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Conversion of Oil Palm Biomass to Ethyl Levulinate via Ionic Liquids

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Biomass is a potential renewable feedstock that can be used as a replacement for fossil resources. A variety of high end chemicals have been produced from biomass including ethyl levulinate, which is a viable biofuel for diesel engines. In this study, the capability of three types of imidazolium based ionic liquids (ILs) catalysts, i.e., 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO_4]) and 1-methylimidazolium hydrogen sulfate ([HMIM][HSO_4]) to convert oil palm empty fruit bunch (OPEFB) and oil palm mesocarp fiber (OPMF) biomass to ethyl levulinate were compared. The procedure entailed a sequential reaction of depolymerisation of biomass at 160 °C for 3 hours, followed by an esterification at 90 °C for 12 h in excess ethanol, with ILs-to-biomass ratio of 5 : 1 by weight and 20 wt% water. It was demonstrated that only the last two acidic [HSO_4]$^-$ counteranion based ILs are able to convert the biomass to ethyl levulinate. Mono-alkylated ILs, [HMIM][HSO_4], consistently gave a higher efficiency than multi-alkylated ILs, [BMIM][HSO_4], for both OPEFB and OPMF biomass conversions, with ethyl levulinate yields of 11.61 % and 13.54 %, and the process efficiencies of 39.26 % and 50.79 %. OPMF appears to be a slightly more efficient feedstock in ethyl levulinate production than OPEFB. This indicates the performance of ILs was dependent upon the character of their cation side chain, seeing that both ILs used have the same acidic [HSO_4]$^-$ counteranion. The experimental results suggested that [HMIM][HSO_4] has the potential to be used in ethyl levulinate production from sustainable biomass feedstocks under mild operating conditions.

1. Introduction

The continuous rise in energy requirements due to the increase of population and rapid industrial growth has been a global concern for centuries. Although a shift to shale gas and away from other fossil fuels is increasingly plausible, the adverse environmental impact associated to these energies remains unresolved. Extensive researches are being carried out to search alternative resources which are cleaner, inexpensive and renewable. Conversion of biomass to biofuel (Elumalai et al., 2016) is a particularly attractive approach, as it transforms waste into useful product. Malaysia has a rich oil palm industry which generates tremendous amount of biomass. Oil palm empty fruit bunch (OPEFB) and oil palm mesocarp fiber (OPMF) contribute a significant amount of 22 % and 13.5 % of the mass of each fruit bunch (FFB) (Aditiya et al., 2016). Cellulose is the main composition of oil palm biomass and serves the major substrate for the catalytic conversion to levulinic acid (Rackemann and Doherty, 2011). Levulinic acid can be further converted to biofuel, i.e., ethyl levulinate, via the esterification with ethanol, as illustrated in Figure 1. Ethyl levulinate contains ~14 mol% oxygen, having similar properties to the biodiesel fatty acid ethyl esters (FAEEs). It provides a cleaner burning with high lubricity, flashpoint stability, reduced sulfur content and improved viscosity in regular diesel engines. It also serves as viable bio-derived petroleum diesel fuel oxygenate additive (Windom et al., 2011).

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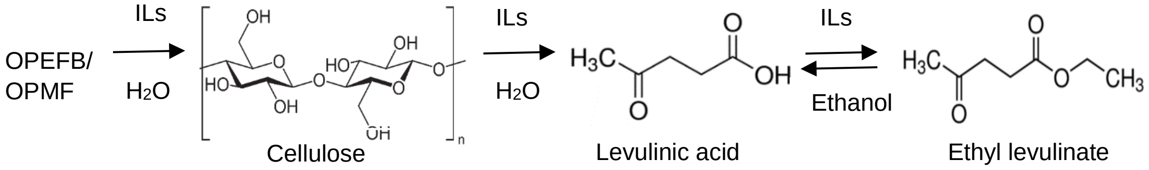

Figure 1: Reaction scheme of ethyl levulinate production catalysed by ILs.

The conversion of ethyl levulinate from lignocellulosic biomass can be enhanced by the presence of homogenous or heterogenous acid catalysts. Heterogenous catalysts are naturally unstable due to its rapid deactivation and homogenous catalysts encounter corrosion issues. The drawbacks drive researchers to seek for alternative catalysts such as ionic liquids (ILs). ILs are new generation catalysts which are green and could serve as dual catalyst-solvent for biomass conversion by primarily disrupting the hydrogen bonds between molecules. ILs exhibit favourable properties that ease the production, such as negligible vapour pressure, high thermal and chemical stabilities and large operational temperature range (Reddy et al., 2015).

Bronsted acidic ILs (BAILs) have been widely used as viable catalysts in the production of levulinate esters from lignocellulosic biomass including oil palm biomass (Ramli and Amin, 2016) and its processed materials such as cellulose (Amarasekara and Wiredu, 2014). Among these, the application of BAILs, which is composed of hydrogen sulfate $[HSO_4]^-$ counteranion based sulfonic acid functionalised ILs (SFILs) was reported to give 12 - 30 % levulinate esters yields. However, BAILs which bearing an alkyl sulfonic acid functionalised group are extremely acidic and can cause serious corrosion in equipment (Tao et al., 2011). The present study focuses on using noncorrosive ILs for conversions of biomass. Three types of ILs, i.e., 1-butyl-3-methylimidazolium chloride [BMIM][Cl], 1-butyl-3-methylimidazolium hydrogen sulfate $[BMIM][HSO_4]$ and 1-methylimidazolium hydrogen sulfate $[HMIM][HSO_4]$ were selected to convert oil palm biomass to ethyl levulinate. Chloride $[Cl]^-$ based ILs is neutral and acted as a control, whereas, the other two are BAILs with sole acid site (i.e., $[HSO_4]^-$ counteranion based ILs) but differ in alkyl chain length. Besides being environmental friendly and noncorrosive (Tao et al., 2011), the acidic nature of $[HSO_4]^-$ would expectedly favour the production of levulinate esters. Mono-alkylated imidazolium (1-alkylimidazolium, $[HC_nim]^+$) based ILs have been reported to be easily synthesise and has a lower cost (Brandt et al., 2011) than multi-alkylated imidazolium based ILs. To the best of our knowledge, $[BMIM][HSO_4]$ and $[HMIM][HSO_4]$ have never been applied in the production of levulinate esters. The purpose of present study was to determine the efficiency of production of ethyl levulinate from OPEFB and OPMF via these two ILs in one-pot reaction system.

2. Materials and Methods

2.1 Materials

OPEFB and OPMF samples were collected at Seri Ulu Langat Palm Oil Mill, Dengkil, Selangor. The samples were dried in an oven at 105 °C for 24 h and ground with a high-speed rotor beater mill to give particle size ranged 0.4 to 1 mm. The samples were then stored in desiccator at room temperature until further use. The ILs, [BMIM][Cl], $[BMIM][HSO_4]$ and $[HMIM][HSO_4]$ were purchased from Sigma-Aldrich, USA, with a purity of ≥ 95 %. Ethyl levulinate (99 %) and other chemicals needed for biomass characterisation studies were also purchased from Sigma-Aldrich, USA. Analytical graded ethanol and ethyl acetate (RCI Labscan) were supplied by EOS Scientific Limited (Selangor, Malaysia).

2.2 Characterisation of OPEFB and OPMF compositions

The compositions of OPEFB and OPMF were determined by thermal gravimetric analysis (TGA) using a Mettler Toledo TGA/DSC1. The biomass samples were heated in a platinum cell with a scanning rate of 10 °C/min, from 30 to 700 °C, under a nitrogen flow rate of 20 mL min^{-1}. Holocellulose, which is the sum of hemicellulose and cellulose, was determined according to the method reported by Teramoto et al. (2009). Briefly, the biomass sample was treated with deionised water containing acetic acid and sodium chlorite ($NaClO_2$) for 1 h at 75 °C. Then, 0.04 mL of acetic acid and 0.2 g of $NaClO_2$ were added to the mixture every 1 h for 3 h. The residue was filtered, washed, and then dried overnight to a constant weight. The holocellulose content was then determined from the solid residues obtained. The cellulose content was determined by shaking 0.2 g of previously obtained holocellulose in a flask with 5 mL of 17.5 % NaOH aqueous solution at 30 °C for 40 min in a water bath shaker. Next, 5 mL of deionised water was added to the mixture with continued shaking for 5 min before the mixture was filtered. The remaining residue was then washed with 8 mL of 10 % acetic acid and boiling water. Finally, the cellulose residue was dried overnight and weighed. The hemicellulose content was calculated as the difference between holocellulose and cellulose contents.

2.3 Two-step sequential reaction system in one-pot: Depolymerisation and esterification reactions

ILs-catalysed conversion of oil palm biomass to ethyl levulinate was conducted in a two-step sequential reaction i.e., depolymerisation, followed by esterification, in one pot. For depolymerisation reaction, the biomass, ILs catalyst and 20 wt% water were first mixed in the pressure vessel. The solution was then heated at 160 °C for 3 h with continuous stirring. Upon the completion, the pressure vessel was quenched immediately with cold water to cease the reaction. The entire solution was then transferred into a single-neck round bottom flask for the subsequent esterification reaction. The esterification reaction was performed under reflux at 90 °C in ethanol medium. At the end of the reaction, the solution was quenched immediately in cold water to room temperature. The resulting product was mixed with ethyl acetate for three times in the ratio of 1 : 1 by volume and transferred into centrifuge tubes. Two layer solution was formed by centrifuging at 2,000 rpm for 5 min: organic phase (upper layer) and aqueous phase (bottom layer). The organic liquid fractions obtained from the upper layer were then evaporated to dryness at 50 °C for 30 min using a rotary evaporator (Heidolph, Germany). The content was then reconstituted into 2 mL ethyl acetate for GC/MS analysis.

2.3 Product analysis

The ethyl levulinate compound was determined by using GC (Perkin Elmer Clarus 680) equipped with a MS detector and fused silica capillary column (HP-FFAP, 30 m length x 0.32 mm diameter x 0.25 µm film thickness). The autosampler injection volume was 1.0 µl in the split mode ratio of 50 : 1. The injection port was maintained at 240 °C, while the operating temperature for the oven was initially set at 90 °C for 3 min, then gradually increased to 230 °C at a heating rate of 10 °C/min, and held at the final temperature for 10 min. A solvent delay of 2 min was applied. Helium was used as carrier gas at a constant flow of 1.0 mL/min. The ethyl levulinate compound was identified with the GC/MS library (NIST MS search library) and were further confirmed with injection of standard. In order to quantify the compound of interest, 5-points standard ethyl levulinate calibration curve was obtained by injecting standard solutions to calculate concentrations of the compound. The actual ethyl levulinate yield, theoretical ethyl levulinate yield and process efficiency were calculated as in Eq(1) - (3):

$$\text{Ethyl levulinate yield (\%)} = \frac{\text{Amount of ethyl levulinate}}{\text{Initial biomass loading}} \text{ x } 100\ \% \tag{1}$$

$$\text{Theoretical ethyl levulinate yield (\%)} = \frac{\text{Cellulose content in biomass x 0.89}}{\text{Initial biomass loading}} \text{ x } 100\ \% \tag{2}$$

where $\frac{\text{Molecular weight of ethyl levulinate}}{\text{Molecular weight of cellulose}} = \frac{144}{162} = 0.89$

$$\text{Process efficiency (\%)} = \frac{\text{Ethyl levulinate yield}}{\text{Theoretical ethyl levulinate yield}} \text{ x } 100\ \% \tag{3}$$

where process efficiency refers to the efficiency of the biomass conversion to ethyl levulinate, based on the cellulose content.

3. Results and Discussions

3.1 Characterisation of OPEFB and OPMF compositions

Figure 2 illustrates the thermal gravimetric analysis (TGA) curves for both samples. Three distinct stages of weight losses for both samples were observed. Initial weight loss was found between 30 and 100 °C, which could be regarded as the evaporation of residual water in the biomass samples. The second stage of weight loss at a temperature range of 200 – 360 °C indicates the decomposition of holocellulose (i.e., cellulose and hemicellulose). The weight losses of last stage at 360 - 650 °C represents the degradation of lignin. The remaining amount is known as residue or commonly defined as ash content.

Table 1 summarises the composition of OPEFB and OPMF biomass samples. The cellulose and hemicellulose contents in OPEFB and OPMF were analysed according to the method reported by Teramoto et al. (2009). The percentages of holocellulose content from both samples were adopted from TGA analysis. OPEFB was found containing higher cellulose content and lower lignin content than OPMF.

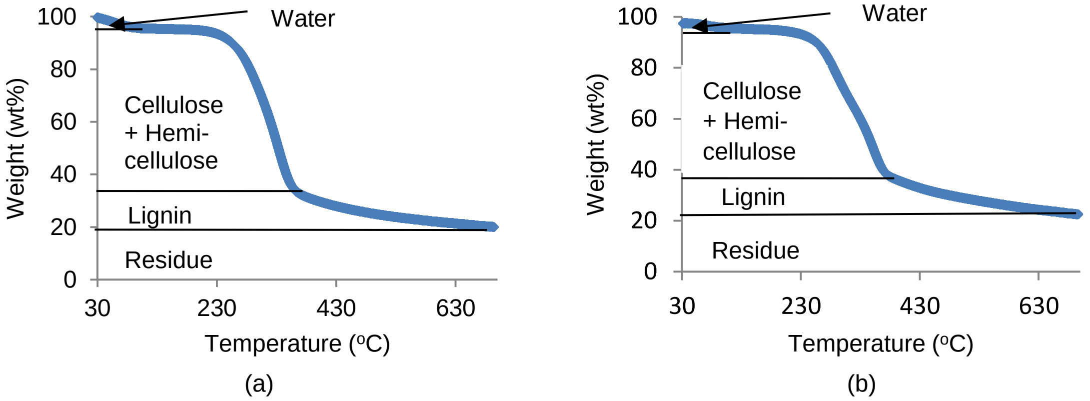

Figure 2: TGA analysis of oil palm biomass (a) OPEFB and (b) OPMF.

Table 1: Composition of oil palm biomass

Components	Composition (wt%)	
	OPEFB	OPMF
Moisture content	4.36	4.31
Holocellulose	58.25	56.28
Cellulose	33.23	29.96
Hemicellulose	25.02	26.32
Lignin	18.52	16.29
Residue	18.87	23.12

3.2 Conversion of oil palm biomass to ethyl levulinate

A two-step sequential reaction system in one-pot (i.e., depolymerisation, followed by esterification) was developed to synthesise ethyl levulinate. There was no ethyl levulinate yield detected in both OPEFB and OPMF conversions via the neutral based ILs, [BMIM][Cl]. This was presumably due to the absence of the acidity nature in the ILs, as acidity was one of the main factor for the catalytic conversion to be possible. Jiang et al. (2011) have reported [BMIM][Cl] is not active in the production of precursors of levulinic acid such as reducing sugars and 5-hydroxymethylfurfural (5-HMF) due to its neutral based properties, and thus unable to produce ethyl levulinate. Ya'aini and Amin (2013) claimed that neutral based ILs favour the biomass dissolution but perhaps not the subsequent organic synthesis reactions of ethyl levulinate. It can be concluded that this neutral based ILs, [BMIM][Cl], was incapable to convert oil palm biomass to ethyl levulinate. The present study also shows that the longer alkyl chain based acidic ILs, [BMIM][HSO_4], gave very low yields of ethyl levulinate (<2.5 %) in both OPEFB and OPMF conversions (Figure 3).

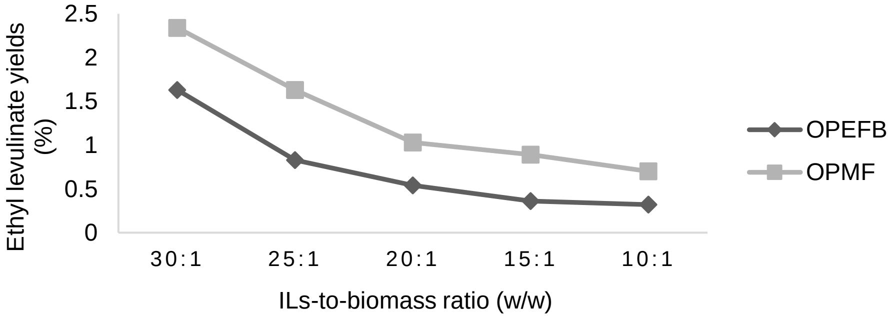

Figure 3: Ethyl levulinate yields in OPEFB and OPMF conversions via [BMIM][HSO_4] at various ILs-to-biomass ratio. (Depolymerisation: 160 °C, 3 h; Esterification: 90 °C, 6 h)

A high ILs-to-biomass ratio of 30 : 1 by weight only produced 1.63 % and 2.34 % ethyl levulinate yields in OPEFB and OPMF conversions. Ethyl levulinate yields decreased as ILs-to-biomass ratio decreased. Higher biomass loading may have increased the chances of reactive compounds colliding with each other, causing cross polymerisation that produces undesired products. Low ethyl levulinate yields obtained from present study, indicates that [BMIM][HSO_4] was unsuitable to catalyse the conversion of oil palm biomass to ethyl levulinate. Mono-alkylated based ILs, [HMIM][HSO_4], being solely alkyl chain, gave better conversions for both OPEFB and OPMF (Figure 4).

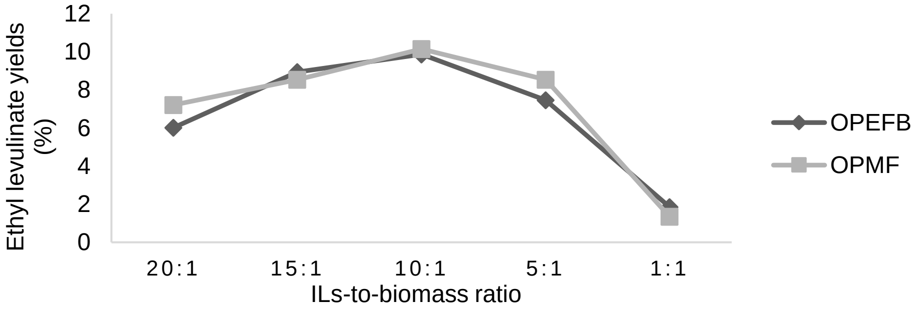

Figure 4: Ethyl levulinate yields in OPEFB and OPMF conversions via [HMIM][HSO_4] at various ILs-to-biomass ratio. (Depolymerisation: 160 °C, 3 h; Esterification: 90 °C, 6 h)

Ethyl levulinate yields at ILs-to-biomass ratio of 10 : 1 by weight were 9.87 % and 10.15 % in OPEFB and OPMF conversions. A gradual decline of ethyl levulinate yield was observed in increasing ILs-to-biomass ratio, indicating excess ILs loading in the reaction system could cause cross polymerisation that lead to undesired by-reactions. The reduced ILs-to-biomass ratio gradually decreased the ethyl levuliante yields, possibly due to insufficient catalyst for the excess biomass loadings. These results are in agreement with Naydenov et al. (2009) who reported that the increase of alkyl chain length of cation in [BMIM][HSO_4] gave lower conversion. Better solubility of ethyl levulinate in longer alkyl chain length based ILs in the catalytic phase, could have promoted the undesirable reverse reaction of esterification (Figure 1) and hence resulted in lower biomass conversions, compared to mono-alkylated based ILs, [HMIM][HSO_4]. It is essential to keep ILs at the minimum dosage of 5 : 1 by weight in the bulk production, to minimise the production cost. Further investigation was conducted on prolonged esterification time up to 24 h while maintaining this ILs-to-biomass ratio at 5 : 1 by weight (Figure 5).

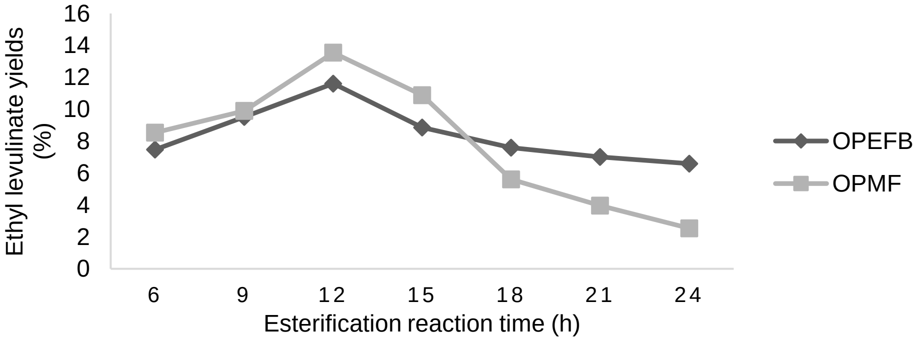

Figure 5: Ethyl levulinate yields in OPEFB and OPMF conversions via [HMIM][HSO_4] with various esterification reaction times. (Depolymerisation: 160 °C, 3 h; Esterification: 90 °C)

The increase of esterification reaction time from 6 to 12 h enhanced the ethyl levulinate yields gradually for both OPEFB and OPMF conversions. This confirms that prolonged esterification reaction time was essential for a sufficient turnover change synthesis. Excess esterification reaction time to more than 12 h caused a fall in ethyl levulinate yields in both OPEFB and OPMF conversions. This was presumably due to the partial hydrolysis of ethyl levulinate. As esterification is a reversible reaction, the hydrolysis rate of ethyl levulinate increases with reaction time, causing a reduction of ethyl levulinate yield. There are formations of by-products such as FAEEs in the biomass conversion alongside with the ethyl levulinate production. The highest ethyl levulinate yields in both OPEFB and OPMF conversions were 11.61 % and 13.54 %, observed at 12 h esterification reaction time. The process efficiencies of OPEFB and OPMF conversions were 39.26 % and 50.79 %. OPMF is a more efficient raw material for the conversion, giving a slight higher ethyl levulinate yields than OPEFB, although the former has a slight less cellulose content. This was presumably due to OPMF has a lower lignin content compared to OPEFB, as lignin is an amorphous polymer that acts as a “glue” binding hemicellulose and cellulose by ester linkages and hydrogen bonds (da Costa Lopes et al., 2013). These molecular interactions increase the recalcitrance of materials against hydrolysis and depress the function of ILs on biomass.

4. Conclusions

Mono-alkylated acidic ILs, [HMIM][HSO_4], efficiently catalysed the one-pot production of ethyl levulinate from oil palm biomass. Under the operating conditions studied, the one-pot reaction was best conducted in two-step sequential reaction system at 160 °C for 3 h in depolymerisation reaction, followed by 90 °C for 12 h in esterification reaction, with ILs-to-biomass ratio of 5:1 by weight in 20 wt% water. In OPEFB and OPMF conversions, 11.61 % and 13.54 % of ethyl levulinate yields were achieved, with the process efficiencies of 39.26 % and 50.79 %. OPMF appears to be a slightly more efficient feedstock in ethyl levulinate production than OPEFB. In addition of being noncorrosive and poses lower environmental impact, the ILs used, [HMIM][HSO_4], has shown to be a promising catalyst in the conversion of oil palm biomass to ethyl levulinate. The study suggests the use of lignocellulosic biomass to generate a bio-based chemical, i.e., ethyl levulinate, in a greener perspective. Future study will focus on the process optimisation and recyclability of catalyst in the proposed technique.

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References

Aditiya H.B., Chong W.T., Mahlia T.M.I., Sebayang A.H., Berawi M.A., Nur H., 2016, Second generation bioethanol potential from selected Malaysia’s biodiversity biomasses: A review, Waste Management 47, 46-61.

Amarasekara A.S., Wiredu B., 2014, Acidic ionic liquid catalyzed one-pot conversion of cellulose to ethyl levulinate and levulinic acid in ethanol-water solvent system, BioEnergy Research 7, 1237-1243.

Brandt A., Ray M.J., To T.Q., Leak D.J., Murphy R.J., Welton T., 2011, Ionic liquid pretreatment of lignocellulosic biomass with ionic liquid-water mixtures, Green Chemistry 13, 2489-2499.

da Costa Lopes A.M., Joao K.G., Morais, A.R.C., Lukasik, E.B., Lukasik, R.B., 2013, Ionic liquids as a tool for lignocellulosic biomass fractionation, Sustainable Chemical Processes 1 (3), 1-31.

Elumalai S., Agarwal B., Runge T.M., Sangwan R.S., 2016, Integrated two-stage chemically processing of rice straw cellulose to butyl levulinate, Carbohydrate Polymers 150, 286-298.

Jiang F., Zhu Q., Ma D., Liu X., Han X., 2011, Direct conversion and NMR observation of cellulose to glucose and 5-hydroxymehtylfurfural (HMF) catalyzed by the acidic ionic liqudis, Journal of Molecular Catalysis A: Chemical 334, 8-12.

Naydenov D., Hasse H., Maurer G., Bart H.-J., 2009, Esterification in ionic liquids with 1-alkyl-3-methylimidazolium cation and hydrogen sulfate anion: Conversion and phase equilibrium, The Open Chemical Engineering Journal 3, 17-26.

Rackemann D.W., Doherty W.O., 2011, The conversion of lignocellulosics to levulinic acid, Biofuels, Bioproducts and Biorefining 5 (2), 198-214.

Ramli N.A.S., Amin N.A.S., 2016, Optimization of biomass conversion to levulinic acid in acidic ionic liquid and upgrading of levulinic acid to ethyl levulinate, BioEnergy Research, 1-14.

Reddy P.N., Padmaja P., Reddy B.V.S., Rambabu G., 2015, Ionic liquid/water mixture promoted organic transformations, RSC Advances 5, 51035-51054.

Tao D.-J., Lu X.-M., Lu J.-F., Huang K., Zhou Z., Wu Y.-T., 2011, Noncorrosive ionic liquids composed of [HSO_4] as esterification catalysts, Chemical Engineering Journal 171, 1333-1339.

Teramoto Y., Lee S.-H., Endo T., 2009, Cost reduction and feedstock diversity for sulfuric acid-free ethanol cooking of lignocellulosic biomass as a pretreatment to enzymatic saccharification, Bioresource Technology 100 (20), 4783-4789.

Windom B.C., Lovestead T.M., Mascal M., Nikitin E.B., Bruno T.J., 2011, Advanced distillation curve analysis on ethyl levulinate as a diesel fuel oxygenate and a hybrid biodiesel fuel, Energy and Fuels 25, 1878-1890.

Ya’aini N., Amin N.A.S., 2013, Catalytic conversion of lignocellulosic biomass to levulinic acid in ionic liquid, BioResources 8 (4), 5761-5772.