Basic and Brønsted Acidic Ionic Liquids as Catalysts in Biodiesel Synthesis

Abdelmalik M. Shakorfow[1] and Abdulaziz H. Mohamed[2]

[1]Chemical and Petroleum Engineering Department, Faculty of Engineering, Elmergib University, Khoms-Libya

[2]Chemical Engineering Department, Faculty of Engineering, Tobruk University, Tobruk-Libya.

Corresponding E-mail: Dr_Eng.Malik@Yahoo.Co.Uk.

Abstract

In this article, use of some basic and Brønsted acidic ionic liquids for the purpose of synthesis of biodiesel has been reviewed. In such a technology, it is evident that use of ionic liquids in general is increasing. Ionic liquids can be tailored with respect to the desirable application. In-house-synthesized basic ionic liquids have sufficiently catalyze the transesterification reaction with an adequate biodiesel yield. Reusability, stable catalytic activity and use of moderate reaction conditions were all reported. Investigations deemed have shown that optimal reaction conditions have been demonstrated. In order to further promote the catalytic activity of a basic ionic liquid, immobilization of some metal chlorides in that basic ionic liquids has been proposed. Biodiesel contamination by metal residues as well as the possibility of release of HCl; however, have encouraged another arrangement. This arrangement relies on using an ionic liquid as a support for those readily available acidic/basic traditional catalysts. Via such an arrangement, high yield, low cost, reusability as well as simplicity of procedure were attained. Another success of ionic liquids as catalysts in biodiesel synthesis is that with the Brønsted acidic ionic liquids good product recovery can be ensured while biodiesel contamination with free molecules of the used catalyst can be prevented. In addition, good features of basic ionic liquids cited above have also been demonstrated while using those Brønsted acidic ionic liquids.

Keywords: Ionic liquid, basic ionic liquid, Brønsted acidic ionic liquid, synthesis.

I. INTRODUCTION

To a large extent; nowadays, world's energy sector is quite heavily dependent on fossil fuels. This is ultra-pronounced in the transportation sector as well as in the sector of energy generation. In order to augment the fuels, quests for sustainable alternative fuel(s) based on renewable fuels can be critical factors in achieving a sustainable while economic development. This can also be an avenue for minimizing the consequential greenhouse gas emissions and; thus, mitigating the phenomenon of global warming. Though several countries that are deemed developing countries and are among the largest oil producers, yet they are bedeviled with insufficient energy supply. Thus, diversification of energy resources by the exploitation of some biomass resources (biodiesel; in particular), that are capable of providing an augmentation in energy supply with a zero effect on the food basket, is; therefore, necessary. Several catalytic techniques are available for biodiesel synthesis. Among the catalysts that have been employed for biodiesel synthesis are the inept rather mediocre homogenous, heterogeneous and enzymatic catalysts. Issues arising due to employment of such catalysts have been addressed elsewhere [1].

The chief focus of this paper was to discuss the employment of two types of ionic liquids (basic and Brønsted acidic), a sub-category of homogenous catalysts, in biodiesel synthesis.

II. IONIC LIQUIDS

Ionic liquids catalysts have also been used for the purpose of biodiesel production with which a faster reaction rate can be obtained compared to that obtained in case another type of catalysts is used, although the mechanism how these ionic liquids catalysts function is still a subject of mystery [2]. Ionic liquids date back to 1914 following a study carried out by Walden, P. and Seddon examining the physical properties of the ionic liquid ethylammonium nitrate $(C_2H_5)NH_3NO_3$ [3]. Although initially such a discipline did not find a wide range of interest and application, it; however, recently seems to have become a significant one following performing thousands of research investigations on the properties of ionic liquids and their vast applications and registering several patents [4]. Among ionic liquids applications are: polymerization [5], industrial separation and extraction processes [6-7], electrochemistry [6], organic synthesis processes [8], spectroscopy [6], nano-materials [9], electrochemistry [7], etc. However, in biodiesel synthesis; in particular, ionic liquids have not found a wide range of interest and application as they

Received: 01 May 2020; revised: 01 June 2020; accepted: 02 June 2020. Available online: 06 June 2020
www.lam.edu.ly

deserve. In the subsequent sections of this paper, available limited literature on the use of some types of ionic liquids in the synthesis of biodiesel is discussed. The first industrial process utilized ionic liquids to remove HCl produced through the synthesis of alkoxyphenylphosphines, which are essential raw materials for photoinitiators in various industries including pharmaceuticals, was reported in 2003 by BASF, USA. French Institute of Petroleum, Degussa and ExxonMobil are also other institutions that consider ionic liquids for their manufacturing processes.

Ionic liquids can be defined as organic salts made up with anions and cations. They are a result of the combination of a small anion with a large cation. At the room temperature, they are liquids indicating their low melting points. Their melting points are often close to or less than room temperature. At extremely low temperatures, -96 °C, they can be fluid due to their large ions [10-14]. A review on ionic liquids for clean technology is available [10] while use of supported acidic ionic liquids in organic synthesis is reviewed elsewhere [15]. Examples of acidic ionic liquids catalysts are: ethylammonium nitrate $(C_2H_5)NH_3NO_3$ [3], chloroaluminate ionic liquid [16-17], dicationic ionic liquid [17-18], MB3B (bentonite modified with 3,3′-(butane-1,6-diyl) bis (6-sulfo-1-(4-sulfobenzyl)-1*H*-benzimidazolium) hydrogensulfate) [19], dialkylimidazolium chloroaluminate, 1-ethylbenzimidazolium tetrafluoroborate ([Hebim]BF4), 1-butylbenzimidazolium tetrafluoroborate ([Hbbim]BF4)] [20], polymeric ionic liquids [21], 1-carboxyethylene-3-(4-zinc acetate sulfobutyl) imidazolium chloride ([CH3COO-Zn-O3S-bim-CH2CH2COOH]Cl), 1-(1,2-dicarboxy) ethylene-3-(4-zinc acetate sulfobutyl) imidazolium chloride ([CH3COO-Zn-O3S-bim-C4H5O4]Cl) [22], Brønsted *N*-methyl-2-pyrrolidonium methyl sulfonate ([NMP][CH_3SO_3]) and quaternary ammonium ionic liquid [(CH3CH2)3N(CH2)3 SO3H][C7H7O3S] [2].

On the other hand, examples of alkaline ionic liquids catalysts include: 1-butyl-3-methylimidazolium cation and imidazolide anion ([Bmim]Im) [23], 1-butyl-3-methyl imidazolium imidazolide [24], 1-butyl-3-methyl morpholine hydroxide ([Hnmm]OH) [7], 1-butyl-3-methylimidazolium hydroxide ([BMIM]OH), chloroaluminate ionic liquid, $Et_3NH]Cl–AlCl_3(x(AlCl_3)$ [17] and bis-(3-methyl-1-imidazolium-)-ethlyene dihydroxide [25]. Since the cations and anions of acidic ionic liquids catalysts compared to alkaline ones can be designed to a number of groups with certain properties that regulate acidity, acidic catalysts have seen a wider application in chemical synthesis [26] compared to alkaline catalysts [27-29] due to high activity [30]. Ionic liquids catalysts are colorless, non-flammable [3,10, 31-32], non-volatile, green [26] and thermally stable [20]. Furthermore, ionic liquid catalysts are characterized with: excellent catalytic activity, low corrosion effects and low viscosity [3, 10, 31-32], that can be readily separable and recyclable [4, 33], outstanding solvating potential [22, 34], negligible vapor pressure and high chemical and thermal stability [22, 35].

Ionic liquids, owing to their unique dual parts configuration, are also easy to manipulate through molecule design in accordance to a certain application aiming at a bespoke set of properties [20,34,36]. Furthermore, throughout use, due to adequate ion attraction, ionic liquids are characterized by zero vapor pressure (no emissions of volatile organic compounds) [4]. Also, with regards to the environment, ionic liquid catalysts are considered environment-friendly for being recyclable [20,37-38]. In fact, although they are currently used in massive amounts in several reactions, ionic liquids can be dealt with and recovered economically. Through using ionic liquids, amount of residual water and procedure(s) of product separation and purification can all be lower than that in case a classical catalyst has been used. In terms of cost; however, some ionic liquids can be generally considered expensive whether as a catalyst or as a solvent. According to suppliers such as Sigma-Aldrich, few grams of an ionic liquid can cost several dollars. In fact, costs of the same amounts of classical acidic/alkaline catalysts are only 4% of an ionic liquid's cost [4]. Although this might be an obstacle towards employing ionic liquids as a catalyst in a transesterification reaction, their use; however, seems inevitable. To this end, due to their effectiveness, chemists have suggested that in-house synthesis of ionic liquids instead of their purchase could reduce their cost to a third. Another way to reduce their cost, ionic liquids can be re-used several times owing to their easy separation from the reaction medium provided that their activity is not compromised [3]. Another important aspect of ionic liquids, that is the details of their synthesis, is beyond the scope of this study while it can be found elsewhere [3,39-41]. In this paper as previously stated; however, use of some basic and Brønsted acidic ionic liquids as catalysts in biodiesel synthesis via esterification and transesterification of several vegetable oils is discussed.

III. BASIC IONIC LIQUIDS AS CATALYSTS IN BIODIESEL SYNTHESIS

Liang, et al. have successfully synthesized several basic binuclear (bication) functional ionic liquids with an imidazolium structure for use as catalysts in the preparation of biodiesel through transesterification from cottonseed vegetable oil with methanol. They demonstrated that bication ionic liquids with an imidazolium structure are suitable catalysts for the synthesis of biodiesel through transesterification. Due to their adequate lengths of the carbon chain in the cations, synthesized ionic liquids exhibited a satisfactory catalytic activity. Part of their investigation was devoted to investigating the effect of catalyst dosage, reaction time, reaction temperature and the molar ratio of methanol to cottonseed oil on the transesterification performance. A dosage of 0.4% of bis-(3-methyl-1-imidazolium-)-ethlyene dihydroxide as a catalyst, running the reaction for four hours at a temperature of 55 °C and using a molar ratio of 12:1 gave a fraction and selectivity of fatty acid methyl ester in the produced biodiesel of 98.5% and 99.9%, respectively [30]. Li and co-workers have also successfully synthesized a new basic ionic liquid paired by 1-butyl-3-methylimidazolium cation and imidazolide anion ([Bmim]Im), in a two-step reaction, for use as a catalyst in the preparation of biodiesel through transesterification of soybean vegetable oil with methanol. They demonstrated that the used ionic liquid is a suitable catalyst for the synthesis of biodiesel through transesterification. Part of their work was also devoted to investigating the effect of catalyst dosage, reaction time, reaction temperature and the molar ratio of methanol to soybean oil on the performance of transesterification. Results indicate that optimal reaction conditions, at which a biodiesel yield of up to 95.76% can be achieved, are: dosage of the used basic ionic liquid as a catalyst is 8% (mass fraction), reaction duration is one hour, temperature of the reaction is 60 °C and molar ratio is 6:1. The used basic ionic liquid was stable and could be repeatedly used [23].

Furthermore, Ren, et al. have synthesized a morpholine alkaline basic ionic liquid, 1-butyl-3-methyl morpholine hydroxide ([Hnmm]OH), for the purpose of biodiesel synthesis through transesterification of soybean vegetable oil with methanol. Their results indicate that among the catalyst concentrations used in this work, catalyst concentration of 4% was the best for a biodiesel yield of 96.6%. Due to ester saponification under alkaline conditions imposed by the used catalyst, beyond this concentration no improvement in biodiesel yield was established. Among the molar ratios chosen in this work, higher molar ratios gave a higher biodiesel yield. A molar ratio of 8:1 gave the maximum biodiesel yield of nearly 91.5% when the catalyst concentration was 3%. In fact, a criticism to this investigation can be made on the ground that examining the effect of molar ratio on biodiesel yield should have been performed while using the best concentration of the used catalyst, 4% not 3%. Initially, increasing the temperature of transesterification reaction up to 70 °C was with a positive effect on biodiesel yield. Nevertheless, the effect of temperatures higher than 70 °C on biodiesel yield was otherwise, perhaps, due to methanol volatilization. Biodiesel yield increased with increasing the reaction time up to 1.5 hours. Afterwards, biodiesel yield started to collapse, due to side reactions of fatty acid methyl esters with glycerol. Also, separation of the used catalyst from the reaction medium, reusability and stable catalytic activity were reported [7].

Also, Li, et al. reported good results of using 1-butyl-3-methylimidazolium hydroxide (\OH), alkaline ionic liquid as a catalyst, to catalyze the synthesis of biodiesel via cornus wilsoniana fruit oil. High activity, stability, reusability for up to 6 times of use, minimum waste and no drop of the yield of methyl ester (biodiesel) with a molar ratio of 6:1 were observed [42]. Furthermore, soybean vegetable oil in addition to rapeseed and sunflower vegetable oils were used to synthesize biodiesel using an alkaline ionic liquid, 1-butyl-3-methylimidazolium imidazolide, as a catalyst. An optimum yield of 96.42% of methyl ester can be achieved provided that: catalyst dosage is 0.9%, reaction temperature is 60 °C, reaction time is 70 min using methanol as an alcohol. It was found that the used catalyst is highly active and can be reused several times with no declination in biodiesel yield which was about 95% [24].

However, in order to avoid the tricky recovery and limited reuse of such ionic liquids cited above as they are dissolved within the reaction medium, immobilization of some metal chlorides in some basic ionic liquids has been investigated. The basic ionic liquid triethylammonium chloroaluminate, [Et_3NH] Cl immobilizing $AlCl_3$ was used as a catalyst for the transesterification of soybean vegetable oil with methanol to synthesize biodiesel. In order to attain a 98.5% conversion, reaction duration was for nine hours, temperature was 70 °C and methanol: oil ratio was 12:1 with 70% mole fraction of $AlCl_3$ in the catalyst. The authors of this work claim the ease f the procedure, reduced catalyst cost and reusability, high yield as well as no saponification. Furthermore, they have compared the efficiency of this basic ionic liquid as a catalyst to that of two acidic traditional catalysts, sulfuric and phosphoric acids. The outcome of this comparison is that the former catalyst was advantageous over the latter two traditional ones with respect to cost and the environmental impact. Having said this; however, biodiesel contamination by aluminum residues arising from the immobilized $AlCl_3$ as well as probable release of HCl, due to instability of an ionic liquid, with aluminum 3 chloride, in an alcoholic solution (methanol in this case), may be consequential risk factors [43]. As a remedy to this issue accompanying immobilization of some metal anions in the structure of the ionic liquid, another scheme was proposed. This scheme utilizes an ionic liquid as a support for those readily available acidic/basic traditional catalysts, i.e., no metal anions are there. In this regard, Lapis and others have tested the performance of dilute H_2SO_4 and K_2CO_3 immobilizing three separate basic ionic liquids; namely: [BMI] [NTF_2], [BMI] [BF_4] and [BMI] [BF_6] for the transesterification of soybean vegetable oil again. A yield of 98%, high purity of the produced biodiesel (98%), ease of product separation and good reusability were all in place while using the first basic ionic liquid with 40 mol.% K_2CO_3 [44]. In another work, Liang, et al. proposed a highly efficient procedure for the synthesis of biodiesel from soybean oil using chloroaluminate ionic liquid, Et_3NH]Cl–$AlCl_3$(x($AlCl_3$), as a catalyst. Efficiency, low cost and reusability of the used catalyst, operational simplicity, high yield of 98.5% and no saponification are the key features of this procedure [17].

Also, in order to synthesize biodiesel, use of basic ionic liquid(s) for esterification of free fatty acids can be coupled with the use of KOH for transesterification of the esterified parent vegetable oil. Elsheikh, Y. has proposed a dual step catalyzed process to synthesize biodiesel from a citrullus colocynthis vegetable oil. In the first step, citrullus colocynthis vegetable oil was esterified by two ionic liquids, namely, 1-methyl-3-(4-sulfobutyl)-imidazolium hydrogensulfate (MSBIMHSO4) and pyrazolium 1-methyl-2-(4-sulfobutyl)-pyrazolium hydrogen sulfate (MSBPHSO4). The former ionic liquid demonstrated a higher free fatty acid esterification conversion, 96.7%, than the latter one. The esterification step was; then, followed by a transesterification step of the esterified citrullus colocynthis vegetable oil using KOH as a catalyst although at reaction conditions that are notably milder than those maintained at the first step of esterification reaction. A summary of reaction conditions for esterification and transesterification reactions is made in Table (1). Synthesized biodiesel was in accordance to the fuel ASTM requirements [45].

Table (1): A summary of reaction conditions for esterification and transesterification reactions [45].

Reaction condition	Esterification reaction	Transesterification reaction
Temperature, °C	130	60
Molar ratio	12:1	6.1
Agitation speed, rpm	600	600
Catalyst dose, wt%	3.8	1.0
Catalyst type	Two Basic Ionic liquids	KOH
Reaction duration, min.	120	50

IV. BRØNSTED ACIDIC IONIC LIQUIDS AS CATALYSTS IN BIODIESEL SYNTHESIS

Also, Brønsted acidic ionic liquids have been employed for esterification as well as transesterification reactions for biodiesel production. Such as an approach can ensure a good product recovery and prevent product contamination with free molecules of the used catalyst. Ghiaci and others have successfully synthesized biodiesel through esterification of a natural fatty acid (oleic acid) with methanol in the presence of a modified bentonite with 1-benzyl-1*H*-benzimidazole-based Brønsted acidic ionic liquid, MB3B (bentonite modified with 3,3′-(butane-1,6-diyl)bis(6-sulfo-1-(4-sulfobenzyl)-1*H*- benzimi dazolium) hydrogensulfate), as a catalyst. They demonstrated that modified bentonite is able to catalyze the esterification of oleic acid to its methyl ester. They examined the effect of catalyst dosage, reaction time, reaction temperature and the molar ratio on the esterification of oleic acid to its methyl ester. Their results indicate that modified bentonite is able to catalyze the esterification of oleic acid to its methyl ester (biodiesel) with a yield of more than 92%, provided that optimized esterification reaction conditions are maintained. Reported optimum esterification reaction conditions can be found elsewhere [19]. Esterification of oleic acid with methanol to biodiesel was also an aim of an investigation carried out by Wu and co-workers. They considered several consistent structure while different polymerization degree of polyether cation bi-functional temperature-sensitive amphiphilic acidic ionic liquids as catalysts for esterification. Among the ionic liquids they have considered, the ionic liquid, MPEG-350-ILs, was the best in terms of catalytic activity due to its strong Brønsted acidity and amphiphilicity. The used ionic liquid can be reused following a decantation separation of the produced biodiesel [46].

Moreover, Guo, et al. have examined the esterification of raw jatropha vegetable oil, that holds a high acid value of 13.8 mg KOH/g, to biodiesel using a Brønsted acidic ionic liquid, 1-butyl-3-methylimidazolium tosylate ([BMIm][CH_3SO_3], with and without metal chlorides, $FeCl_3$, although at the same temperature of 120 °C. The yield of biodiesel was only 12% compared to 99.7% when $FeCl_3$ was added to the used ionic liquid. The role of $FeCl_3$ is that it provides metal ions within the used ionic liquid granting Lewis acidic sites much of which can be provided by trivalent metallic ions than those of bivalent ions. Separation of reaction mixture from the synthesized biodiesel was easily performed. Reusability of the used separated ionic liquid was again demonstrated [47]. Also, Zhang, et al. have used the Brønsted acidic ionic liquid *N*-methyl-2-pyrrolidonium methyl sulfonate ([NMP][CH_3SO_3]) as a catalyst to synthesize biodiesel with low molecular weight alcohols as substrates. The conversion of fatty acid alkyl esters could reach between 93.6% and 95.3%. Despite several uses of the used ionic liquid catalyst, the used catalyst demonstrated a high catalytic activity and required no additional organic solvent(s), provided that water is removed and the reaction conditions are moderate [48].

In an investigation by Wu and co-workers, the transesterification of cottonseed oil using methanol as an alcohol was reported. They used the Brønsted acidic ionic liquid, 1-(4-sulfouric acid)- butylpyridinium hydrogen sulfate ([BSPy] [HSO_4]). It contains the cations of 1-n-butyl-3methylimidazolium or 1-butylpyridinum. In order to attain a 92% yield, reaction duration was for five hours, temperature was 170 °C and methanol: oil ratio was 12:1. The authors of this investigation have compared the efficiency of this Brønsted acidic ionic liquid as a catalyst to that of a concentrated sulfuric acid. They have found that a comparable biodiesel yield was obtained out of both systems they have compared since it was 65% out of the former reaction system and 69% out of the reaction system. Hence, they suggested that the former reaction system is the most suitable catalytic system for this transesterification reaction taking into account the environmental benefits of the ionic liquids in general, as indicated earlier, in comparison to the harmful concentrated sulfuric acid [49]. Brønsted acidic ionic liquids could also be efficiently while environmentally friendly used for the purpose of biodiesel synthesis based on low-cost feedstocks, waste oils, where the content of free fatty acids is literally high. Han et al. have used this just aforementioned Brønsted acidic ionic liquid to transesterify a feedstock oil of such a category. In this work, it was noted that a high temperature of 170 °C and four hours as a reaction duration were required to achieve a biodiesel yield of 93.5%. It was also noted that the reusability of the ionic liquid used was maintained for nine uses without a significant declination in biodiesel yield [28].

V. CONCLUSIONS

It seems that in-house-synthesis of different ionic liquids as catalysts for biodiesel production via different oil feedstocks is increasing. Promising results in terms of biodiesel yield, reasonable catalyst reusability, minimum waste as well as catalytic activity, in moderate reaction conditions, have been reported. In order to enhance the performance of a basic ionic liquid as a catalyst in biodiesel synthesis, with respect to reusability, high yield and minimal side reactions (sabonification), immobilization of some metal chlorides in this basic ionic liquid can be beneficial, although biodiesel contamination is envisaged. Enhancement of the performance of a basic ionic liquid as a catalyst can also be achieved via coupling it with an acidic or a basic non-ionic liquid catalyst. In case the feedstock used to synthesize biodiesel *does* require to undergo two consecutive esterification and transesterification reactions, a basic ionic liquid is usually employed as a catalyst for the first reaction and that a traditional non-ionic liquid catalyst is chosen to catalyze the second reaction, respectively. Finally, contamination of the produced biodiesel; in particular, can be avoided if a Brønsted acidic ionic liquid has been used as a catalyst instead of a non- Brønsted acidic ionic liquid. Furthermore, it has been observed that an improved reusability can be associated with the use of Brønsted acidic ionic liquids. Use of Brønsted acidic ionic liquids as catalysts in biodiesel synthesis is always desirable in case the content of free fatty acids in the used feedstock oil is high.

REFERENCES

[1] Abdelmalik M. Shakorfow and Abdulaziz H. Mohamed. Immobilized Enzymatic Catalysts for Biodiesel Production: A Review. International Science and Technology Journal, Vol. 21, April 2020.

[2] Jing-Juan Qi, Jin-Qing Lin and Hong-Quan Fu. One-step production of biodiesel from waste cooking oil catalysed by SO_3H-functionalized quaternary ammonium ionic liquid. CURRENT SCIENCE, VOL. 110, No. 11, 10 June 2016.

[3] Plechkova, N. V., Seddon, K. R., Applications of ionic liquids in the chemical industry. Chemical Society Reviews, 37, No. 1, 123-150 (2008).

[4] L. Andreani and J. D. Rocha. USE OF IONIC LIQUIDS IN BIODIESEL PRODUCTION: A REVIEW. Brazilian Journal of Chemical Engineering. Vol. 29, No. 01, pp. 1 - 13, January - March, 2012. ISSN 0104-6632.

[5] Kubisa, P., Ionic liquids as solvents for polymerization processes – Progress and challenges. Progress in Polymer Science, 34, No. 12, 1333-1347 (2009).

[6] Anderson, J. L., Armstrong, D. W., Wei, G. -T., Ionic liquids in analytical chemistry. Analytical Chemistry, 78, No. 9, 2892-2902 (2006).

[7] Qinggong Ren, Tongmei Zuo, Jingjing Pan, Changle Chen and Weimin Li . Preparation of Biodiesel from Soybean Catalyzed by Basic Ionic Liquids [Hnmm]OH. Materials 2014, 7, 8012-8023; doi:10.3390/ma7128012. ISSN 1996-1944.

[8] Forbes, et al., 2006 Forbes, D. C., Law, A. M., Morrison, D. W., The Knoevenagel reaction: analysis and recycling of the ionic liquid medium. Tetrahedron Letters, 47, No. 11, 1699-1703 (2006).

[9] Li, E., and Rudolph, V. Transesterification of vegetable oil to biodiesel over MgO-functionalized mesoporous catalysts. Energy & Fuels 2008;22:145-149.

[10] Seddon, K.R. Ionic liquids for clean technology. J. Chem. Technol. Biotechnlol. 1997, 68, 351–356.

[11] Judeh, Z.M.A.; Shen, H.-Y.; Chi, B.C.; Feng, L.-C.; Selvasothi, S. A facile and efficient nucleophilic displacement reaction at room temperature in ionic liquids. Tetrahedron Lett. 2002, 43, 9381–9384.

[12] Claudio, A.F.M.; Ferreira, A.M.; Shahriari, S.; Freire, M.G.; Coutinho, J.A.P. Critical assessment of the formation of ionic-liquid-based aqueous two-phase systems in acidic media. J. Phys. Chem. B 2011, 115, 11145–11153.

[13] L. Andreani and J. D. Rocha. USE OF IONIC LIQUIDS IN BIODIESEL PRODUCTION: A REVIEW. Brazilian Journal of Chemical Engineering. Vol. 29, No. 01, pp. 1 - 13, January - March, 2012. ISSN 0104-6632.

[14] Fauzi, A.H.M.; Amin, N.A.S. An overview of ionic liquids as solvents in biodiesel synthesis. Renew. Sust. Energ. Rev. 2012, 16, 5770–5786.

[15] Rita Skoda-Földes. The Use of Supported Acidic Ionic Liquids in Organic Synthesis. Molecules 2014, 19, 8840-8884.

[16] B. Gilbert, H. Olivier-Bourbigou and F. Favre. Chloroaluminate Ionic Liquids: from their Structural Properties to their Applications in Process Intensification. Oil & Gas Science and Technology – Rev. IFP, Vol. 62 (2007), No. 6, pp. 745-759 Copyright © 2007, Institut français du pétrole DOI: 10.2516/ogst:2007068.

[17] Liang, X. Z., Gong, G. Z., Wu, H. H. and Yang, J. G., Highly efficient procedure for the synthesis of biodiesel from soybean oil using chloroaluminate ionic liquid as catalyst. Fuel, 2009, 88, 613–616.

[18] Fang, D., Yang, J. M. and Jiao, C. M., Dicationic ionic liquids as environmentally benign catalysts for biodiesel synthesis. ACS Catal., 2010, 1, 42–47.

[19] Ghiaci, M.; Aghabarari, B.; Gil, A. Production of biodiesel by esterification of natural fatty acids over modified organoclay catalysts. Fuel 2011, 90, 3382–3389.

[20] Cao, F.; Chen, Y.; Zhai, F.; Li, J.; Wang, J.; Wang, X.; Wang, S.; Zhu, W., (2008). Biodiesel production from high acid value waste frying oil catalyzed by superacid heteropolyacid. Biotech. Bioengin., 101 (1), 93-100

[21] Liang, X. Z., Xiao, H. Q. and Qi, C. Z., Efficient procedure for biodiesel synthesis from waste oils using novel solid acidic ionic liquid polymer as catalysts. Fuel Processing Technology. Volume 110, June 2013, Pages 109-113.

[22] Hualiang An, Lijuan Kang, Wei Gao, Xinqiang Zhao, Yanji Wang. Synthesis and Characterization of Novel Brønsted-Lewis Acidic Ionic Liquids. Green and Sustainable Chemistry, 2013, 3, 32-37 doi:10.4236/gsc.2013.32A005 Published Online May 2013 (http://www.scirp.org/journal/gsc).
[23] Li, X.F.; Wang, Y.; Zhao, H.; Li, C.H. Synthesis of a new basic ionic liquid and its application in catalyzing preparation of biodiesel. Petroleum Prog. Sect. 2012, 28, 201 206.
[24] Luo, H., Fan, W. Y., Li, Y. and Nan, G. Z., Biodiesel production using alkaline ionic liquid and adopted as lubricity additive for low-sulfur diesel fuel. Bioresour. Technol., 2013, 140, 337–341.
[25] Jin-hua LIANG. Xiao-qian REN, Jin-tang WANG, ming JINAG and Zheng-jinag LI. Preparation of biodiesel by transesterification from cottonseed oil using the basic dication ionic liquids as catalysts. Journal of Fuel Chemistry and Technology Volume 38, Issue 3, June 2010a, pages 275-280.
[26] Khashayar Ghandi. A Review of Ionic Liquids, Their Limits and Applications. Green and Sustainable Chemistry, 2014, 4, 44-53 Published Online February 2014 (http://www.scirp.org/journal/gsc) http://dx.doi.org/10.4236/gsc.2014.41008.
[27] S. Ahrens, A. Peritz and T. Strassner, “Tunable Aryl Alkyl Ionic Liquids (TAAILs): The Next Generation of Ionic Liquids. Angewandte Chemie International Edition, Vol. 48, No. 42, 2009, pp. 7908-7910.
[28] Minghan Han, Wulang Yi, Qin Wu, Ying Liu, Yongchun Hong and Dezheng Wang. Preparation of biodiesel from waste oils catalyzed by a Brønsted acidic ionic liquid.Bioresource Technology. Volume 100, Issue 7, April 2009, Pages 2308-2310.
[29] Ji Li, Xiao Peng, Meng Luo, Chun-Jian Zhao, Cheng-Bo Gu, Yuan-Gang Zu and Yu Jie Fu. Biodiesel production from Camptotheca acuminate seed oil catalyzed by novel Brönsted–Lewis acidic ionic liquid. Appl. Energy, 2014, 115, issue C, 438–444.
[30] Liang, X. Z. and Yang, J. G., Synthesis of a novel multi SO_3H functionalized ionic liquid and its catalytic activities for biodiesel synthesis. Green Chem., 2010b, 12, 201–204.
[31] Earle, M. J., Seddon, K. R., Ionic liquids. Green solvents for the future. Pure and Applied Chemistry, 72, No. 7, 1391-1398 (2000).
[32] Welton, T., Ionic liquids in catalysis. Coordination Chemistry Reviews, 248, No. 21-24, 2459-2477 (2004).
[33] Greaves, T. L. and Drummond, C. J., Protic ionic liquids: properties and applications. Chem. Rev., 2008, 108, 206–237.
[34] Welton, T., Room-temperature ionic liquids. Solvents for synthesis and catalysis. Chemical Reviews, 99, No. 9, 2071-2083 (1999).
[35] N. Meine, F. Benedito and R. Rinaldi, “Thermal Stability of Ionic Liquids Assessed by Potentiometric Titration,” Green Chemistry, Vol. 12, No. 10, 2010, pp. 1711-1714.
[36] Roosen, C., Muller, P., Greiner, L., Ionic liquids in biotechnology: applications and perspectives for biotransformations. Applied Microbiology and Biotechnology, 81, No. 4, 607-614 (2008).
[37] Cole, A. C. et al., Novel Brønsted acidic ionic liquids and their use as dual solvent–catalysts. J. Am. Chem. Soc., 2002, 124, 5962–5963.
[38] Brandt, A., Grasvik, J., Hallett, J. P. and Welton, T., Deconstruction of lignocellulosic biomass with ionic liquids. Green Chem., 2013, 15, 550–583.
[39] John S. Wilkes, Joseph A. Levisky, Robert A. Wilson, and Charles L. Hussey. Dialkylimidazolium chloroaluminate melts: a new class of room-temperature ionic liquids for electrochemistry, spectroscopy and synthesis. Inorg. Chem., 1982, 21 (3), pp 1263–1264 DOI: 10.1021/ic00133a078.
[40] John D. Holbrey, W. Matthew Reichert, Richard P. Swatloski, Grant A. Broker, William R. Pitner, Kenneth R. Seddon and Robin D. Rogers. Efficient, halide free synthesis of new, low cost ionic liquids: 1,3-dialkylimidazolium salts containing methyl- and ethyl-sulfate anions. 2002. Journal of Green Cemistry, Issue 5.
[41] Claúdia C**. Cassol, Günter Ebeling, Bauer** Ferrera and Jairton Dupont. A Simple and Practical Method for the Preparation and Purity Determination of Halide-Free Imidazolium Ionic Liquids. 2006. Journal of Advanced Synthesis & Catalysis. Volume 348, Issue 1-2 January 2006 Pages 243–248.
[42] Li, C.Z.; Zhang, A.H.; Xiao, Z.H.; Jiang, L.J.; Li, P.W. Preparation of biodiesel from cornus wilsoniana fruit oil with basic ionic liquids as catalyst. J. Cent. South. Univ. For. Technol. 2011, 31, 38–43.
[43] Earle, M. J., Plechkova, N. V., Seddon, K. R., Green synthesis of biodiesel using ionic liquids. Pure and Applied Chemistry, 81, No. 11,2045-2057(2009).
[44] Gamba, M., Lapis, A. A. M., Dupont, J., Supported ionic liquid enzymatic catalysis for the production of biodiesel. Advanced Synthesis and Catalysis, 350, No. 1, 160 164 (2008).
[45] Elsheikh, Y.A. Preparation of Citrullus colocynthis biodiesel via dual-step catalyzed process using functionalized imidazolium and pyrazolium ionic liquids for esterification step. Ind. Crops Prod. 2013, 49, 822–829.
[46] Qin Wu, Hualin Wan, Hansheng Li, Haoran Song and Tonghua Chu. Bifunctional temperature-sensitive amphiphilic acidic ionic liquids for preparation of biodiesel. Catalysis Today. Volume 200, 1 February 2013, Pages 74-79.
[47] Feng Guo, 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.Bioresource Technology. Volume 102, Issue 11, June 2011, Pages 6469-6472
[48] Zhang, L.; Xian, M.; He, Y.C.; Li, L.Z.; Yang, J.M.; Yu, S.T.; Xu, X. A Brønsted acidic ionic liquid as an efficient and environmentally benign catalyst for biodiesel synthesis from free fatty acids and alcohols. Bioresour. Technol. 2009, 100, 4368 4373.
[49] Wu, P.; Yang, Y.; Colucci, J. A.; Grulke, E. A., (2007). Effect of ultrasonication on droplet size in biodiesel mixtures. J. Am. Oil Chem. Soc., 84 (9), 877-884.