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Effect of Ionic Liquids on Oil Palm Biomass Fiber Dissolution

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Ionic liquids (ILs) were used in the dissolution of oil palm biomass, primarily empty fruit bunches (EFB), oil palm fronds (OPF), and oil palm trunks (OPT). These ILs acted as alternative solvents that could dissolve biopolymer molecules up to 5 wt.%. The IL, [emim][OAc] was the best solvent, dissolving EFB, OPF, and OPT of 99%, 100%, and 97%, respectively, at 100 ºC and 16 h. The lignin content of the regenerated oil palm solids for all biomass was quantified and showed significant reduction up to 35%; fiber length was also reduced as the heating time increased after IL dissolution. Also, the effect of ILs on the different parts of oil palm biomass fibers was thoroughly studied. The lignin content was quantified.

INTRODUCTION

The oil palm *Elaeis guineensis*, a species in the Arecaceae family, is one of the most economical perennial oil-producing crops in tropical regions, such as West Africa and Southeast Asia. It has been domesticated and grown in plantations by the oil-producing fruit industry. The oil palm is the main agricultural crop in Malaysia, with a total planted area of 4.917 million hectares in 2011 (Goh *et al.* 2010). Notably, Malaysia generated 20,000 million USD from the export of palm oil and palm oil-based products in 2008. Eighty million tons (dry weight) of oil palm biomass were generated in 2011, and it is estimated that an additional 20 million tons will be generated by 2020. This total includes not only the mesocarp fibers (MF) and palm kernel shells (PKS), but also the empty fruit bunches (EFB), oil palm fronds (OPF), and oil palm trunks (OPT). This biomass needs to be utilized to ensure the sustainability of the oil palm industry.

Dissolution of biomass in common solvents is very difficult because lignin binds the plant cell walls together and provides mechanical strength to the plant. Different methods have been used to dissolve this lignin network and facilitate further processing for various applications. In 1939, Graenacher and Sailmann reported that tertiary amine oxides are capable of dissolving up to 10% cellulose. Then, 20 years later, Dee Lynn Johnson of Eastman Kodak patented a solvent system based on cyclic amine oxides, including *N*-methylmorpholine *N*-oxide (NMMO), for solubilizing cellulose (Johnson 1969). This NMMO is a better solvent compared with trimethylamine oxide because NMMO dissolves

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cellulose and other polymers as well. The dissolution of cellulose in NMMO, cellulose precipitation, and subsequent cellulose molding have been investigated since the 1970s (McCorsley and Varga 1979).

The mechanism of dissolution and the structure of cellulose-NMMO solutions remain unclear. The NMMO dissolution technique is well established for producing regenerated cellulose, with an output of 220 kilotons/year of Lyocell fibers. NMR analyses have shown that neither cellulose derivation nor cellulose complex formation takes place with NMMO (Gagnaire *et al.* 1980). Fink *et al.* (2001) has reviewed the structure formation of regenerated cellulose materials from NMMO solutions. A study by Chanzy *et al.* (1982) revealed that the reaction is favored by the formation of hydrogen bonds between the oxygen of the strong N-O dipoles in NMMO with other compounds containing hydroxyl groups, such as water, alcohol, and cellulose. However, water and cellulose will compete with each other to bind with NMMO molecules, which seem to prefer water. Despite many advantages, the NMMO process has several disadvantages such as severe fibrillation of the fibers manufactured and the fiber profile which is closer to cotton. Moreover, the use of NMMO - a thermally unstable solvent requires a major investment in safety technology. This is where ionic liquids (ILs) come into play as a new class of solvents. They have significant advantages over dissolution of biomass compared to NMMO solvent. ILs are thermally stable solvents. They can be effective for dissolving cellulose, yielding clear viscous solutions. The dissolved cellulose can subsequently be precipitated by adding water or protic organic solvents such as ethanol. Moreover, the crystallinity of the regenerated cellulose is reduced, which significantly accelerates subsequent hydrolysis with cellulases.

Traditionally, production of regenerated cellulose fibers and films was largely based on viscose technology, which requires the use of harmful carbon disulfide and produces hydrogen sulfide (Ghittori *et al.* 1998). Other organic solvent systems, such as paraformaldehyde-dimethyl sulfoxide (PFA-DMSO) or dimethyl formamide-dinitrogen tetroxide (DMF-N_2O_4), transform cellulose into unstable derivatives, from which cellulose can easily be regenerated by precipitation in water (at a higher concentration) (Fink *et al.* 2001) or alcohol. Traditional cellulose dissolution processes, are often cumbersome, expensive, and require unusual solvents with a high ionic strength and harsh dissolution conditions (Kirk-Othmer 1993; Feng and Chen 2008). These solvents include NMMO, mixtures of *N,N*-dimethylacetamide and lithium chloride (DMAC/LiCl), dimethylimidazolone/LiCl, concentrated aqueous inorganic salt solutions (*e.g.*, $ZnCl_2/H_2O$ or $Ca(SCN)_2/H_2O$), concentrated mineral acids (H_2SO_4/H_3PO_4), or molten salt hydrates (*e.g.*, $LiClO_4$•$3H_2O$ and LiSCN•$2H_2O$).

Recently, ILs have emerged as a new class of solvents for chemical reactions and biocatalysts, either alone or as co-solvents. The use of ILs has attracted much attention from researchers. These solvents have gained popularity because these organic salts have a wide liquid range, high thermal stability, non-volatility, and excellent dissolution capabilities for both organic and inorganic compounds (Paulechka *et al.* 2003; Wasserscheid and Welton 2008). The near limitless potential to combine anions and cations to tailor solvent properties has led to room temperature ILs (RTILs) being termed as 'designer solvents' (Freemantle 1998). The cation (usually organic) and anion (usually inorganic) comprising ILs are paired such that the resulting organic salts cannot pack compactly (Bourbigou and Magna 2002). As a result, ILs do not easily crystallize and remain liquid over a wide range of temperatures. Recently, ILs were used to partially dissolve cellulose and wood chips/fibers (Fort *et al.* 2007; Kilpeläinen *et al.* 2007).

Cellulose-dissolving ILs usually contain anions of chloride, formate, acetate, or alkylphosphonate because they form strong hydrogen bonds with cellulose and other carbohydrates at elevated temperatures, which allows these biopolymers to dissolve (Remsing *et al.* 2006; Youngs *et al.* 2006; Liebert and Heinze 2008; Remsing *et al.* 2008; Zhao *et al.* 2008; Leskinen *et al.* 2011, 2013). As for 1-butyl-3-methylimidazolium chloride ([bmim][Cl]), Remsing *et al.* (2006) and Moulthrop *et al.* (2005) have reported that the chloride anion is much more involved than the cation in the disruption of the hydrogen bond system (18 to 25 wt.%) and the solubilization of the chains. The postulated Cl-OH-cellulose interaction is comparable to the structure discussed for the cellulose/DMAc/LiCl system, but it should be more efficient because the anion is free due to its looser binding with the large asymmetric cation (El Seoud *et al.* 2007).

The packed structure of lignocellulosic materials practically limits the ability of common solvents to dissolve them. Lignin is highly cross-linked and also linked to both cellulose and hemicelluloses in lignocellulosic material (Chandra *et al.* 2007). Lignin, as a network polymer, binds with the carbohydrates (hemicelluloses and cellulose) to form a tight and compact structure. Therefore, pretreatment of biomass with ILs is necessary to disrupt the packed structure of lignocellulosic materials.

Most studies on tropical agri-biomasses have focused on sugarcane bagasse (Kuo and Lee 2009) and on other lignocellulosic materials such as pine (*Pinus radiata*), poplar, switchgrass, avicel, and corn stover (Binder and Raines 2010; Brandt *et al.* 2010; Samayam and Schall 2010). However, there is limited research on the dissolution of oil palm biomass by ILs. In this study, oil palm biomass was dissolved in 1-butyl-3-methylimidazolium chloride ([bmim][Cl]), 1-ethyl-3- methylimidazolium chloride ([emim][Cl]), and 1-ethyl-3-methylimidazolium acetate ([emim][OAc]) ILs. Correlations between the dissolution of oil palm biomass and cellulose fibers from EFB, OPF, and OPT, together with lignin extraction into the ILs, were evaluated. ILs have advantages that will enable the development of improved process strategies for manufacturing advanced biopolymer-based materials.

EXPERIMENTAL

Materials

The oil palm biomass waste fibers selected for this study were empty fruit bunch (EFB), oil palm frond (OPF), and oil palm trunk (OPT); this waste biomass was obtained from the Malaysian Palm Oil Board (MPOB), Biomass Technology Centre located in Bangi, Selangor, Malaysia. The fibers were dried in the sun before being shredded and refined into loose fibrous materials using a thermochemical refiner at a medium density fiberboard (MDF) pilot plant in the MPOB Biomass Technology Center. Subsequently, the samples were sieved to obtain particles that were less than 150 µm in diameter to ensure the dissolution of the refined material in the ILs. Three ionic liquids (ILs), [bmim][Cl], [emim][Cl], and [emim][OAc], were purchased from Merck (Germany) (Fig. 1). Microcrystalline cellulose (MCC) was purchased from Merck (Germany) and was used as a cellulose standard. All other chemicals were of analytical-reagent grade and were purchased from Merck (Germany).
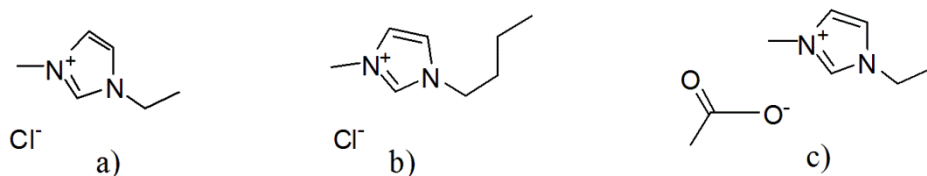
Fig. 1. ILs used in this study: a) [emim][Cl], b) [bmim][Cl], and c) [emim][OAc]

Oil Palm Biomass and Cellulose Fiber Pre-Treatment

Oil palm biomass fibers (EFB, OPF, and OPT) were denoted as raw materials, while cellulose fiber was defined as the product of treatments following Technical Association of Pulp and Paper Industry (TAPPI) analysis methods. The chemical composition of the oil palm biomass fibers was determined in accordance with TAPPI standard methods, as summarized in Table 1.

Oil palm biomass and the cellulose fibers from EFB, OPF, and OPT (particle size =150 µm) were dried in a vacuum oven for 3 h, and ILs were dried for 8 h at 70 °C to remove trace amounts of water prior to the dissolution experiments. Approximately 5 wt.% suspensions of oil palm biomass and cellulose fibers (MCC, EFB, OPF, or OPT) were prepared by mixing the ILs ([bmim][Cl], [emim][Cl] or [emim][OAc]) with DMSO-d_6 in a 80:15 ratio (w/w) in a 50-mL beaker. The inclusion of small amounts of DMSO-d_6 as a co-solvent had no noticeable effect on the solubility of the carbohydrates in ILs; in fact, the DMSO-d_6 reduced the viscosity of the mixtures. All reactions were carried out under a nitrogen (N_2) atmosphere. This preparation method enabled the rapid filling of all fiber voids in the specimens and maximized surface contact between fibers and ILs, which resulted in uniform swelling of the fibers and improved homogeneity.

Table 1. TAPPI Standard Methods Used to Determine Chemical Composition

Content	Standard Method for Analysis
Extractive	*TAPPI (Technical Association of the Pulp and Paper Industry): " Alcohol-benzene and dichloromethane soluble in wood and pulp," T 204 om-88*, 1988 TAPPI (Technical Association of the Pulp and Paper Industry): 'Preparation of wood for chemical analysis,' T 264 om-88," 1988
Holocellulose	Wise *et al.* 1946*
α-Cellulose	*TAPPI (Technical Association of the Pulp and Paper Industry): "Alpha-, beta-, and gamma-cellulose in pulp," T 203 os-74*, 1988
Lignin	*TAPPI (Technical Association of the Pulp and Paper Industry): "Acid-insoluble lignin in wood and pulp," T 222 om-88*, 1988
Ash	*TAPPI (Technical Association of the Pulp and Paper Industry): "Ash in wood and pulp," T 211 om-93*, 1988

*Used with some modifications

The oil palm biomass fiber/ILs or cellulose fiber/ILs solutions were thoroughly mixed. The heterogeneous mixtures were placed into an oil bath and heated at 100 °C with vigorous magnetic stirring (300 rpm). All reactions were carried out under a nitrogen

atmosphere. The reactions were heated for different time intervals, and the time taken to complete fiber dissolution was recorded. Following the reaction, insoluble residues were separated by filtration (if needed) through heated glass wool; the clear liquors obtained were saved for further analysis. Scheme 1 shows the experimental procedure for dissolution process.
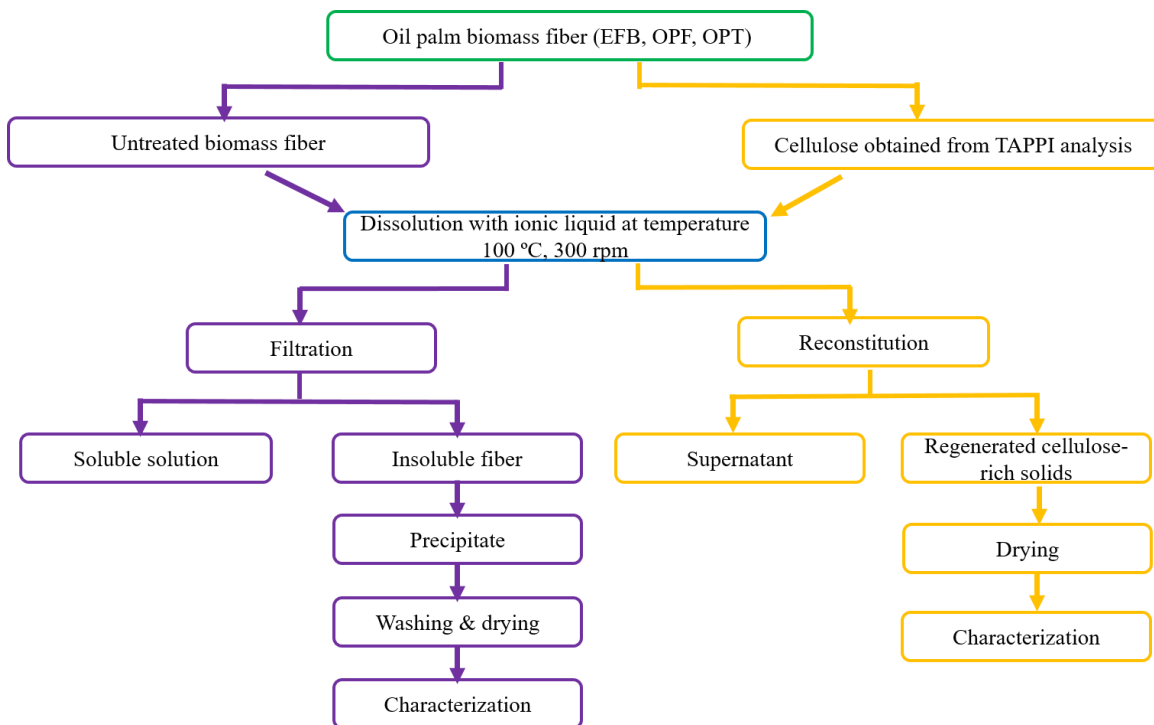
Scheme 1. Flowchart for the dissolution of oil palm biomass and cellulose in ionic liquid

Evaluation of Dissolved Solution

After treatment, 10 mL of DMSO was added to the dissolved solutions to reduce viscosity (Heinze *et al.* 2005); the mixture was mixed vigorously and centrifuged at high speed (3000 rpm) for 10 min. The supernatant was then separated from the precipitate, which was washed with DMSO (3 x 10 mL) to remove any residual dissolved substances. The residue was further washed with deionized water (3 x 30 mL), dried overnight in an oven at 90 °C, and weighed. The percentage of fibers dissolved was calculated as shown in Eq. 1,

$$\text{Fiber dissolved (\%)} = \frac{m_{ow} - m_{res}}{m_{ow}} \times 100 \qquad (1)$$

where m_{ow} represents the mass of the initial fiber added and m_{res} is the mass of the residue recovered after centrifugation.

Regeneration of Dissolved Materials

The dissolved materials mixture was added to 300-mL beaker containing 100 mL of acetone/water (1:1 v/v), which acts as a precipitator. The beaker was sealed with Parafilm®, and the mixture was stirred at room temperature for 1 h. Subsequently, the regenerated cellulose-rich solids were centrifuged. The supernatant containing the ILs was

removed, and the precipitates were washed twice with acetone/water to remove residual ILs. Precipitates were filtered through nylon filter paper in a ceramic funnel on a Bŭchner flask under soft vacuum. The precipitated and regenerated cellulose-rich solids were dried at 60 °C overnight in an oven. The lignin content of the regenerated material was determined using the TAPPI standard method (Table 1). The length and width of oil palm biomass fibers before and after treatment with ILs were measured using digital imaging microscopy (Nikon Infinity 2 MP digital camera with i-solution software, Japan) under 10x and 20x magnification.

RESULTS AND DISCUSSION

Effect of ILs

Three ILs, [bmim][Cl], [emim][Cl] and [emim][OAc], were selected based on their different cation lengths and types of anions. These ILs are good solvents that dissolve cellulose fibers (Table 2). They dissolved 5 wt.% (w/w) of cellulose fibers and formed a homogeneous clear solution after 2 h at 100 °C. This finding was similar to the pioneering work by Richard *et al.* (2002), who found that ILs containing the chloride anion [Cl]$^-$ have successfully dissolved fibrous cellulose (Aldrich) and Whatman cellulose filter papers. The [Cl]$^-$ anion has also been used as reaction medium in the chemical modification of cellulose, such that carboxyl groups are grafted onto the cellulose (Liu *et al.* 2006). The dissolution of cellulose by ILs is believed to be caused by the disruption of inter- and intra-molecular hydrogen bonds in cellulose chains, followed by the formation of new hydrogen bonds between cellulose hydroxyl protons and anions of the ILs (Remsing *et al.* 2006).

Table 2. Dissolution of Cellulose Fibers and Oil Palm Biomass by ILs

ILs	Cellulose fibers[a]				Oil palm biomass[b]		
	MCC*	EFB	OPF	OPT	EFB	OPF	OPT
[emim][Cl]	/	/	/	/	X	X	X
[bmim][Cl]	/	/	/	/	X	X	X
[emim][OAc]	/	/	/	/	/	/	/

[a] Maximum heating time is 4 h at 100 °C; [b] Heating time is 16 h at 100 °C; /, complete dissolution; X, partial dissolution; *MCC, microcrystalline cellulose.

[Cl]$^-$ anions are advantageous because they have large electronegativity values and small atomic radii (Dadi *et al.* 2006), which allows them to act as a small hydrogen bond acceptor. However, chloride salts of ILs are highly hygroscopic, have high melting temperatures, and have high liquid viscosities, which makes their handling difficult (Vitz *et al.* 2009). On the other hand, carboxylate containing IL such [OAc]$^-$ anion was used for comparison. This IL overcomes the drawbacks of the chloride salts. In this study, cellulose fibers were quickly dissolved in [emim][OAc] at 100 °C. The strength of an anion to form hydrogen bonds with hydroxyl group of cellulose is depends on its β value (basicity) determined by Kamlet-Taft parameters (Anderson *et al.* 2002; Stark *et al.* 2012). Kamlet and Taft introduced multi-parameter polarity scales which composed of the complimentary scales of hydrogen bond acidity (α), (Taft and Kamlet 1976) hydrogen bond basicity (β) (Kamlet and Taft 1976) and dipolarity/ polarizability effects (π*) (Kamlet *et al.* 1977). The basicity of ILs could be significantly enhanced via weakening of the cation−anion

interaction or employing an anion-tethered strategy (Xu *et al*. 2014). This previous report showed that the [OAc]⁻ anion was a considerably stronger hydrogen bond acceptor than the [Cl]⁻ anion, whereas the *β* values of these anions were 1.20 and 0.83, respectively.

The [emim][Cl] and [bmim][Cl] partially dissolved the oil palm biomass fibers, whereas [emim][OAc] completely dissolved these fibers (Table 3). The solubility of fibers in [bmim][Cl] and [emim][Cl] versus [emim][OAc] are in agreement with other studies (Fort *et al*. 2007; Kilpeläinen *et al*. 2007). Different lengths of time were required to completely dissolve 5 wt.% oil palm biomass fibers in the different ILs. A standard heating time of 16 h was selected for subsequent experiments, as more than 90% w/w fibers were dissolved in [emim][OAc] within this time.

Table 3. Percentage of Oil Palm Biomass Dissolved in ILs

Entry	Ionic Liquids	Type of Biomass	Dissolution (%)*
1	[emim][Cl]	EFB	47 ± 1.5
2	[emim][Cl]	OPF	47 ± 1.0
3	[emim][Cl]	OPT	47 ± 1.8
4	[bmim][Cl]	EFB	48 ± 0.9
5	[bmim][Cl]	OPF	48 ± 1.0
6	[bmim][Cl]	OPT	47 ± 1.5
7	[emim][OAc]	EFB	99 ± 1.0
8	[emim][OAc]	OPF	100 ± 1.2
9	[emim][OAc]	OPT	97 ± 1.0

* relative to the initial fiber loading (5 wt.%)

From the results, [emim][Cl] and [bmim][Cl] dissolved less than half (< 50%) of the EFB, OPF, and OPT fibers (Table 3). There was little difference in the amount of fibers dissolved by [emim][Cl] and [bmim][Cl] (16 h at 100 °C). There is a less noticeable effect of different alkyl chain of cation (less than six carbons) towards the dissolution of oil palm biomass, unless the carbon of the alkyl chain is more than six carbons (Richard *et al.* 2002). Moreover, the effectiveness of [Cl]⁻ anion concentration was reduced within these liquids. Of the anions used, the [OAc]⁻ anion IL showed a better ability to solubilize biomass fibers than its [Cl]⁻ anion counterpart. In addition, ILs containing the [OAc]⁻ anion tend to be less corrosive, less viscous, and more basic than ILs with halide anions. These factors make it more efficient than the [Cl]⁻ anion at disrupting the inter- and intra-molecular hydrogen bonding in biopolymers, such as cellulose (Richard *et al.* 2002). Nearly 100% of the OPF dissolved in [emim][OAc] at 100 °C, followed by EFB and 99% and 97%, of the EFB and OPT, respectively, were dissolved.

In ILs, hydrogen bonds and $\pi-\pi$ interactions are present apart from ionic interactions (Anderson *et al.* 2002). Therefore, ILs compete with the lignocellulose components to form hydrogen bonding especially with cellulose, thus it was expected to disrupt the intricate three-dimensional network structure of oil palm fibers cell wall (Moulthrop *et al.* 2005). This effect is attributed to the anions of ILs (Richard *et al.* 2002; Remsing *et al.* 2006; Kilpeläinen *et al.* 2007; Dadi *et al.* 2007). The higher proportion of cellulose compared to lignin and hemicellulose seems to have favored dissolution. In addition, [OAc]⁻ anion has π-electrons not only within its imidazolium ring, but also on the anion which is expected to favor the formation of hydrogen bonding with cellulose and promotes faster dissolution of lignocellulose components compared to [Cl]⁻ anion. Thus, [emim][OAc] is a better candidate for the dissolution of a variety lignocellulosic biomass

sources. It is worth to note that cation has indirect effect towards the dissolution process which has been studied by Sashina *et al*. (2012) and Heinze *et al*. (2005).

Effect of Fibers of Different Oil Palm Biomass
Solubility

The ability of ILs to dissolve fibers is not totally dependent on the solvent itself; the composition of the fibers also plays a major role in dissolution. Oil palm biomass is categorized as fibrous material containing three major biopolymers including cellulose (43-49%), hemicellulose (23-30%) and lignin (19-21%) content (Table 4). It has considerably high lignin content and is particularly recalcitrant to many pre-treatments (Saka 2000; Kumar *et al.* 2009). Lignin provides wood with mechanical strength and rigidity to resist external forces, such as wind, and forms a barrier against microbial attack (Fujita and Harada 1991). The percentage of cellulose in all three fibers was similar, with the OPT fibers having the lowest value ($43.7 \pm 1.1\%$). The lignin content of OPT fibers was slightly higher than EFB and OPF fibers.

Table 4. Chemical Composition of Oil Palm Biomass

Fiber/ Wood	Ash Content (%)	Alcohol- Benzene Extractives (%)	Holocellulose (%)	Hemicellulose (%)	Lignin (%)	Cellulose (%)
EFB	2.6 ± 0.1	2.9 ± 0.3	73.5 ± 2.7	25.6 ± 1.0	19.9 ± 1.4	47.3 ± 0.8
OPF	0.7 ± 0.2	2.6 ± 0.4	71.6 ± 1.5	23.1 ± 2.1	19.4 ± 1.3	49.4 ± 0.8
OPT	1.6 ± 0.3	2.7 ± 0.2	73.6 ± 0.8	30.1 ± 1.1	21.3 ± 2.1	43.7 ± 1.1

This result was expected because mature tissues at the base (trunk) accumulate more metabolic products than the younger parts at the top (fronds and branches) (Ververis *et al.* 2004). However, this result was not in agreement with some findings (Husin *et al.* 1985; Sreekala *et al.* 2001). Those researchers found that EFB contained the highest percentage of lignin. This discrepancy in the proportion of these wood components within a fiber depends on its age, the nature of the plant, the environmental conditions, the source of the fiber, and the extraction method used to obtain the fibers (Batra 1985). Chemical composition varies from plant to plant and within different parts of the same plant.

While EFB and OPF took almost 16 h to be dissolved in [emim][OAc] at 100 °C, OPT required more than 16 h (Fig. 2). However, more than 90% of EFB and OPF fibers were dissolved after being heated for 48 h or longer in [emim][Cl] or [bmim][Cl] (Figs. 3 and 4, respectively). The OPT fibers, on the other hand, took more than 50 h to be 90% dissolved in the IL chloride salts. Longer dissolution times require more energy input into the process (Lu and Ralph 2003). The OPT required the longest time for complete dissolution, probably because of its higher lignin content (Table 4). This result was expected because mature tissues at the base (trunk) accumulate more metabolic products than the younger parts at the top (fronds and branches) (Ververis *et al.* 2004). Furthermore, parenchymatous tissue along the trunk can hinder solvent penetration of the cell wall (Yusoff 2006). The combination of these two factors resulted in the lower solubility of OPT fibers in ILs, which prolonged the heating time.
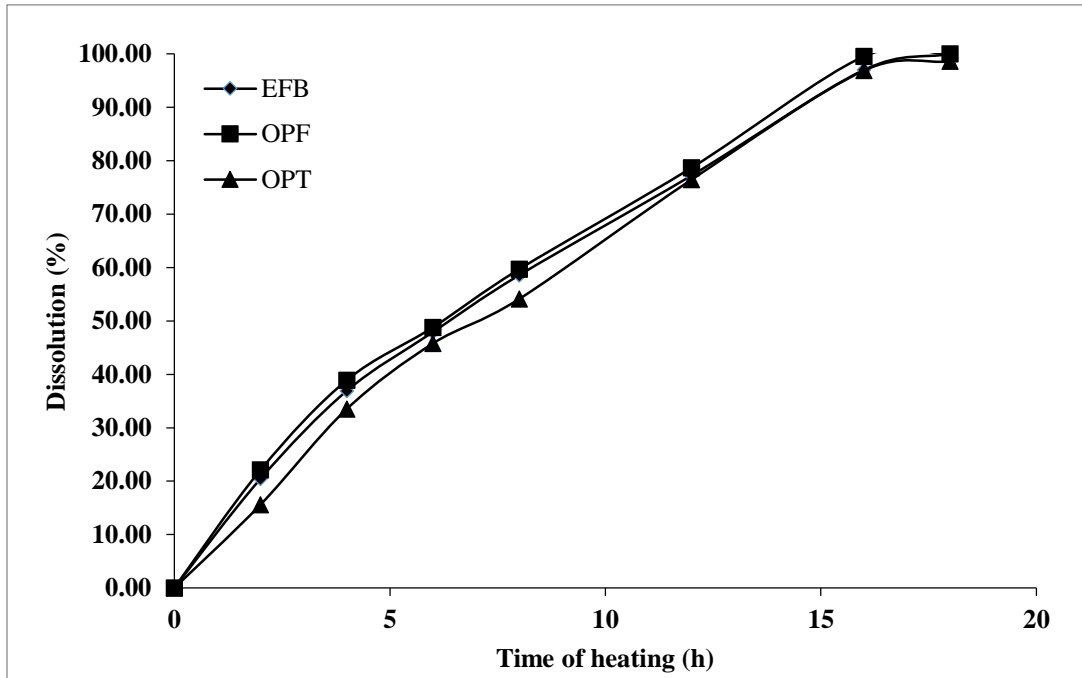
Fig. 2. Percentage of dissolution as a function of heating time for oil palm biomass in [emim][OAc] (particle size = 150 µm) at 100 °C
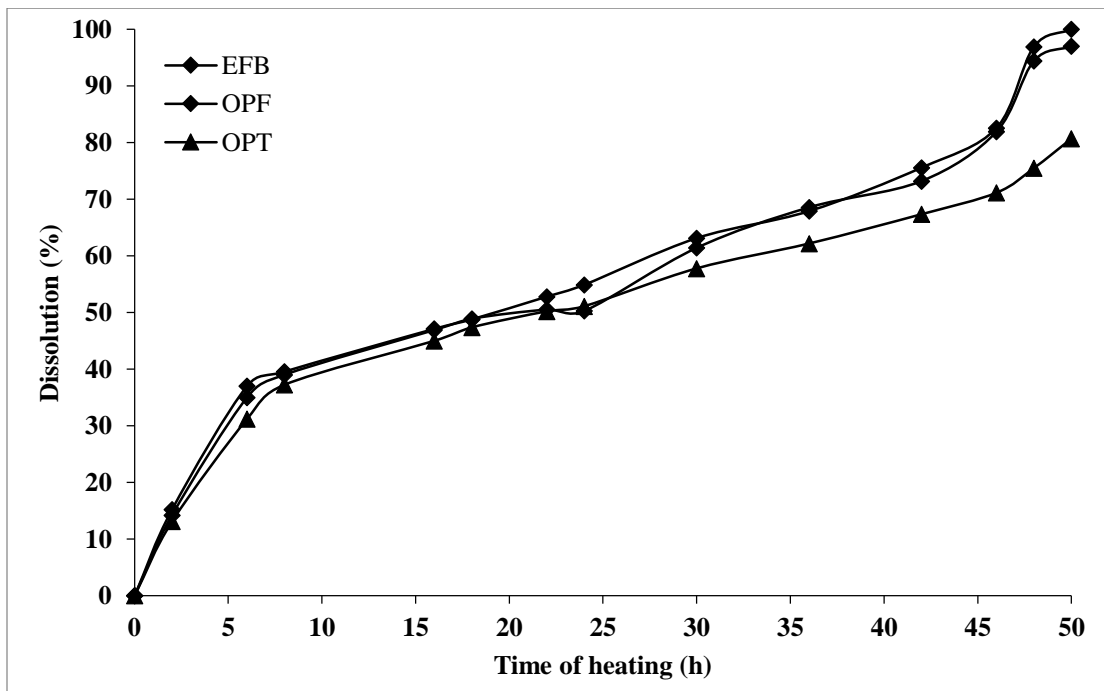

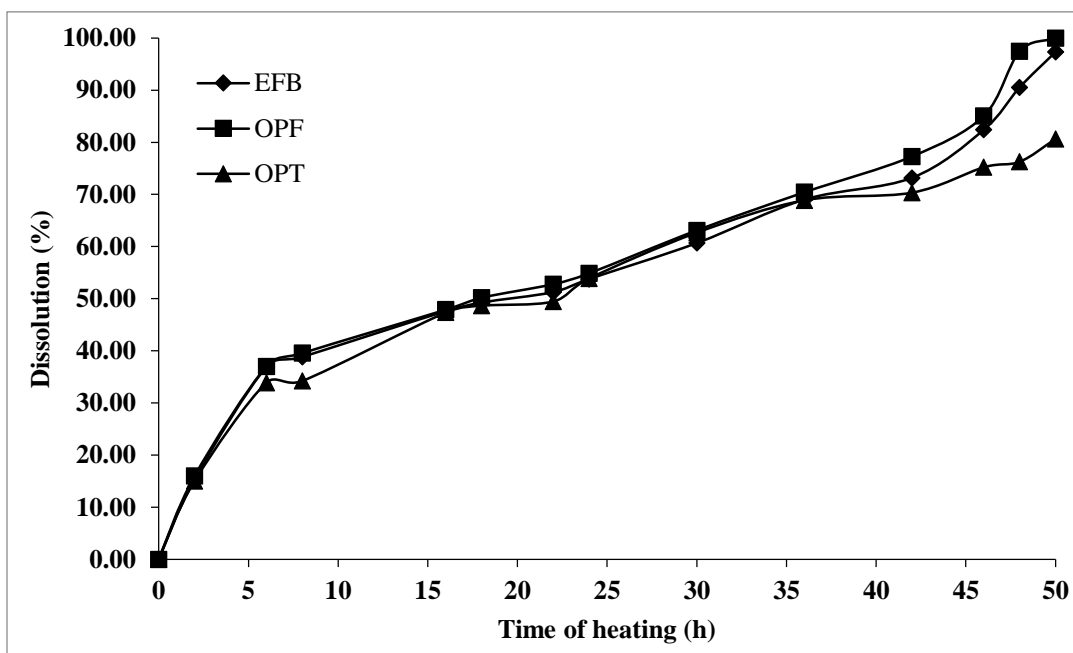**Fig. 3.** Percentage of dissolution as a function of heating time for oil palm biomass in [emim][Cl] (particle size = 150 µm) 100 °C

Fig. 4. Percentage of dissolution as a function of heating time for oil palm biomass in [bmim][Cl] (particle size = 150 μm) 100 °C

The fibers treated with [emim][OAc] were more than 95% dissolved after being heated for 16 h. Notably, [emim][OAc] can achieve 95% dissolution of wood particles as large as 1.0 mm and solubilize plant cell walls at mild heating temperatures (Singh *et al.* 2009). The initial step in delignification is the hydrolytic fragmentation of the lignin polymer, which is followed by the solubilization of lignin fragments (Tan *et al.* 2009). Regeneration of the cellulose *via* the addition of water as a precipitation agent could considerably hinder delignification and lignin fragment solubilization. [emim][OAc] would be more economical at the industrial scale because the energy needed to dissolve the biomass is minimum (with all other factors being equal) (Sun *et al.* 2009). Moreover, [emim][OAc] can be considered as biodegradable and reasonably non-toxic and non-corrosive (Liebert 2010). Otherwise, microwave heating could help to shorten dissolution times (Fort *et al.* 2007; Kilpeläinen *et al.* 2007).

Fiber length

The lengths of oil palm biomass fibers before and after treatment in ILs were measured using digital imaging microscopy (DIM) (Fig. 5). For particle sizes of 150 μm, OPT exhibited the longest fiber length (1910 μm), followed by OPF (1827 μm) and EFB (1242 μm). Similar observations have been reported by Abdul Khalil *et al.* (2008). Fiber length was reduced by half after 12 h in [emim][Cl] (Fig. 6). On the other hand, the time taken as the fiber length was reduced by half. The time was decreased to 11 h and 8 h when the oil palm biomass was treated in [bmim][Cl] and [emim][OAc], respectively (Figs. 7 and 8). In general, fiber length decreased as the heating time increased. Reduction in fiber length for all the oil palm biomass sources was probably a result of holocellulose solubilization by ILs. The solubilization of fibers and their modes of interaction have been previously examined (Cuissinat and Navard 2006a,b; Rahman *et al.* 2012).

However, the trend of fiber length reduction versus heating time for complete dissolution were not the same for the various fiber types and various ILs used. The

differences in the chemical compositions of the fibers and of IL solvent properties should be explained by these trend.
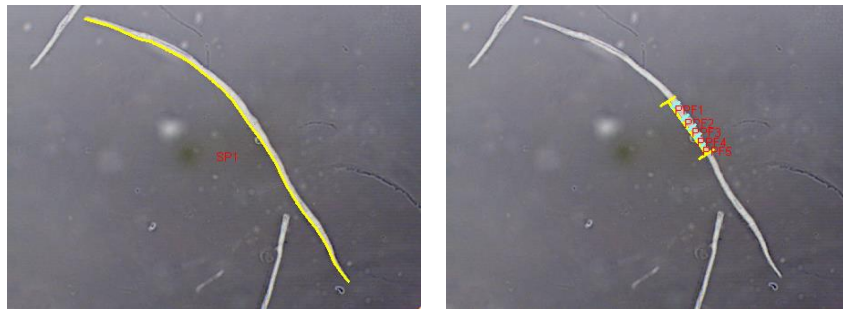

Fig. 5. The length and width of oil palm biomass fiber measured using digital imaging microscopy

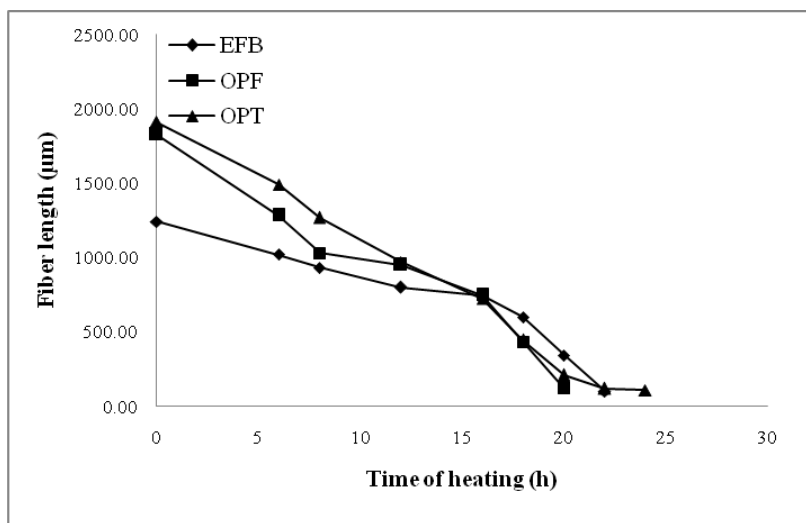**Fig. 6**. Graph of fiber length of oil palm biomass EFB, OPF, and OPT as a function of heating time in [emim][Cl] at 100 °C (particle size = 150 µm)
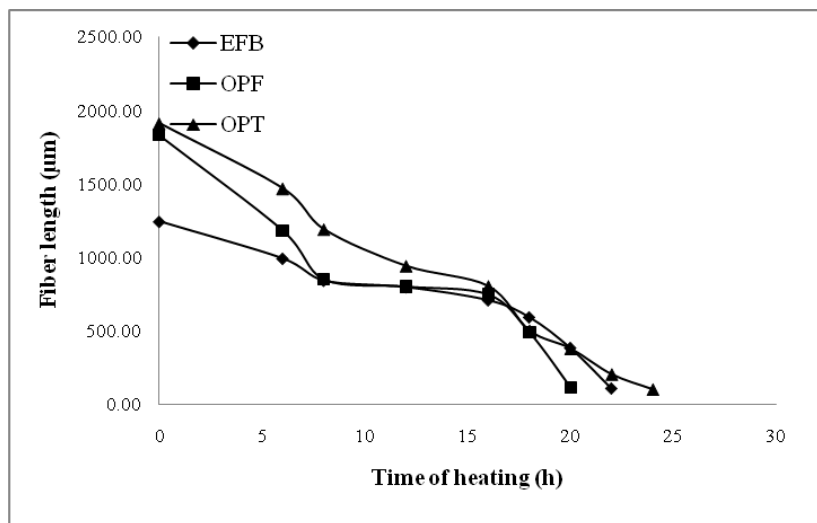

Fig. 7. Graph of fiber length of oil palm biomass EFB, OPF, and OPT as a function of heating time in [bmim][Cl] at 100 °C (particle size = 150 µm)
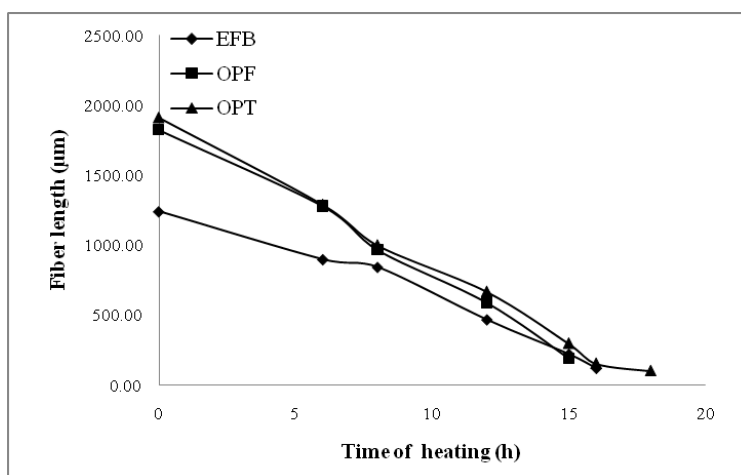
Fig. 8. Graph of fiber length of oil palm biomass EFB, OPF, and OPT as a function of heating time in [emim][OAc] at 100 °C (particle size = 150 μm)

Quantification of lignin content

The percentage of lignin initially present in oil palm biomass was compared to the amount in the fiber after dissolution in ILs and its subsequent regeneration (Table 5). All regenerated materials had a considerably lower lignin content when compared to the original fiber (up to 35% reduction).

Table 5. Lignin in Raw Oil Palm Biomass and Regenerated Oil Palm Solids

Type of fiber	Materials	L_K (%)		
		[emim][Cl][a]	[bmim][Cl][b]	[emim][OAc][c]
EFB	Oil palm biomass fiber	$19.9 \pm 1.4^{L}{}_K$	$19.9 \pm 1.4^{L}{}_K$	$19.9 \pm 1.4^{L}{}_K$
	Regenerated solid	14.9 ± 1.1^{a}	15.4 ± 1.6^{b}	13.0 ± 0.9^{c}
OPF	Oil palm biomass fiber	$19.4 \pm 1.3^{L}{}_K$	$19.4 \pm 1.3^{L}{}_K$	$19.4 \pm 1.3^{L}{}_K$
	Regenerated solid	14.7 ± 0.2^{a}	14.2 ± 0.5^{b}	12.6 ± 1.0^{c}
OPT	Oil palm biomass fiber	$21.3 \pm 2.1^{L}{}_K$	$21.3 \pm 2.1^{L}{}_K$	$21.3 \pm 2.1^{L}{}_K$
	Regenerated solid	16.4 ± 1.2^{a}	15.5 ± 0.2^{b}	14.7 ± 0.3^{c}

L_K, Klason lignin.
Regenerated material from 0.50 g fiber in 10 g ILs; after dissolution in a) [emim][Cl], b) [bmim][Cl] after 24 h of heating, respectively, and in c) [emim][OAc] after 16 h of heating, at 100 °C under N_2 atmosphere.

Lignin content in all regenerated oil palm solids had decreased significantly after dissolution in ILs. The [emim][OAc] IL most efficiently removed lignin during the dissolution process, followed by [bmim][Cl] and [emim][Cl]. Carbohydrates that contain fewer or no covalent bonds with lignin are preferentially dissolved in ILs (Sun *et al.* 2009). For example, 85% of the original lignin was extracted from maple wood floor after pre-treatment with [emim][OAc] for 70 h at 90 °C (Lee *et al.* 2009). Others reported studies have also showed that [OAc] IL show good performance for pretreatment of biomass such as energy cane bagasse (Qiu and Aita 2013), cypress wood (Moniruzzaman and Ono 2013), and rubber wood (Darji *et al*. 2015).

The differences in lignin solubility in IL can best be explained by several hypotheses. First, the effective pre-treatments generally include higher temperatures and longer incubation times, in which an effective lignin glass transition temperature (T_g) must

be exceeded to efficiently abrupt the softening of the lignin. Second, ability of IL anion to form bonding with lignin and also cellulose by formation of H-bonding between the IL anion and -OH group of cellulose (Youngs *et al*. 2006) have promoted lignin solubilization. For instance, anion having hydrogen donating ability such as amino-acid anion influences the dissolution of lignin. Liu *et al*. (2012) reported that lignin showed better solubility results than cellulose in amino-acid based IL. In another study, Shill *et al*. (2011) indicated that the p–p interactions of the IL cation with lignin assisted in lignin solubilization. However, complete delignification of biomass is difficult due to the location of lignin within the lignin–carbohydrate complex, strong poly-ring bonds of C–O–C, C–C, and hydrophobicity (Kim *et al*. 2003). Third, the extent and degree of biomass recalcitrance varies as a function of biomass itself (*i.e.*, non-wood (*e.g*., grass), hardwood, and softwood); other influencing factors include variations in biomass age, harvest method, extent of drying, and storage conditions. For example, the difference and complexity of lignin–carbohydrate bonding make softwoods inaccessible, non-extractable and more recalcitrant to delignification (Tadesse and Luque 2011). In advance studies, pretreatment of the biomass, such as by steam explosion of rice straw (Jiang *et al*. 2011) and autohydrolysis pretreatment of silver birch (*Betula pendula*) (Hauru *et al*. 2013), improves lignin solubility and thus allows lignin extraction with ILs. The high solubilization of lignin in ILs may have important practical applications for wood delignification, for example in the pulp and paper industry (Li *et al.* 2009; King *et al*. 2014).

Cost of Ionic Liquids

Ionic liquids have been proven to be significantly potential in many areas of research at laboratory scale, within a timeframe of more than two decades. However, the cost of ionic liquids has been the subject of considerable recent attention as for industrial prospects. Plechkova and Seddon (2008) have critically reviewed the cost of ILs, at least giving an overview of the potential ILs to be used in chemical industry. ILs are typically between 2 and 100 times the cost of organic solvents. Obviously, they are far expensive than traditional solvents and catalysts used in chemical reactions. For example, the cost of commonly used ILs, 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium hexafluorophosphate are USD 1,972 and USD 2,360 per kilogram (kg), respectively which is 25 times far expensive if compare to NaOH which only cost USD 80 per kg (Andreani and Rocha 2012). For instance, choline-based and tetraalkylphosphonium or tetraalkylammonium salts are intrinsically less expensive than others (Pernak *et al*. 2007). Besides, the ability to tailor the properties of ILs by its combination of the inorganic cation, organic anion and starting materials could significantly vary the cost of ILs to a wide range. Through large-scale bulk production, the cost of ILs can be reduced. Chen *et al*. (2014) gave information about the costs of protic ILs; triethylammonium hydrogen sulfate (simpler ammonium salt) was determined to cost just USD 1.24 per kg to produce, while 1-methyl- imidazolium hydrogen sulfate (imidazolium complex) would be USD 2.96 per kg. The tunability properties of ILs (eg., viscosity, density, or thermal conductivity) perhaps can be fine-tuned to optimise the chemistry, the chemical engineering, and the cost of the system. Overall, more effort should be dedicated by means of synthesizing new ILs from affordable raw materials in a very few steps, thus can reduce the cost of these liquids.

Due to the high cost of RTILs, solvent recycling will be necessary to process biomass on an industrial scale. For example, Lee *et al*. (2009) observed that [emim][OAc] can be recycled at least four times without any deleterious effect on lignin extraction or

generation of fermentable sugars following enzymatic hydrolysis of the residual lignocellulose. A side benefit of this extraction process is the potential to provide a highly pristine lignin. Qiu and Aita (2013) shows that, [emim][OAc] can be recycled up to four times for the pretreatment of energy cane bagasse. It also shows that the enzymatic digestibility decreased as the number of pretreatment recycles increased.

CONCLUSIONS

1. Ionic liquids (ILs) can be used as an alternative solvent for the pre-treatment of oil palm biomass fibers. In this study, [emim][OAc] was the most effective in fully dissolving tropical oil palm biomass and cellulose fibers within 16 to 18 h and 2 to 3 h of heating at 100 °C, respectively.

2. Complete dissolution of oil palm biomass took longer than cellulose fibers, probably because of the compact structure of oil palm biomass. Additionally, [emim][OAc] resulted in better dissolution compared with [bmim][Cl] and [emim][Cl] because of its high basicity originated from [OAc]⁻ anion. The [OAc]⁻ anion played a key role in the dissolution of oil palm biomass among the studied ILs.

3. [emim][OAc] has fully dissolved OPF fibers, followed by EFB (99%) and OPT (97%) at 100 °C at 16 h. Fiber lengths in each oil palm biomass were reduced significantly as heating time and percentage of biomass dissolution increased.

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