure must be taken into consideration during handling of the substance. In the search to find replacement for the methanol, IL has been identified to be greener in nature and possesses similar capability as solvent in biodiesel preparation.

2. Ionic Liquid

Generally, IL can be described as an organic salt constitutes of cations and anions that exists as liquid at room temperature [6]. Modern technology enables more groups of IL to be synthesis. Since IL constitutes anion and cation of two different salts, its formation is controllable by finely tuning the strength of the anion and cation according to desired final product. As listed by Ramadhan, Pornwongthong, Rattanaporn, and Sriariyanun [7], there are six groups of cation that are widely used in IL formation. They are imidazolium, pyridinium, pyrrolinium, cholinium, ammonium, and phosphonium. In addition, trifluoromethanesulfonate, methyl sulfate, hexafluoroantimonate, methane sulfonate, tetrachloroaluminate, tetrafluoroborate, hexafluorophosphate, , iodide, thiocyanate, nitrate, hydrogen sulfate, and dihydrogen phosphate are the 12 groups of anion which also well known for having broad applications in various industries [8] and are popular in IL synthesis.

In 1914, Paul Walden became the first person to discover possess physical properties of IL [9]. As mentioned by D. Han, Tang, Lee, and Row [10] IL has low flammability and negligible vapor pressure, high ionic, high thermal conductivity, and high dissolution capability towards many substrate, non-toxic, and non-volatile. Besides, as a substance that can act as solvent, IL is more favorable compared to other substance because of its properties such as polarity and hydrophobicity can be finely tuned by customized selection of cations and anions [11].

Due to superior properties of IL, literature review shows that besides being used in biodiesel synthesis, IL as catalyst and solvent can be found in broad applications such as Knoevenagel condensation [12-13], Fridel-craft acylation [14-15], Markovnikov's addition reaction [16-18], liquid extraction [10], Feist-Benary reaction [19] and Erlenmeyer synthesis of azlactones [20]. Famous claim is that IL is more costly compared to other catalyst and solvent and that remains the major limitation for application of IL at large scale. However, as revealed by Zhao *et al*. [18], apart from bulk purchase [21], it is possible to overcome this well-established downside of IL by coupling some suitable complexing agents with desired solid organic salts to produce deep eutectic solvent; a solvent having similar features as those in IL but simpler in terms of preparation and relatively cheaper with high purity [22].

A. Multiple Functions of Ionic Liquid

Earle [14] in their study divided IL into three major categories; Brønsted acidic IL, Brønsted base, and Lewis acid IL. In contrast, Ratti [23] categorized IL into two major groups; simple salts and binary IL. Being differ to both, Andreani and Rocha [9] reviewed that IL can be clustered into two major groups; one is based on chlorometallate anions and another containing no metals. Either way of grouping, IL can be acidic or basic depending on which functional groups are attached to cation and anion of the IL [23]. In comparison to conventional catalyst and solvent, IL in application of biodiesel preparation bears one distinguished specialty which is capability to act as catalyst, solvent and co-solvent. In any reaction, the solvent is important to dissolve all reacting components to maximize contact [24] hence ensuring reaction occurs. Due to negligible vapor pressure, IL is attractive in biodiesel production it broadens the range of temperature in which the reaction takes place without easily vaporize to surrounding [25]. As reported in many literature, conventional solvent such as methanol evaporates at considerably low temperature and decomposes at elevated temperature [24]. Continuous reaction beyond that point degrades biodiesel yield caused by loss of the solvent and increasing in viscosity that results from decomposition of the solvent which later dissolves in reaction mixture [26-27]. This notion is supported by Onukwuli, Emembolu, Ude, Aliozo, and Menkiti [28] whereby in their response surface study they proved that methanol is in direct relationship with temperature until some point along the reaction, increasing in temperature retards the oil conversion due to loss of solvent from evaporation.

Another feature of IL which is attractive to biodiesel production is adjustable solubility and miscibility of the solvent with other organic and inorganic solvent [8]. The ability of the solvent to form biphase or multiphase layer in reaction mixture facilitates product separation and eases catalyst and solvent recovery [29]. Application of IL as a solvent in liquid phase microextraction (LPME) technology improves the extraction process by exerting additional ionic interaction which is mutual electrostatic attraction to existing dipole-dipole and van der Waals interaction [10]. In extraction of lipid from *Chlorella sorokiniana,* 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO_4]) in the present of microwave irradiation enhances the process by 1990% relative to conventional heat as the IL actively dissolves the lipid and the mixture gains more energy to separate more efficiently [30].

Possibility on designing desired features in IL attracts a great interest to utilize biodiesel in biodiesel synthesis [31-32]. Previously, many ionic liquids contain imidazole cations. This notion is in line with the one agreed by F. Zhou, Xin, and Hao [33] whereby they mentioned that imidazolium-based IL is one of common IL. Thus, in 2004 they improved the existing ionic liquid by eliminating halogen element from the substance to produce a 'greener' solution with sulfate anions. Manipulation of imidazole-based ionic liquid requires less laborious task since the procedures are considered simple and straight forward [34].

In esterification, imidazolium-containing IL affects the reaction differently when the material is reacted with and without functionalized groups of chemical species. [33] reported that, coupling with HSO_3 - functional Brønsted acidic IL improves the esterification reaction tremendously. In fact, functionalized imidazolium IL increases biodiesel synthesis even when it performs dual-function IL in the conversion of waste vegetable oil [35]. In comparative study by Ha et al. [21], transesterification of soybeans in 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Emim][TfO]) as the reaction solvent is faster than those in tert-butanol and three times higher in terms of product yield than that in solvent-free condition. In terms of technical advantage, scientists agree that imidazolium- based IL is easy to be separated from reaction mixture, thus simplify catalyst recovery process at the end of production [35]. Many reactions using reactions listed proceeds between reaction temperatures of 55 to 70℃ [36-37] in 2 to 8 hours [38]. The reaction temperature is mild considering that methanol evaporates approximately at 60C. Therefore, under this reaction condition methanol loss due to prolong heating is negligible. This feature, although not applicable to all ILs, in one way can compensate for the major drawback of IL which is high cost for its synthesis.

IL compared to other conventional catalyst possesses good catalytic performance. Because it can be separated in less complicated procedures, solvent can be used repeatedly without dramatic decrease in biodiesel yield. This is supported by the fact that recovered solvent is high in purity and minimal loss due to mixing with glycerol. From environmental point of view, high reusability of IL serves the nature in a safer mode since it minimizes waste generation thus influence the environment with the least impact [39]. Transesterification of soybean using seven different ILs has shown that the catalyst is recyclable for at least three times without rapid reduction in product yield. Among the IL used, $[(CH_3CH_2)_3N(CH_2)_3SO_3H]HSO_4$ [40] and $[Et_3NH]Cl–AlCl_3$ [41]are better in reusability compared to cholinium hydroxide [42], BMI·NTf_2 [43], choline chloride·$x ZnCl_2$ [44] and [Hnmm]OH [45].

B. Acidic Ionic Liquid

Acidic IL is similar to conventional acid catalyst thus its strength, as proposed by Q. Wu, Chen, Han, Wang, and Wang [46] the strength of acidic IL is linked to dissociation of H^+. Presumably, since IL is thermally stable. Increase in temperature promotes more liberation of H^+, hence improves its catalytic performance with increasing acidity [37]. As highlighted earlier, there is possible customization in IL formation according to specific reaction requirement. It gives significant difference in many applications. For instance, observed that during the reaction of IL which is synthesized with zwitterionic precursor, no obvious fumes or vapour pressure observed as does in conventional strong acids.

Tran *et al*. [45] compared catalytic transesterification of soybean and *Botryococcus braunii* using strong acid such as sulphuric acid and sulfuryl chloride as acidic IL. The result indicates that slight increment in IL dosage enhances the biodiesel conversion remarkably with catalyst increment from 3 to 21%. Meanwhile, no similar effect takes place when conventional acid catalyst is used. Similar results were obtained when the reaction was conducted in low-frequency, high-intensity ultrasonic-assisted condition [48] whereby little increment in catalyst loading improves the biodiesel yield tremendously. IL is similar to conventional acid such that it functions better even in the reaction using feedstock consists of high free fatty acid [7]. In the attempt to conduct direct transesterification of *Jatropha curcas* sp.; feedstock well-known for its high free fatty acid, 1-butyl-3-methylimidazolium tosylate $[BMIm][CH_3SO_3]–FeCl_3$ was reported to produce higher yield of biodiesel with 99.7% of biodiesel yield in the present of 6:1 of methanol to oil ration at 120°C in 7 hours [6]. In contrast, when the same feedstock was tested with cholinium hydroxide (ChOH); a basic IL, the yield depreciates to 95% while the optimum ratio of methanol to oil increases at reduced temperature and reaction time [49].

Since Brønsted acid can operate in mild temperature and possess bigger acid group number, it forms the IL which is widely used in biodiesel synthesis [7]. In esterification reaction, Brønsted acid IL pretreats low grade feedstock to achieve acceptable level of free fatty acid that inhibits saponification [50]. In the development of green catalyst for esterification of carboxylic acid in alcoholic condition, 1-methylimidazolium tetrafluoroborate ([Hmim]BF) was reported to convert a minimum of 94% of the reactant and the product was easily separated due to obvious immiscibilty [51]. Liu, Wang and Xie [50] screened 9 Brønsted acid IL constitute of immidazolium cation. The result revealed that 1-(3-sulfonic acid)propyl-3-3-methylimidazole hydrosulfate, $[HO_3S\text{-pmim}]H_2SO_4$ is superior in catalytic performance over others which are $[Hmim]HSO_4$, $[Hmim]H_2PO_4$, $[Hmim]BF_4$, $[C_4mim]HSO_4$, $[C_4mim]H_2PO_4$, $[C_4mim]BF_4$, $[HO_3S\text{-pmim}]HSO_4$, and $[HO_3S\text{-pmim}]BF_4$ with 93% biodiesel yield in 8 hours at 120°C and waste oil and methanol ratio of 1:12. From the finding, they concluded that the acidity of IL influences catalytic activity of material.

C. Acidic Ionic Liquid

Acidic IL is similar to conventional acid catalyst thus its strength, as proposed by Q. Wu *et al*. [46] the strength of acidic IL is linked to dissociation of H^+. Presumably, since IL is thermally stable. Increase in temperature promotes more liberation of H^+, hence improves its catalytic performance with increasing acidity [37]. As highlighted earlier, there is possible customization in IL formation according to specific reaction requirement. It gives significant difference in many applications. For instance, observed that during the reaction of IL which is synthesized with zwitterionic precursor, no obvious fumes or vapour pressure observed as does in conventional strong acids.

Tran *et al*. [45] compared catalytic transesterification of soybean and *Botryococcus braunii* using strong acid such as sulphuric acid and sulfuryl chloride as acidic IL. The result indicates that slight increment in IL dosage enhances the biodiesel conversion remarkably with catalyst increment from 3 to 21%. Meanwhile, no similar effect takes place when conventional acid catalyst is used. Similar results were obtained when the reaction was conducted in low-frequency, high-intensity ultrasonic-assisted condition [48] whereby little increment in catalyst loading improves the biodiesel yield tremendously. IL is similar to conventional acid such that it functions better even in the reaction using feedstock consists of high free fatty acid [7]. In the attempt to conduct direct transesterification of *Jatropha curcas* sp.; feedstock well-known for its high free fatty acid, 1-butyl-3-methylimidazolium tosylate [BMIm][CH_3SO_3]–$FeCl_3$ was reported to produce higher yield of biodiesel with 99.7% of biodiesel yield in the present of 6:1 of methanol to oil ration at 120℃ in 7 hours [6]. In contrast, when the same feedstock was tested with cholinium hydroxide (ChOH); a basic IL, the yield depreciates to 95% while the optimum ratio of methanol to oil increases at reduced temperature and reaction time [49].

Since *Brønsted* acid can operate in mild temperature and possess bigger acid group number, it forms the IL which is widely used in biodiesel synthesis [7]. In esterification reaction, Brønsted acid IL pretreats low grade feedstock to achieve acceptable level of free fatty acid that inhibits saponification [50]. In the development of green catalyst for esterification of carboxylic acid in alcoholic condition, 1-methylimidazolium tetrafluoroborate ([Hmim]BF) was reported to convert a minimum of 94% of the reactant and the product was easily separated due to obvious immiscibilty [51]. Liu, Wang and Xie [50] screened 9 Brønsted acid IL constitute of immidazolium cation. The result revealed that 1-(3-sulfonic acid)propyl-3-3-methylimidazole hydrosulfate, [HO_3S-pmim]H_2SO_4 is superior in catalytic performance over others which are [Hmim]HSO_4 , [Hmim]H_2PO_4 , [Hmim]BF_4 , [C_4mim]HSO_4 , [C_4mim]H_2PO_4, [C_4mim]BF_4 , [HO_3S-pmim]HSO_4 , and [HO_3S-pmim]BF_4 with 93% biodiesel yield in 8 hours at 120℃ and waste oil and methanol ratio of 1:12. From the finding, they concluded that the acidity of IL influences catalytic activity of material.

D. Enzymatic Reaction in Ionic Liquid

A feature that make it superior than other volatile organic solvent is its ability to form variety of new compound by correct combination of cation and anion. Despite this advantage, one cannot simply couple a cation group with anion such that the newly formed compound might be too hydrophobic or hydrophilic. This is because too hydrophobic of an IL can poorly dissolve lipids while the highly hydrophilic property of IL inhibits enzyme activity [52]. Besides, high cost [53] and instability of enzyme remains the major setback to bring the application of biocatalyst with IL for biodiesel synthesis [54] to industrial level. Nevertheless, there are few reports related to biocatalyzed application of IL in the deliberate attempts to study the efficiency of IL as catalyst support or reaction solvent as listed in Table 1.

Table 1
Application of ionic liquid for biodiesel production in enzymatic condition

Ionic liquid	Ionic liquid functions	Biocatalyst	Ref.
[Emim][TfO]	Solvent	Novozym 435	[21]
[BMI·NTf$_2$]	Catalyst support	*Pseudomonas cepacia* lipase	[55]
[Emin][BF$_4$]	Solvent	Wild type *R. Oryzae* fungal strain	[56]
[Omim][PF$_6$]	Solvent	Novozym 435	[57]
[BMIM][PF$_6$]	Solvent	Novozym 435	[54]
[BMIM][PF$_6$]	Solvent	*Penicillium expansum* lipase	[58]
[OmPy][BF$_4$]	Solvent	*Burkholderia cepacia* lipase	[59]
[BMIM][PF$_6$]	Solvent	*Penicillium expansum* lipase	[60]
[C$_{18}$mim][NTF$_2$]	Solvent	Novozym 435	[61]
Ammoeng 102	Solvent	Novozym 435	[62]
[omim][PF$_6$]	Solvent	Novozym 435	[63]
[C$_{16}$MIM][NTf$_2$]	Solvent	Novozym 435	[64]
[BMIm][PF$_6$]	Solvent	*Penicillium expansum* lipase	[65]
[C$_{18}$tma][NTf$_2$]	Solvent	Novozym 435	[66]
[BMIm][PF$_6$]	Catalyst	Lipozyme RM IM	[67]

Several enzymes that are attractive in biodiesel production in IL system are Novozym 435 [21], *Pseudomonas cepacia* lipase [55], *Penicillium expansum* [58], *Burkholderia cepacian* [59], Lipozyme TL IM [62], Lipozyme RM IM [6267], and *Pseudomonas fluorescens* lipase [64] with Novozym 435 being the most frequent tested enzyme. Except for a few, application of IL alongside biocatalyst is to act as solvent instead of co-solvent or co-catalyst. Due to hydrophilic adverse effects of IL to the enzyme performance [68-69] most transesterification oil lipid and oil are done using other than methanol organic solvent. In most cases, *tert*-butanol and hydrophilic IL has been the popular choice [58]. To ensure high biodiesel yield, it is essential to select the accurate group IL so that the IL-enzyme synergistic effect of the reaction will result in high tolerance of the mixture towards the methanol [56]. The same view is shared by K.-P. Zhang et al. [60] as they concluded in their study that different IL groups depicts contradicted resistance towards methanol when it is used as the solvent.

Based on the numerous studies reports, one obvious similarity between them is that glycerol forms the final of transesterification. In a purer state, it may be valuable for commercialization of various market. But that is not always the case in transesterification, especially those using high free fatty acid feedstock. In the enzymatic reaction, glycerol inhibits the activity of the catalyst thus reducing the efficiency of the whole reaction and decrease the possibility of recycling the biocatalyst. One alternative to avoid the formation is by directing the reaction to the formation of biodiesel as the main and triacetylglycerol instead of glycerol of the by-product [54]. The alternative, although it seems promising in terms of solving problems related to denaturation of enzyme [70], it however creates further complication in separation the by-product. Owing to the fact IL is capable to dissolves many compound, Lozano et al. [66] demonstrated that it is possible to separate the transesterification of triolein and its by-product in a straight forward manner by taking the unique properties of IL to behave in a sponge-like compound. To understand this notion, the manipulation on IL state is done by ensuring formation of liquid monophasic homogeneous system between IL and other reacting materials at early stage of transesterification for maximum enzyme-reactant contact and formation of solid-liquid state at towards the end of the reaction. Using IL as solvent in the system, study by Lozano et al. [71] suggested that it is possible to establish this system by choosing IL consisting long chain alkyl side-chains.

4. Limitation

Until very recently, minimum number on published literature can be found that relates application of IL in biodiesel production. Therefore, the iconicity, flammability, and causticity of some IL are unknown [72]. The fact that IL is claimed to be 'green chemical' but for ILs which are newly discovered the status is yet to be determined [73]. Nevertheless, information on qualitative qualities such as nuclear magnetic resonance (NMR) spectroscopy thermal characteristics, as suggested by [Noda et al. [74]] and Schwenzer, Kerisit, and Vijayakumar [75] can be determined using Walden plots. Although IL is known to be ideal for biodiesel separation and glycerol removal, little is known about the effect of accumulated by-product to the recovery of biodiesel [76].

As for acidic IL, no specific method in which it can be employed to determine acidity of substance, this acidity of IL remains unknown [46]. Mentioned in previous section is high reusability of IL. But in case where solid IL is used in the reaction, solidifying of the mixture and removal of the entire product by solvent extraction might cause IL loss its catalytic strength in consequent reaction [31]. In terms of catalytic performance in enzymatic condition, despites its high efficiency to produce high biodiesel yield, IL is mostly likely to deactivate the active site of the enzyme, thus reduces its reusability [56] and necessitates for longer reaction time [21].

4. Conclusion

Ionic liquid has attracted a great interest in biodiesel synthesis due to its superior features which is feasible for biodiesel production. As a 'green chemical' IL is highly potential to completely replace conventional catalyst and solvent which are currently used at industrial level. Although high price of it remains the main obstacle in employing IL at large scale, proper planning and deeper studies from economic aspect helps in allocating minimum total cost. Besides, IL which is highly reusable would compensate for high cost of the raw materials for IL synthesis.

Acknowledgement
This research was funded by Ministry of Higher Education of Malaysia MOHE/FRGS 2013 grant (FRGS 13-079-0320) and RIGS16-089-0253 from International Islamic University Malaysia (IIUM).

References

[1] Thanh, Le Tu, Kenji Okitsu, Luu Van Boi, and Yasuaki Maeda. "Catalytic technologies for biodiesel fuel production and utilization of glycerol: a review." *Catalysts* 2, no. 1 (2012): 191-222.

[2] Lee, Dae-Won, Young-Moo Park, and Kwan-Young Lee. "Heterogeneous base catalysts for transesterification in biodiesel synthesis." *Catalysis Surveys from Asia* 13, no. 2 (2009): 63-77.

[3] Vicente, Gemma, Mercedes Martınez, and Jose Aracil. "Integrated biodiesel production: a comparison of different homogeneous catalysts systems." *Bioresource technology* 92, no. 3 (2004): 297-305.

[4] Qiu, Ting, Xiaoting Guo, Jinbei Yang, Lihua Zhou, Ling Li, Hongxing Wang, and Yu Niu. "The synthesis of biodiesel from coconut oil using novel Brønsted acidic ionic liquid as green catalyst." *Chemical Engineering Journal* 296 (2016): 71-78.

[5] Gude, Veera Gnaneswar, Prafulla Patil, Edith Martinez-Guerra, Shuguang Deng, and Nagamany Nirmalakhandan. "Microwave energy potential for biodiesel production." *Sustainable Chemical Processes* 1, no. 1 (2013): 5.

[6] Guo, Feng, Zhen Fang, Xiao-Fei Tian, Yun-Duo Long, and Li-Qun Jiang. "“One-step production of biodiesel from Jatropha oil with high-acid value in ionic liquids”[Bioresour. Technol. 102 (11)(2011)]." *Bioresource technology* 140 (2013): 447-450.

[7] Ramadhan, A. R., Pornwongthong, P., Rattanaporn, K., & Sriariyanun, M. (2015). Review of Ionic Liquid as a Catalyst for Biodiesel Prodution. *J Sci Technol MSU, 34*(4).

[8] Fauzi, Ahmad Hafiidz Mohammad, and Nor Aishah Saidina Amin. "An overview of ionic liquids as solvents in biodiesel synthesis." *Renewable and Sustainable Energy Reviews* 16, no. 8 (2012): 5770-5786.

[9] Andreani, L., and J. D. Rocha. "Use of ionic liquids in biodiesel production: a review." *Brazilian Journal of Chemical Engineering* 29, no. 1 (2012): 1-13.

[10] Han, Dandan, Baokun Tang, Yu Ri Lee, and Kyung Ho Row. "Application of ionic liquid in liquid phase microextraction technology." *Journal of separation science* 35, no. 21 (2012): 2949-2961.

[11] Zhao, Hua, Cheng Zhang, and Tanisha D. Crittle. "Choline-based deep eutectic solvents for enzymatic preparation of biodiesel from soybean oil." *Journal of Molecular Catalysis B: Enzymatic* 85 (2013): 243-247.

[12] Gong, Kai, Zhi-Wei He, Ying Xu, Dong Fang, and Zu-liang Liu. "Green synthesis of 5-benzylidene rhodanine derivatives catalyzed by 1-butyl-3-methyl imidazolium hydroxide in water." *Monatshefte für Chemie/Chemical Monthly* 139, no. 8 (2008): 913-915.

[13] Priede, Elina, Sindija Brica, Eduards Bakis, Niklavs Udris, and Andris Zicmanis. "Ionic liquids as solvents for the Knoevenagel condensation: understanding the role of solvent–solute interactions." *New Journal of Chemistry* 39, no. 12 (2015): 9132-9142.

[14] Earle, Martyn J., Natalia V. Plechkova, and Kenneth R. Seddon. "Green synthesis of biodiesel using ionic liquids." *Pure and Applied Chemistry* 81, no. 11 (2009): 2045-2057.

[15] Liu, Z. C., X. H. Meng, Rui Zhang, and C. M. Xu. "Friedel-Crafts acylation of aromatic compounds in ionic liquids." *Petroleum Science and Technology* 27, no. 2 (2009): 226-237.

[16] Sun, Hui, Dongju Zhang, Fang Wang, and Chengbu Liu. "Theoretical study of the mechanism for the Markovnikov addition of imidazole to vinyl acetate catalyzed by the ionic liquid [bmIm] OH." *The Journal of Physical Chemistry A* 111, no. 20 (2007): 4535-4541.

[17] Xu, Jian-Ming, Bo-Kai Liu, Wei-Bo Wu, Chao Qian, Qi Wu, and Xian-Fu Lin. "Basic ionic liquid as catalysis and reaction medium: a novel and green protocol for the Markovnikov addition of N-heterocycles to vinyl esters, using a task-specific ionic liquid,[bmIm] OH." *The Journal of organic chemistry* 71, no. 10 (2006): 3991-3993.

[18] Zhao, Hua, Gary A. Baker, and Shaletha Holmes. "New eutectic ionic liquids for lipase activation and enzymatic preparation of biodiesel." *Organic & biomolecular chemistry* 9, no. 6 (2011): 1908-1916.

[19] Ranu, Brindaban C., Laksmikanta Adak, and Subhash Banerjee. "Ionic liquid promoted interrupted Feist–Benary reaction with high diastereoselectivity." *Tetrahedron Letters*49, no. 31 (2008): 4613-4617.

[20] Patil, S. G., R. R. Bagul, V. M. Kamble, and V. A. Navale. "A green protocol for Erlenmeyer Plöchl reaction by using [bmIm] OH." *J. Chem. Pharm. Res* 3, no. 4 (2011): 285-290.

[21] Ha, Sung Ho, Mai Ngoc Lan, Sang Hyun Lee, Sung Mi Hwang, and Yoon-Mo Koo. "Lipase-catalyzed biodiesel production from soybean oil in ionic liquids." *Enzyme and Microbial Technology* 41, no. 4 (2007): 480-483.

[22] Dai, Yuntao, Jaap van Spronsen, Geert-Jan Witkamp, Robert Verpoorte, and Young Hae Choi. "Natural deep eutectic solvents as new potential media for green technology." *Analytica chimica acta* 766 (2013): 61-68.

[23] Ratti, R. (2014). Ionic Liquids: Synthesis and Applications in Catalysis. *Advances in Chemistry, 2014*, 16. doi: 10.1155/2014/729842

[24] Fauzi, Ahmad Hafiidz Mohammad, and Nor Aishah Saidina Amin. "An overview of ionic liquids as solvents in biodiesel synthesis." *Renewable and Sustainable Energy Reviews* 16, no. 8 (2012): 5770-5786.

[25] Han, B., W. Zhang, Y. Chen, F. Yin, S. Liu, X. Zhao, J. Liu, L. Xu, C. Wang, and H. Yang. "Synthesis of methyl laurate catalyzed by Brønsted acid ionic liquids." *J Chem Pharm Res*6 (2014): 435-40.

[26] El-Gendy, Nour Sh, A. Hamdy, and Salem S. Abu Amr. "An investigation of biodiesel production from wastes of seafood restaurants." *International journal of biomaterials* 2014 (2014).

[27] Muciño, Gabriel Galván, Rubi Romero, Armando Ramírez, Sandra Luz Martínez, Ramiro Baeza-Jiménez, and Reyna Natividad. "Biodiesel production from used cooking oil and sea sand as heterogeneous catalyst." *Fuel* 138 (2014): 143-148.

[28] Onukwuli, Dominic Okechukwu, Lovet Nwanneka Emembolu, Callistus Nonso Ude, Sandra Ogechukwu Aliozo, and Mathew Chukwudi Menkiti. "Optimization of biodiesel production from refined cotton seed oil and its characterization." *Egyptian Journal of Petroleum* 26, no. 1 (2017): 103-110.

[29] Ramalho, Hugo F., Karlla MC di Ferreira, Paula MA Machado, Renato S. Oliveira, Luciano P. Silva, Marcos J. Prauchner, and Paulo AZ Suarez. "Biphasic hydroformylation of soybean biodiesel using a rhodium complex dissolved in ionic liquid." *Industrial Crops and Products* 52 (2014): 211-218.

[30] Pan, Jingying, Tapaswy Muppaneni, Yingqiang Sun, Harvind K. Reddy, Jie Fu, Xiuyang Lu, and Shuguang Deng. "Microwave-assisted extraction of lipids from microalgae using an ionic liquid solvent [BMIM][HSO 4]." *Fuel* 178 (2016): 49-55.

[31] Hajipour, A. R., and F. Rafiee. "Basic ionic liquids. A short review." *J. Iran. Chem. Soc* 6, no. 4 (2009): 647-678.

[32] Zhou, Xian Si, Bing Jia Liu, Feng Wen Luo, Wen Yi Zhang, and Hang Song. "Novel Brønsted-acidic ionic liquids based on benzothiazolium cations as catalysts for esterification reactions." *Journal of the Serbian Chemical Society* 76, no. 12 (2011): 1607-1615.

[33] Zhou, FengYan, BingWei Xin, and JingCheng Hao. "HSO3-functionalized Brønsted acidic ionic liquids promote esterification of aromatic acid." *Chinese Science Bulletin* 58, no. 26 (2013): 3202-3207.

[34] Xu, Jian-Ming, Wei-Bo Wu, Chao Qian, Bo-Kai Liu, and Xian-Fu Lin. "A novel and highly efficient protocol for Markovnikov's addition using ionic liquid as catalytic green solvent." *Tetrahedron letters* 47, no. 10 (2006): 1555-1558.

[35] Yassin, Fathy A., Fathy Y. El Kady, Hoda S. Ahmed, Latifa K. Mohamed, Seham A. Shaban, and Ahmed K. Elfadaly. "Highly effective ionic liquids for biodiesel production from waste vegetable oils." *Egyptian Journal of Petroleum* 24, no. 1 (2015): 103-111.

[36] Ullah, Zahoor, Mohamad Azmi Bustam, and Zakaria Man. "Biodiesel production from waste cooking oil by acidic ionic liquid as a catalyst." *Renewable Energy* 77 (2015): 521-526.

[37] Wu, Jianxiang, Yilong Gao, Wei Zhang, Yueyue Tan, Aomin Tang, Yong Men, and Bohejin Tang. "Esterification of cooking oil for biodiesel production using composites Cs2. 5H0. 5PW12O40/ionic liquids catalysts." *Applied Petrochemical Research* 4, no. 3 (2014): 305-312.

[38] Zhang, Lei, Mo Xian, Yucai He, Liangzhi Li, Jianming Yang, Shitao Yu, and Xin Xu. "A Brønsted acidic ionic liquid as an efficient and environmentally benign catalyst for biodiesel synthesis from free fatty acids and alcohols." *Bioresource Technology* 100, no. 19 (2009): 4368-4373.

[39] Clark, James H., Thomas J. Farmer, Duncan J. Macquarrie, and James Sherwood. "Using metrics and sustainability considerations to evaluate the use of bio-based and non-renewable Brønsted acidic ionic liquids to catalyse Fischer esterification reactions." *Sustainable Chemical Processes* 1, no. 1 (2013): 23.

[40] Yanfei, He, Han Xiaoxiang, Chen Qing, and Zhou Lingxiao. "Transesterification of Soybean Oil to Biodiesel by Brønsted-Type Ionic Liquid Acid Catalysts." *Chemical Engineering & Technology* 36, no. 9 (2013): 1559-1567.

[41] Liang, Xuezheng, Guozhen Gong, Haihong Wu, and Jianguo Yang. "Highly efficient procedure for the synthesis of biodiesel from soybean oil using chloroaluminate ionic liquid as catalyst." *Fuel* 88, no. 4 (2009): 613-616.

[42] Fan, Mingming, Jianglei Huang, Jing Yang, and Pingbo Zhang. "Biodiesel production by transesterification catalyzed by an efficient choline ionic liquid catalyst." *Applied energy*108 (2013): 333-339.

[43] Lapis, Alexandre AM, Luciane F. de Oliveira, Brenno AD Neto, and Jairton Dupont. "Ionic Liquid Supported Acid/Base-Catalyzed Production of Biodiesel." *ChemSusChem* 1, no. 8-9 (2008): 759-762.

[44] Tao, L. O. N. G., D. E. N. G. Yuefeng, G. A. N. Shucai, and C. H. E. N. Ji. "Application of choline chloride· xZnCl2 ionic liquids for preparation of biodiesel." *Chinese Journal of Chemical Engineering* 18, no. 2 (2010): 322-327.

[45] Ren, Qinggong, Tongmei Zuo, Jingjing Pan, Changle Chen, and Weimin Li. "Preparation of biodiesel from soybean catalyzed by basic ionic liquids [Hnmm] OH." *Materials* 7, no. 12 (2014): 8012-8023.

[46] Wu, Qin, He Chen, Minghan Han, Dezheng Wang, and Jinfu Wang. "Transesterification of cottonseed oil catalyzed by Brønsted acidic ionic liquids." *Industrial & Engineering Chemistry Research* 46, no. 24 (2007): 7955-7960.

[47] Tran, Hai-Linh, Young-Jin Ryu, Dong Ho Seong, Sang-Min Lim, and Choul-Gyun Lee. "An effective acid catalyst for biodiesel production from impure raw feedstocks." *Biotechnology and bioprocess engineering* 18, no. 2 (2013): 242-247.

[48] Guo, Weilin, Helian Li, Guanglei Ji, and Guangyou Zhang. "Ultrasound-assisted production of biodiesel from soybean oil using Brønsted acidic ionic liquid as catalyst." *Bioresource technology* 125 (2012): 332-334.

[49] Reddy, Eragam Ramamohan, Mukesh Sharma, Jai Prakash Chaudhary, Hetal Bosamiya, and Ramavatar Meena. "One-pot synthesis of biodiesel from high fatty acid Jatropha curcas oil using bio-based basic ionic liquid as a catalyst." *Curr. Sci* 106, no. 10 (2014): 1394-1400.

[50] Das, Subrata, Ashim Jyoti Thakur, and Dhanapati Deka. "Two-stage conversion of high free fatty acid Jatropha curcas oil to biodiesel using Brønsted acidic ionic liquid and KOH as catalysts." *The Scientific World Journal* 2014 (2014).

[51] Zhu, Hua-Ping, Fan Yang, Jie Tang, and Ming-Yuan He. "Brønsted acidic ionic liquid 1-methylimidazolium tetrafluoroborate: a green catalyst and recyclable medium for esterification." *Green Chemistry* 5, no. 1 (2003): 38-39.

[52] Zhao, Hua, Zhiyan Song, Olarongbe Olubajo, and Janet V. Cowins. "New ether-functionalized ionic liquids for lipase-catalyzed synthesis of biodiesel." *Applied biochemistry and biotechnology* 162, no. 1 (2010): 13-23.

[53] Islam, M. T., Alam, M. Z., Al-Mamun, A., Elgharbawy, A. A., & Riyadi, F. A. (2017). Development of enzymatic pretreatment of palm oil mill effluent for monomers towards biogas production *Journal of Advanced Research in Materials Science, 38*(1), 39-44

[54] Ruzich, Nicholas Ivan, and Amarjeet S. Bassi. "Investigation of enzymatic biodiesel production using ionic liquid as a co-solvent." *The Canadian Journal of Chemical Engineering* 88, no. 2 (2010): 277-282.

[55] Gamba, Muriell, Alexandre AM Lapis, and Jairton Dupont. "Supported ionic liquid enzymatic catalysis for the production of biodiesel." *Advanced synthesis & catalysis* 350, no. 1 (2008): 160-164.

[56] Arai, Shogo, Kazunori Nakashima, Takanori Tanino, Chiaki Ogino, Akihiko Kondo, and Hideki Fukuda. "Production of biodiesel fuel from soybean oil catalyzed by fungus whole-cell biocatalysts in ionic liquids." *Enzyme and Microbial Technology* 46, no. 1 (2010): 51-55.

[57] Lozano, Pedro, Juana María Bernal, Rungtiwa Piamtongkam, Dirk Fetzer, and Michel Vaultier. "One-Phase Ionic Liquid Reaction Medium for Biocatalytic Production of Biodiesel." *ChemSusChem* 3, no. 12 (2010): 1359-1363.

[58] Yang, Zhen, Kai-Pei Zhang, Ying Huang, and Zhi Wang. "Both hydrolytic and transesterification activities of Penicillium expansum lipase are significantly enhanced in ionic liquid [BMIm][PF 6]." *Journal of Molecular Catalysis B: Enzymatic*63, no. 1 (2010): 23-30.

[59] Liu, Yun, Dawei Chen, Yunjun Yan, Cheng Peng, and Li Xu. "Biodiesel synthesis and conformation of lipase from Burkholderia cepacia in room temperature ionic liquids and organic solvents." *Bioresource technology* 102, no. 22 (2011): 10414-10418.

[60] Zhang, Kai-Pei, Jing-Qi Lai, Ze-Lin Huang, and Zhen Yang. "Penicillium expansum lipase-catalyzed production of biodiesel in ionic liquids." *Bioresource technology* 102, no. 3 (2011): 2767-2772.

[61] Lozano, Pedro, Juana M. Bernal, and Michel Vaultier. "Towards continuous sustainable processes for enzymatic synthesis of biodiesel in hydrophobic ionic liquids/supercritical carbon dioxide biphasic systems." *Fuel* 90, no. 11 (2011): 3461-3467.

[62] Devi, B. L. A., Zheng Guo, and Xuebing Xu. "Characterization of ionic liquid-based biocatalytic two-phase reaction system for production of biodiesel." *AIChE Journal* 57, no. 6 (2011): 1628-1637.

[63] De los Ríos, A. P., FJ Hernández Fernández, D. Gómez, M. Rubio, and G. Víllora. "Biocatalytic transesterification of sunflower and waste cooking oils in ionic liquid media." *Process biochemistry* 46, no. 7 (2011): 1475-1480.

[64] De Diego, Teresa, Arturo Manjón, Pedro Lozano, Michel Vaultier, and José L. Iborra. "An efficient activity ionic liquid-enzyme system for biodiesel production." *Green Chemistry*13, no. 2 (2011): 444-451.

[65] Lai, Jing-Qi, Zhang-Li Hu, Peng-Wei Wang, and Zhen Yang. "Enzymatic production of microalgal biodiesel in ionic liquid [BMIm][PF 6]." *Fuel* 95 (2012): 329-333.

[66] Lozano, Pedro, Juana M. Bernal, Gregorio Sánchez-Gómez, Gregorio López-López, and Michel Vaultier. "How to produce biodiesel easily using a green biocatalytic approach in sponge-like ionic liquids." *Energy & Environmental Science* 6, no. 4 (2013): 1328-1338.

[67] Manurung, Renita, Rosdanelli Hasibuan, Taslim Taslim, Nur Sri Rahayu, and Aira Darusmy. "Enzymatic Transesterification of DPO to Produce Biodiesel by Using Lipozyme RM IM in Ionic Liquid System." *Procedia-Social and Behavioral Sciences* 195 (2015): 2485-2491.

[68] Sunitha, S., Kanjilal, S., Reddy, P., & Prasad, R. (2007). Ionic liquids as a reaction medium for lipase-catalyzed methanolysis of sunflower oil. *Biotechnology letters, 29*(12), 1881-1885.

[69] Liu, Liping, Yang Hu, Peng Wen, Ning Li, Minhua Zong, Beining Ou-Yang, and Hong Wu. "Evaluating the effects of biocompatible cholinium ionic liquids on microbial lipid production by Trichosporon fermentans." *Biotechnology for biofuels* 8, no. 1 (2015): 119.

[70] Talha, Nur Syakirah, and Sarina Sulaiman. "Overview of catalysts in biodiesel production." *ARPN Journal of Engineering and Applied Sciences* 11, no. 1 (2016): 439-448.

[71] Lozano, Pedro, Celia Gomez, Angel Nicolas, Ramon Polo, Susana Nieto, Juana M. Bernal, Eduardo García-Verdugo, and Santiago V. Luis. "Clean enzymatic preparation of oxygenated biofuels from vegetable and waste cooking oils by using spongelike ionic liquids technology." *ACS Sustainable Chemistry & Engineering* 4, no. 11 (2016): 6125-6132.

[72] Ghandi, Khashayar. "A review of ionic liquids, their limits and applications." *Green and sustainable chemistry* 4, no. 01 (2014): 44.

[73] Potdar, Mahesh K., Geoffrey F. Kelso, Lachlan Schwarz, Chunfang Zhang, and Milton TW Hearn. "Recent developments in chemical synthesis with biocatalysts in ionic liquids." *Molecules* 20, no. 9 (2015): 16788-16816.

[74] Noda, Akihiro, Md Abu Bin Hasan Susan, Kenji Kudo, Shigenori Mitsushima, Kikuko Hayamizu, and Masayoshi Watanabe. "Brønsted acid− base ionic liquids as proton-conducting nonaqueous electrolytes." *The Journal of Physical Chemistry B* 107, no. 17 (2003): 4024-4033.

[75] Schwenzer, Birgit, Sebastien N. Kerisit, and M. Vijayakumar. "Anion pairs in room temperature ionic liquids predicted by molecular dynamics simulation, verified by spectroscopic characterization." *RSC Advances* 4, no. 11 (2014): 5457-5464.

[76] Xu, X., Guo, Z., & Cheong, L.-Z. (2016). Chapter 1 - Are Ionic Liquids Ready for Lipids Processing? *Ionic Liquids in Lipid Processing and Analysis* (pp. 1-9): AOCS Press.