LIGNIN AND CELLULOSE EXTRACTION FROM COCONUT SHELL USING IONIC LIQUIDS

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DISSERTATION SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR

2017

UNIVERSITY OF MALAYA
ORIGINAL LITERARY WORK DECLARATION

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Matric No: **SGR150069**

Name of Degree: **Master**

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Lignin and Cellulose Extraction from Coconut Shell using Ionic Liquids

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LIGNIN AND CELLULOSE EXTRACTION FROM COCONUT SHELL USING IONIC LIQUIDS

ABSTRACT

Coconut shell, a natural lignocellulosic biomass, is available in high amount as an agriculture waste in many countries. To utilize this biomass and convert it into high-value products, there is a need to find alternative solvents that efficiently dissolve lignocellulosic biomass. Recently, ionic liquids (ILs) have attracted much attention due to its unique characteristics; such as negligible vapor pressure, non-flammability, and a low melting point. It has been demonstrated that ILs can dissolve biomass partially or completely, depending on the type of biomass. In this study, we have investigated protic and aprotic ionic liquids as pretreatment solvents for the dissolution of coconut shell. The extraction efficiency was greatly influenced by temperature, duration time, particle size, and types of cations and anions of the ionic liquids. The effects of pretreatment variables on the chemical composition, surface morphology, crystallinity, and thermal stability of regenerated lignin and cellulose from coconut shell were investigated. The solubility tests showed that aprotic ionic liquids have good solubility performance (7 wt %) compared to protic ionic liquids (1 wt %). Thus, a series of aprotic ionic liquids (AILs), [Bmim][Ace], [BMIM]Cl, [Emim][Ace], and [Emim]Cl, were chosen and used in the dissolution and regeneration process of coconut shell. The optimum process pretreatment for dissolution was at 110°C and the particle size of ranges are from 10 - 63 µm. The results indicated that the dissolution of coconut shell (up to 70 mg of coconut shell per g of solvent) were obtained in aprotic ionic liquids at 110°C (6 h) and 150°C (2 h). At 150°C, the regenerated lignin from precipitation of [Emim][Ace] was 10.3 %, while the regenerated cellulose was 70 %. Increasing the temperature caused the regenerated lignin to increase, while the regenerated cellulose was decrease. Among the ILs explored, imidazolium acetate is the best IL to regenerate lignin, whereas imidazolium chloride is suitable to regenerate cellulose. The structural and chemical changes of the raw coconut shell and regenerated fractions (lignin and cellulose) properties were characterized by Fourier transform infra-red (FTIR) spectroscopy, thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), differential scanning calorimetry (DSC), X-ray diffraction (XRD) analysis, and proton nuclear magnetic resonance (^{1}H NMR). Recycling and reuse of ILs can develop cost-friendly and green technique process for utilization and fractionation of biomass. The aprotic ionic liquids, [Bmim]Cl, [Bmim][Ace], [Emim][Ace], and [Emim] Cl were recovered and reused up to four times with 90 % recovery. ^{1}H NMR spectra showed no structural changes which indicate no side products were formed during pretreatment process in the recycled aprotic ionic liquids. Thus, it shows that ionic liquids can be environmentally friendly pretreatment solvents to dissolve and fractionate lignin and cellulose.

Keywords: coconut shell, ionic liquids, cellulose, lignin, biomass

MENGEKSTRAK LIGNIN DAN SELULOSA DARIPADA TEMPURUNG KELAPA MENGGUNAKAN CECAIR IONIK

ABSTRAK

Tempurung kelapa, merupakan biomas lignoselulosa semula jadi, yang boleh didapati dengan jumlah yang banyak dalam bentuk sisa pembuangan pertanian di sesebuah negara. Bagi memanfaatkan biomas ini dan menukarkannya kepada produk bernilai tinggi, pelarut alternatif yang efisien diperlukan untuk melarutkan biomas lignoselulosa. Baru-baru ini, cecair ionik telah menarik perhatian kerana ciri-cirinya yang unik; seperti pengabaian tekanan wap, tidak mudah terbakar, dan mempunyai takat lebur yang rendah. Cecair ionik telah menunjukkan bahawa ia boleh melarutkan biomas secara separuh atau sepenuhnya, bergantung kepada jenis biomas. Dalam kajian ini, kami telah menyiasat cecair ionik protik dan aprotik sebagai pelarut prarawatan bagi melarutkan tempurung kelapa. Kecekapan pengekstrakan dipengaruhi oleh suhu, masa, saiz zarah, dan jenis kation dan anion dalam cecair ionik. Kesan pembolehubah prarawatan ini dikaji ke atas komposisi kimia, permukaan morfologi, kehabluran, dan kestabilan haba pada lignin dan selulosa dari tempurung kelapa. Ujian kelarutan biomas ini menunjukkan bahawa cecair ionik aprotik mempunyai prestasi kelarutan yang baik (7 wt %) berbanding cecair ionik protik (1 wt %). Oleh itu, satu siri cecair ionik aprotik, [Bmim][Ace], [Bmim]Cl, [Emim][Ace] dan [Emim]Cl, telah dipilih dan digunakan dalam proses pelarutan dan regenerasi bagi tempurung kelapa. Proses prarawatan optimum untuk pelarutan adalah pada suhu 110°C, manakala julat dari saiz zarah adalah dari 10 ke 63 mikron. Hasil keputusan menunjukkan bahawa pelarutan untuk tempurung kelapa (70 mg tempurung kelapa dalam 1 g pelarut) boleh berlaku dalam cecair ionik aprotik pada 110°C (6 jam) dan 150°C (2 jam). Pada 150 ° C, regenerasi lignin terhasil daripada mendakan [Emim][Ace] adalah 10.3%, manakala regerasi selulosa adalah 70%. Peningkatan suhu mempengaruhi penghasilan regenerasi lignin untuk meningkat, manakala regenerasi selulosa pula menurun. Berdasarkan cecair ionik yang dikaji, imidazolium asetate adalah terbaik untuk regenerasi lignin, manakala imidazolium klorida adalah sesuai untuk regenerasi selulosa. Struktur dan perubahan kimia bagi tempurung kelapa mentah dan regenerasi bagi lignin dan selulosa dianalisa dengan menggunakan spektroskopi inframerah transformasi Fourier (FTIR), analisis termogravimetri (TGA), pancaran pengimbas mikroskop elektron (FESEM), pengimbasan pengkamiran kalorimeter (DSC), pembelauan X-ray (XRD), dan spektroskopi resonan magnet nuklear (^{1}H NMR). Pengitaran semula cecair ionik juga dikaji bagi pengurangan kos dan juga memperkenalkan proses mesra alam untuk meningkatkan penggunaan biomass. Ia telah menunjukkkan bahawa [Bmim]Cl, [Bmim][Ace], [Emim][Ace] dan [Emim]Cl boleh dikitar semula sehingga empat kali dengan perolehan semula sebanyak 90%. ^{1}H NMR spektra tidak menunjukkan sebarang perubahan struktur dimana tiada produk sampingan telah terbentuk semasa proses prarawatan dalam cecair ionik aprotik yang dikitar semula. Oleh itu, ia menunjukkan bahawa cecair ionik boleh menjadi pelarut prarawatan yang mesra alam untuk pelarutan dan regenerasi lignin dan selulosa.

Kata kunci: tempurung kelapa, cecair ionik, selulosa, lignin, biomas

ACKNOWLEDGEMENTS

First and foremost, all praise to Allah, The Almighty God for His Mercy has given me the strength, patience, and blessings to complete this work.

I would like to extend my deepest gratitude to my supervisors, Dr. Azila binti Mohd Idris and Prof. Dr. Yatimah binti Alias for their invaluable guidance, suggestions, tolerance and encouragement throughout my journey.

Not to forget, a warm thank you to all research group members at Centre of Ionic Liquids of University Malaya (UMCiL) and D220 laboratory colleagues for their helps and advices.

Finally, I owe my deepest appreciation to my family for their love, concern and support. None of this would have been possible without their love and support.

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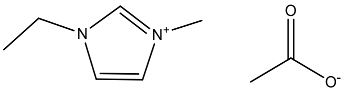
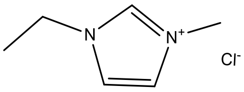
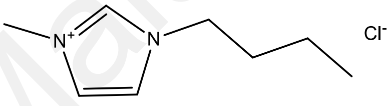
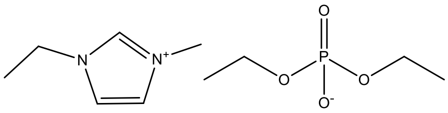
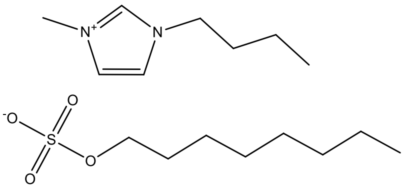
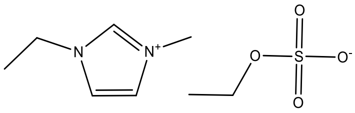
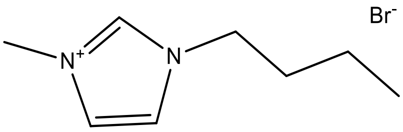
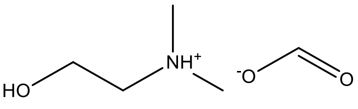
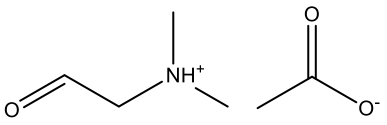
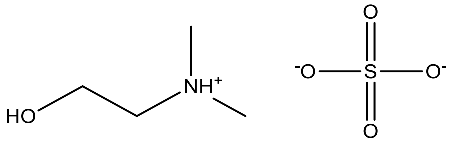
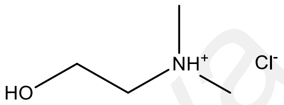
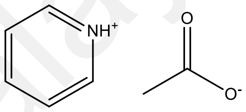
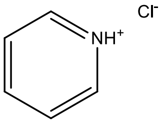
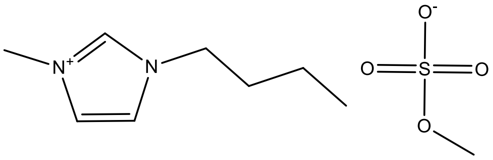
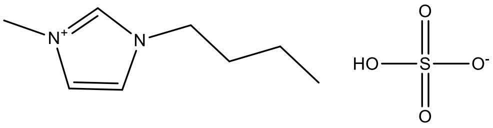
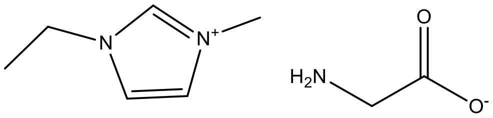
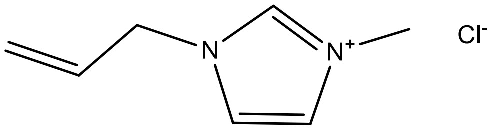
LIST OF SYMBOLS AND ABBREVIATIONS

Abbreviation	Full Name	
[Emim][Ace]	1-ethyl-3-methylimidazolium acetate	
[Emim]Cl	1-ethyl-3-methylimidazolium chloride	
[Bmim][Ace]	1-butyl-3-methylimidazolium acetate	
[Bmim]Cl	1-butyl-3-methylimidazolium chloride	
[Emim][DEP]	1-ethyl-3-methylimidazolium diethyl phosphate	
[Bmim][OS]	1-butyl-3-methylimidazolium octyl sulfate	
[Emim][ESO$_4$]	1-ethyl-3-methylimidazolium ethyl sulfate	
[Bmim]Br	1-butyl-3-methylimidazolium bromide	
[DMEA][HCOO]	*N*,*N*-dimethylethanolammonium formate	

[DMEA][Ace]	*N*,*N*-dimethylethanalommonium acetate	
[DMEA][HSO_4]	*N*,*N*-dimethylethanolammonium sulfate	
[DMEA]Cl	*N*,*N*-dimethylethanolammonium chloride	
[Pyr][Ace]	Pyridinium acetate	
[Pyr]Cl	Pyridinium chloride	
[Bmim][$MeSO_3$]	1-butyl-3-methylimidazolium methyl sulfate	
[Bmim][HSO_4]	1-butyl-3-methylimidazolium hydrogen sulfate	
[Emim][Gly]	1-ethyl-3-methylimidazolium glycine	
[Amim]Cl	1-allyl-3-methylimidazolium chloride	
°C	Degree Celcius	
cm^{-1}	Reciprocal centimeter	
g	Gram	
mg	milligram	
min	minutes	
µm	micrometer	

LIST OF APPENDICES

CHAPTER 1 : INTRODUCTION

1.1 Background

The accumulation of greenhouse gases resulting from over-dependence on nonrenewable fossil fuel, has caused an increase in global warming (Xie & Gathergood, 2013). To counteract this problem, researchers have considered utilizing waste biomass materials and converting them into biorefinery products. Biomass includes all organic matter produced by photosynthesis (Sriram & Shahidehpour, 2005). Lignocellulosic feedstock biorefinery products are derived from agricultural crops or waste biomass, such as wood chips, maize, and corn (Kamm & Kamm, 2004; Cherubinin, 2010; Chandra et al., 2012). Biomass is a great and important source of renewable energy in agriculture-based countries because of the abundant supply and low cost (Stöcker, 2008). This resource could be used in a more efficient manner as a preliminary material in the chemical industry.

Lignocellulosic biomass are derived from plant cell wall (source of biopolymer) that has three main constituents; cellulose, hemicellulose (xylan) and lignin (Guererro et al., 2016). The industrial exploitation of biomass resources are highlighted as a sustainable alternative to petrochemicals. In Malaysia, we have abundant resources of biomass like coconut, palm oil, rubber tree and paddy. In terms of total planted area, coconut is the fourth crucial industrial crop after palm oil, rubber and paddy in our country, while it is an oldest agro-based industry (Sivapragasam, 2008). In future, biorefinery products from agriculture waste can be a source of income in Malaysia. Coconut shell (*Cocos nucifera L.*) is a promising resource for lignocellulosic feedstock biorefinery. Usually the coconut is processed to produce milk, while huge amounts of coconut shell waste are discarded, which is detrimental to the environment because of its poor biodegradability (Goh et al., 2010; FAO, 2013; Kanojia & Jain, 2017). So, the exploitation of coconut shell, trunk and root are yet to be explored and turning these waste into bio-based products. This will reduce the dependence on fossil fuels for the industrial productions.

The role of green chemistry in biomass processing gives the good influence to the environment, economy and consumer. The biomass can be converted into bio-based chemical products, such as glucose, ethanol, furfural, lactic acid, levulinic acid and carbon fibers (Bozell & Petersen, 2010; Gallezot, 2012; Pileidis & Titirici, 2016). The utilization of lignocellulosic biomass into the value added products is presented in

Figure **1.**1.

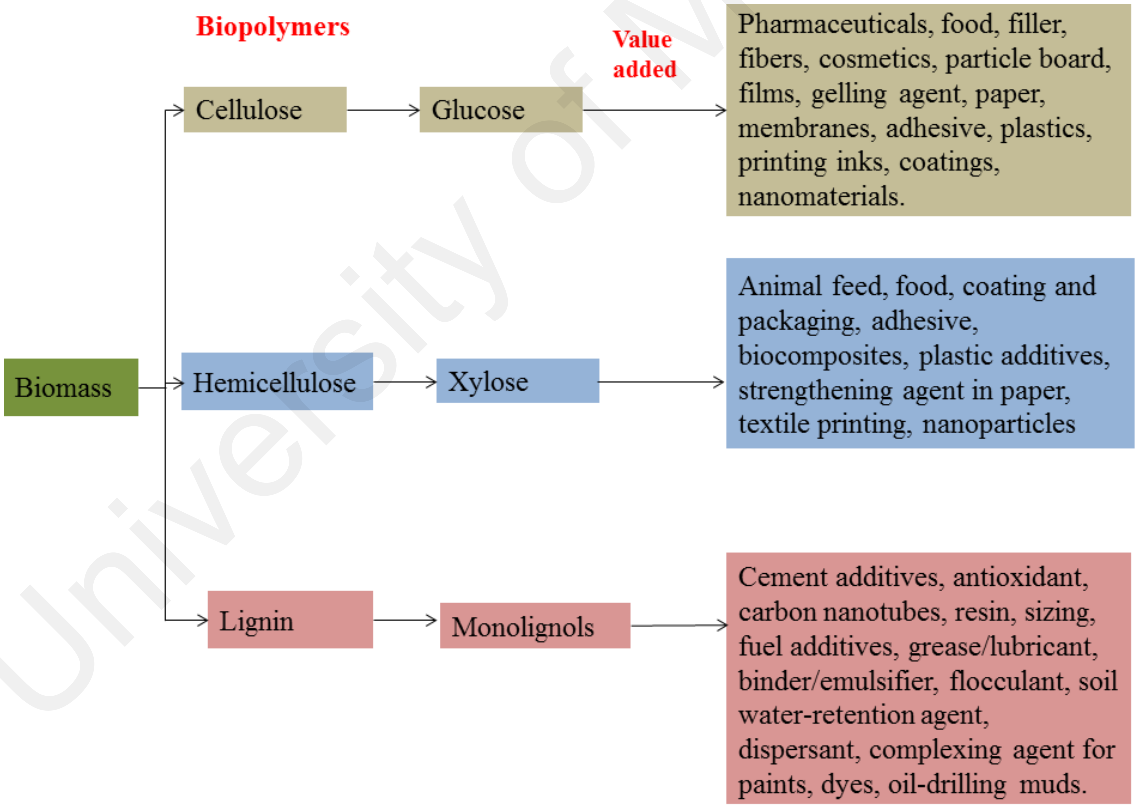


Figure 1.1: Value added products from lignocellulosic biomass (Guererro et al., 2015)

1.2 Problem statement

The excessive dependent on fossil fuels as the main source of energy has led to the diminishing of this non-renewable supply. On the other hand, extreme usage of fossil fuels bring another looming disaster to human being and the mother earth, namely global warming. This has encouraged researchers to replace fossil fuels with inexpensive, ecofriendly and renewable biopolymers. To meet the demands of greener technology industry, lignocellulosic biomass resources are chosen as alternative of renewable biobased materials. Therefore, the development of biomass processing represents the key to access the integrated production of chemicals, food, and energy in the future.

Compositions of plant biomass are highly depending on its source such as hardwoods, softwoods and grasses (Welker et al., 2015). Cellulose fibres are cross-linked in the plant cell walls with hemicellulose, along with the hydrophobic network of lignin that inhibit the production of fermentable sugars from cellulose. While, the structural heterogeneity and recalcitrance of lignin makes it difficult for conversion of cell wall biomass to gain economic value at the industrial level (Li et al., 2011; da Costa Lopes et al., 2013). In order to penetrate into the lignin-carbohydrate complex, the lignocellulosic biomass must undergo the pretreatment process.

Biomass is difficult to dissolve in typical organic solvents and water due to the high crystalline structure of lignocellulosic biomass, which are compact and rigid. The presence of lignin also is a major barrier to enzymatic hydrolysis of cellulose, and inhibit the fermentation of sugar to produce ethanol (Pu et al., 2007; Chaturvedi & Verma, 2013). In order to utilize this biopolymer and convert them into usable materials, there is a need for alternative solvents that efficient to dissolve lignocellulosic biomass.

Ionic liquids (ILs) are generally defined as salts with a melting point below 100 °C, and they contain organic cations and organic/inorganic anions (Welton 1999; Sheldon et al., 2002; Wasserscheid & Welton, 2007). ILs are considered to be green solvents compared with inorganic acids (sulfuric acid, hydrochloric acid, and nitric acid) because ILs have unique characteristics and they are suitable for use in safer and cleaner industries (Sriram & Shahidehpour, 2005). Some distinctive features include a negligible vapour pressure, non-flammability, a low melting point, and they are found in liquid form at ambient atmosphere (Baranyai et al., 2004; Dorn et al., 2008; da Costa Lopes et al., 2013; Xie & Gathergood, 2013).

ILs have been used as the solvent media to dissolve lignocellulosic biomass such as rice husk, Norway spruce sawdust, corn stover, and bamboo (Kilpeläinen et al., 2007; Ang et al., 2012; Yang et al., 2013; Mood et al., 2014). It has been demonstrated that ILs can dissolve these materials partially or completely, depending on the type of lignocellulosic biomass (Sun et al., 2009; Brandt et al., 2011; Mora-Pale et al., 2011). Their tunable properties make ILs capable of being widely used in different fields of applications, such as pharmaceutical, electrochemistry, catalysis, energy, and nanotechnology fields (Pârvulescu & Hardacre 2007; Ohno, 2011; Armand et al., 2009; Wishart, 2009; Dupont & Scholten, 2010; Marrucho et al., 2014).

1.3 Objectives of the study

The overall aim of this project was to investigate the solvency efficiency of ionic liquids in dissolution of coconut shell and evaluate the physiochemical properties of regenerated materials (lignin and cellulose). The physiochemical properties were evaluated on chemical composition, surface morphology, cellulose crystallinity, and thermal stability.

Specifically, this study has the following objectives:

1. To explore the efficiency of protic and aprotic ionic liquids as pretreament solvents in dissolving coconut shell. The ionic liquids were based on;
    i. Imidazolium salts
    ii. Hydroxyl ammonium ionic liquids
2. To study the ionic liquids for dissolution of coconut shell under a variety of conditions including:
    i. Influence of temperature and duration of time
    ii. Influence of particle sizes
    iii. The cation and anion effects on dissolution process
3. To characterise the regenerated lignin and cellulose from the pretreatment process.
4. To investigate the recyclability of ionic liquids for dissolution of coconut shell.

1.4 Thesis outline

This thesis is divided into five chapters which consists of:

Chapter 1: Introduction

In this chapter mentions the main purpose of lignocellulosic biomass that is utilized for the development of sustainable, environmentally friendly, chemicals and materials. The problem statements and objectives were also described in this section.

Chapter 2: Literature Review

This chapter consists of relevant literature of lignocellulosic biomass (hardwoods, softwoods, and grasses). It starts with a brief introduction of the history and background of lignocellulosic biomass followed by the usage of coconut shell as the chosen biomass. The structure of lignocellulosic biomass and the pretreatment techniques related to their utilization are described. The properties of the ionic liquids in the dissolution processes for lignocellulosic biomass are reviewed in details.

Chapter 3: Methodology

The methodology involved the dissolution of coconut shell in protic and aprotic ionic liquids, and conversion into regenerated lignin and cellulose. The regenerated materials are characterized using FTIR, XRD, TGA, ^{1}H NMR, FESEM, DSC, CHNS elemental analysis, and CP-MAS NMR.

Chapter 4: Results and Discussions

This chapter is described the results obtained from the dissolution process and the best ionic liquids to dissolve the coconut shell. The pretreatment process is run under a variety of conditions such as temperature, duration of time, particle sizes and the effect of cation and anion of ionic liquids. Finally, it involves the results and discussion on the recyclability of ionic liquid for dissolution of coconut shell.

Chapter 5: Conclusions and Future Works

This chapter summarizes the main conclusions of this thesis and presents an outlook for future work.

CHAPTER 2 : LITERATURE REVIEW

This chapter consists of the background of lignocellulosic biomass (hardwoods, softwoods, and grasses) followed by the usage of coconut shell as a chosen biomass. The pretreatments methods to dissolve the lignocellulosic biomass and the selection of ionic liquids are reviewed thoroughly.

2.1 Lignocellulosic biomass

Biomass can refer to the mass of one or more species, or to community biomass of all species includes microorganisms, plants, or animals (Xie & Gathergood, 2013). Lignocellulosic biomass is used as a source of raw material and a good alternative to reduce the dependence on the fossil fuels and oil derivatives. Nowadays, biomass has a potential sustainable benefit to ensure the long term feedstock of chemicals, fuels and materials. Lignocellulosic feedstock biorefinery is regenerated in a massive amount of agricultural residues, animal wastes, plant fibers and trees (Kam & Kamm, 2004; Cherubinin, 2010; Chandra et al., 2012). Last decade, there are various types of biomass that undergo lignocellulosic processing, such as bagasse, bamboo, switchgrass, and crop residues (Laopaiboon et al., 2010; Yang et al., 2013; Montalbo-Lomboy & Grewell, 2014). Figure 2.1 shows the examples of various types of lignocellulosic biomass.


Palm tree waste


Crop residue


Switchgrass


Bagasse


Bamboo


Sugarcane

Figure 2.1: Various types of lignocellulosic biomass wastes

Raw lignocellulosic biomass are abundant, cheap, and rich with diversity of species, thus it is an important source of renewable energy in agricultural countries (Stöcker, 2008). This resource could be used in more efficient manner as a preliminary material in the chemical industry.

2.1.1 Compositions of lignocellulosic biomass

Biomass has a strong recalcitrance structure that holds the lignocellulosic building block together (Reddy, 2015). Lignocellulosic biomass is mostly composed of three chemical fractions or precursors, which are cellulose (a glucose polymer), hemicellulose (a sugar polymer predominantly containing pentoses), and lignin (a polymer of phenols) (Sivapragasam, 2008; Xie & Gatherhood 2013). The fraction of cellulose, hemicellulose and lignin contents varies significantly from hardwood, softwood to grasses. For instance, in hardwood, the composition of cellulose, hemicellulose, lignin and others (water extractives and ash content) is around 40-50%, 25-35%, and 5-20% respectively

(Tan et al., 2009). Figure 2.2 displays the source of lignocellulosic biomass derived from the hardwood, softwood, or grasses.

Figure 2.2: The grass, hardwood and softwood lignocellulosic biomass (Schrems et al., 2011; Anwar et al., 2014)

2.1.1.1 Lignin

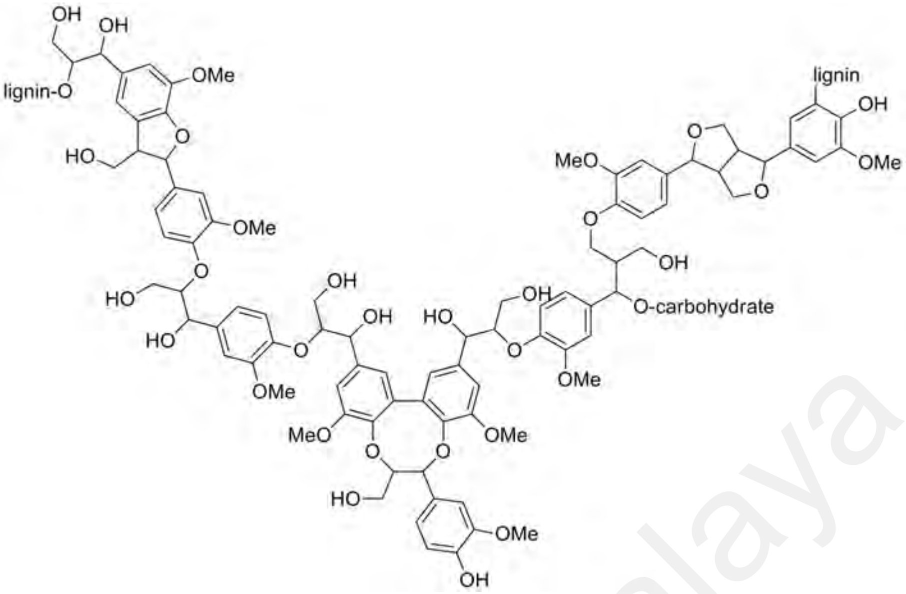


Figure 2.3: Aromatic structure of lignin (Freudenberg & Nash, 1968; Sadeek et al., 2015)

Lignin is a second largest renewable and biodegradable aromatic copolymer in lignocellulosic biomass (Ji et al., 2012). The basic structure of lignin is shown in Figure 2.3. Due to the complexity of lignin structure, the conversion of lignin into chemical products is poorly understood and acknowledged. The growing interest in developing new polyaromatic-based products is driven mainly by the following two facts: first, lignin is a low-cost bioresource with unique functionalities and second, lignin is an environmentally friendly. Lignin has been used as dispersant (Ouyang et al., 2009), binder (Mathiasson & Kubat, 1994), in pharmaceutical process; such as surface coatings, nanoglues (nanoparticles) (Lievonen, 2015).and recently, it gains interest in conversion into carbon fiber (Kubo & Kadla, 2005; Baker & Rials, 2013).

Lignin is derived from the Latin word for wood (lignum) and introduced by de Candolle in 1819. It has a highly complex aromatic heteropolymer and mainly play a biological role in plants to increase cell wall integrity (Brown & Chang, 2014). Furthermore, the amourphous and polyphenolic structure of lignin has arisen from polymerization of phenolpropanoid monomers including: coniferyl, sinapyl, and *p*-coumaryl alcohol (Mathiasson & Kubat, 1994; Pandey, 1999; Kubo & Kadla 2005; Pu et al., 2007; Sivapragasam, 2008; Ouyang et al., 2009; Cesarino et al., 2012; Baker & Rials, 2013). Three monolignol monomers of lignin are presented in Figure 2.4. The composition monomers of lignin and degree of methoxylation are dependent on the source of the species, for example, softwood, hardwood and grasses (Bugg et al., 2011). The softwood lignins are rich in coniferyl alcohol (90%), while hardwood lignins are made of about equal amount of coniferyl and sinapyl alcohols. Whereas, grasses consist of coniferyl and sinapyl alcohol and significant amount of *p*-coumaryl alcohol (10-20%) (Klinke et al., 2004).

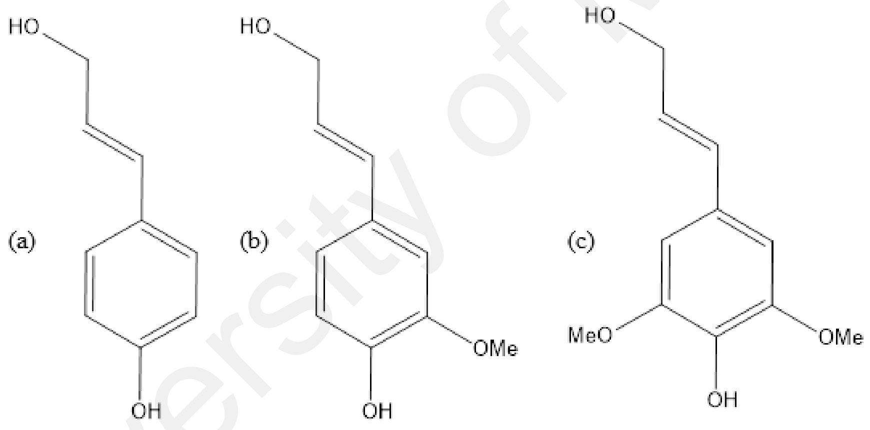


Figure 2.4: Three monolignol monomers of lignin. (a) *p*-coumaryl alcohol, (b) coniferyl alcohol and (c) sinapyl alcohol (Ralph et al., 2004; Doherty Mora-Pale et al., 2011)

Previous literature by Kilpeläinen and co-workers, the lignin provides mechanical strength and high rigidity to resist external forces as it binds the plant cells together (Kilpeläinen et al., 2007). Lignin is a highly branched aromatic polymer that binds cellulose and hemicellulose via strong hydrogen bonding and ester linkages. It acts as "glue binding" in the whole lignocellulosic biomass. This mechanical strength of plants holds the cell walls together and act as a barrier preventing enzymatic attack to cellulose and hemicelluloses. These linkages and molecular interactions cause rigidity and microbial resistance in the lignocellulosic biomass. Lignin behaves differently in solutions compared to cellulose to some extent, therefore the dissolution mechanisms for lignin and cellulose are different. The solubility of cellulose increases almost linearly with hydrogen bonding strength, however, lignin is contradicted (Horwath, 2006; Lee et al., 2009; Vitz et al., 2009; Hart et al., 2015). The strong structure of lignin causes it difficult to be dissolved or extracted in normal organic solvents (Cesarino et al., 2012).

The heterogeneous molecular structure of lignin and depolymerization methods causes the application of lignin to focus on low value products. Lignin is a major obstacle to transform it in biorefining process (Espinoza-Acosta et al., 2014). Thus, selection of the most advantageous pretreatment is a primary concern in order maximize the production of lignocellulosic materials. The effective pretreatment will successfully disrupt the lignin barrier, reduce the crystallinity of cellulose, and recover the biopolymer components. Consequently, some pretreatments have been improved to increase the delignification process. Delignification is defined as a complex process to separate lignin from biomass (Ruiz et al., 2011).

Composition of lignin is dependent on the method of pretreatments, such as physical (microwave, irradiation or milling), chemical (alkaline hydrolysis, organosolv process, wet oxidation and dilute and concentrated of acid hydrolyses) and biological (brown, white and soft fungi) (Sun & Cheng, 2002; Taherzadeh & Karimi, 2008; Kumar et al., 2009; Galbe & Zacchi, 2012). This technique for separation lignocellulosic biomass are mostly destructive where obtained lignin can only be used as low value by products or burnt as a low grade fuel (Zakrzewska et al., 2010; Zhang, 2013). Therefore, an efficient, low-cost technique for the removal and recovery of lignin is important to facilitate easier access to the polysaccharides and produce the valuable side-product streams based on lignin. So, the fractionation of biomass is vital for the implementation of a biorefinery based economy.

2.1.1.2 Cellulose

Carbohydrate is most abundant of polysaccharides and can be divided into; storage polysaccharides (starch, insulin and sucrose) and structural polysaccharides (cellulose, hemicellulose and chitin) (Tzia et al., 2012). Cellulose is a sustainable biopolymer material which it is obtained from lignocellulosic biomass through photosynthesis pathway. It is linked together with β-1,4- glycosidic linkages and has highly crystalline structure due to Van der Waals interactions and hydrogen bonds as shown in Figure 2.5 (Jacobsen & Wyman, 2000; Parthasarathi et al., 2011; Guerriero et al., 2016).

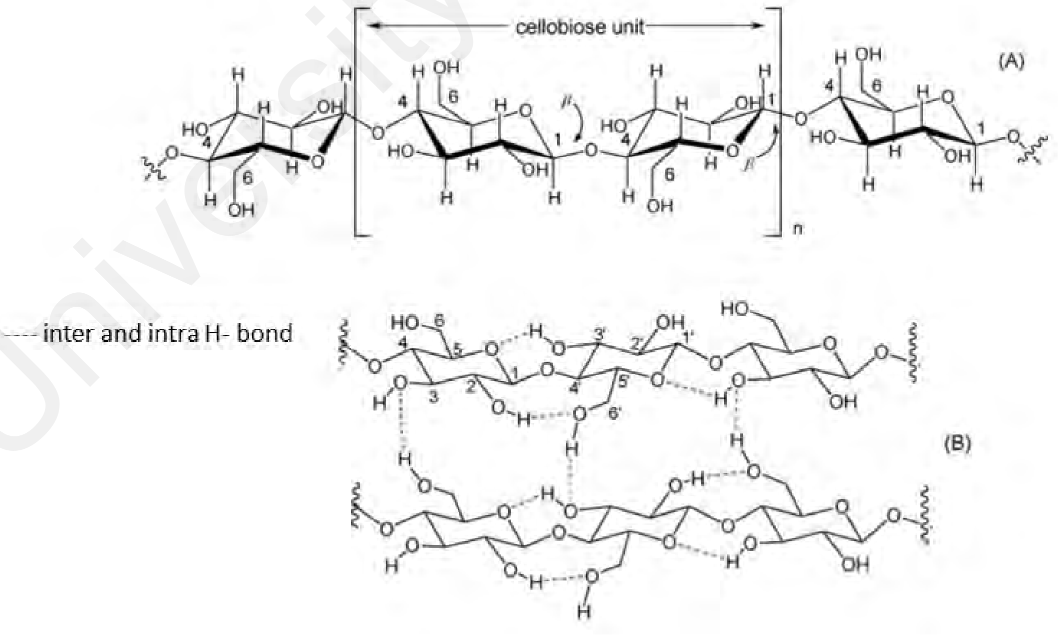


Figure 2.5: The repeating unit of glucose in cellulose structure of the lignocellulosic biomass. (A:Cellulose chain and B:inter and intra-molecular hydrogen (H) bonding present in cellulose) (Olivier-Bourbigou et al., 2010)

The cellulose chains is joined together by hydrogen bonding and held together with hemicellulose and lignin. This allows the growth of large aerial of plants that can withstand the weather and resist the attack by organisms and insects (Clough et al., 2015). The strong interactions bonding cause the biopolymer to be insoluble in the majority of conventional organic solvents. Thus, the recalcitrant structure of cellulose becomes a major challenge to implement these abundant resources (O'sullivan, 1997; Nishiyama et al., 2002; Qian et al., 2005).

Contrary to lignin, cellulose and its derivatives have been widely used in industry, for instance, fibers, tissues, papers, membranes, polymers, paints and medicines. It provides a number of benefits for extensive applications, such as chemical, food and pharmaceutical applications (Farran et al., 2015). To gain access into fermentation sugar production, the complicated structure of this biomass must be broken into biopolymers. Due to physical protection by hemicellulose and lignin, it inhibits the enzymatic hydrolysis (Wyman, 1996). The pretreatment of biomass is required to unlock the strong network in order to increase the enzyme accessibility and to develop the digestibility of cellulose (Sheldon et al. 2009). At the biochemical route, there are three main steps to improve the process, (1) undergoes pretreatment process, (2) conversion polysaccharide to monosaccharide through enzymatic hydrolysis and (3) fermentation of sugars to a combustible fuel (Doherty et al., 2009).

Cellulose is a major part of lignocellulosic biomass that made up of 40-50 % and source of fermentable monosaccharide and bioethanol. Earlier, attention has focused particularly on the pretreatment of lignocellulosic biomass to make the cellulose more accessible to enzymatic hydrolysis. As reported by Chang and Holtzapple (2000), other factors that affect enzymatic hydrolysis are degree of polymerization (DP), moisture content, available surface area and lignin content. Thus, pretreatment process is an important step to improve the digestibility of lignocellulosic biomass as it affects the fractionation of biopolymer productions. It aims to escalate the accessibility and reactivity of the cellulose part from lignocellulosic biomass, while maximize the release of fermentable sugars (monomers) (Doherty et al., 2009).

Currently the pretreatment process to improve the accessibility to ethanol fermentation has been increased significantly (Chaturvedi & Verma, 2013). Pretreatment methods can be categorized into physical (milling), chemical (acid or alkaline hydrolysis), physicochemical (steam explosion, ammonia fiber explosion, supercritical fluids), and biological (white rot fungi). Each pretreatment has different effect on the three main components of biomass, which are cellulose, hemicellulose and lignin.

2.1.1.3 Hemicellulose

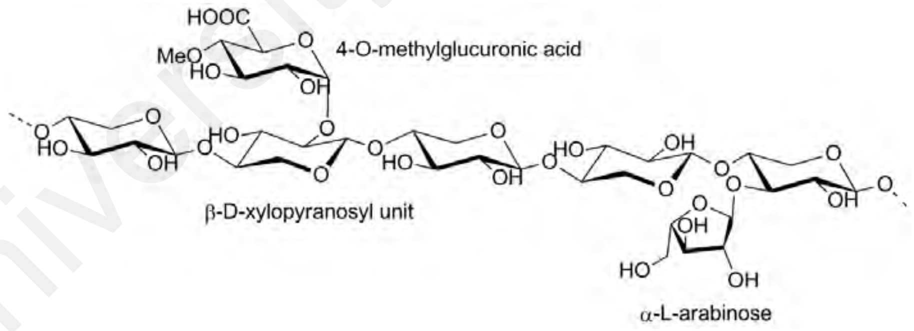


Figure 2.6: Structure of hemicellulose (Balat, 2011)

Hemicellulose is a complex carbohydrate structure which consists of heteropolymer, such as pentoses (xylose and arabinose), hexoses (glucose, galactose, and mannose) and sugar acids (acetic) as shown in Figure 2.6. It is made up 25–35 % of total lignocellulosic biomass and its monomer can be fermented to ethanol similar to cellulose (Jacobsen & Wayman, 2000). The connection between hemicellulose-lignin and cellulose fibers produces strong rigidity network of biomass (Laureano-Perez et al., 2005). Hemicellulose surrounds the cellulose fibers, while it is bonded between cellulose and lignin (about 28 %), while phenylpropane units bound together by ether and carbon-carbon bonds (Farran et al., 2015). The monomer of hemicellulose is dependent on the source of biomass, for example softwood consists of glucomannans, whereas hardwood and agricultural plants contains xylans (Fengel & Wegener, 1984; Saha, 2003; Hendriks & Zeeman, 2009). In acid or alkaline condition, xylan from hardwood can be easily extracted, while alkaline environment is suitable to extract glucomannan (softwood) (Balaban & Ucar, 1999; Fengel & Wegener, 1984; Lawther et al., 1996). Hemicellulose has lower molecular weight which the branches with short lateral chains comprise of different sugars. Therefore, it is easy to hydrolyze the sugar of hemicellulose rather that cellulose (Fengel & Weneger, 1984).

2.2 Lignocellulosic biomass from coconut shell

In this study, coconut shell (Figure 2.7) was selected as a lignocellulosic biomass because it is abundant and not been used commercially. Due to its poor biodegradability, the accumulation of coconut shell is causing environmental and ecological problems (Goh et al., 2010; FAO, 2012; Kanojia & Jain, 2017). The coconut tree, *Cocos nucifera* L., is a source of income, especially in developing countries (Sivapragasam, 2008). It is primarily a plantation crop in Brazil, the Philippines, India, Indonesia, Malaysia, and Sri Lanka (Kumar, 2011). In Malaysia, the production of coconut was estimated around 171 million kg per year (Ratnasingam et al., 2015). The endocarp or inner stone (15–20 %) of coconut is known as shell which the hardest part of coconut (La Mantia et al., 2005; Sarki et al., 2011; Mitan & Razimi, 2016).

Previously, powdered coconut shell was utilized for the biosorption of heavy metals such as cadmium, chromium, and arsenic, which can be extracted by ultrasound to obtain high amounts of phenolic compounds (Pino et al., 2006). Coconut shell can also be used as an effective material precursor in water treatment and removal of impurities, and it produces high-quality activated charcoal (Cobb et al., 2012; Ewansiha et al., 2012). Besides, the green coconut shell also used for adsorption of carbon dioxide (CO_2) from flue gas (Das et al., 2016).

Figure 2.7: Coconut shell from coconut tree

The main components of coconut shell are cellulose, lignin, and hemicelluloses (Rodrigues & Pinto, 2007). It has same main components like wood and contains good properties, such as, small macropores structure, high fixed carbon content and low ash content (Das et al., 2016). Therefore, coconut shell has potential lignocellulosic biomass to be converted into biofuels. In return, it can reduce the waste disposal and alleviate the carbon dioxide (CO_2) emission.

2.3 Types of pretreatment of lignocellulosic biomass

Many factors limit the digestibility of biomass, such as the crystallinity of cellulose, rigidity of lignin content, incompatible solvents and particle sizes (Hendriks & Zeeman, 2009). The lignocellulosic biomass components (cellulose, hemicellulose and lignin) are interlinked together through hydrogen and covalent bonds (Remsing et al., 2008). Hence, the efficient pretreatment must improve the digestibility of the lignocellulosic biomass, increase the accessibility of the cellulose for enzymatic hydrolysis, and increase the percentage yields of biopolymer.

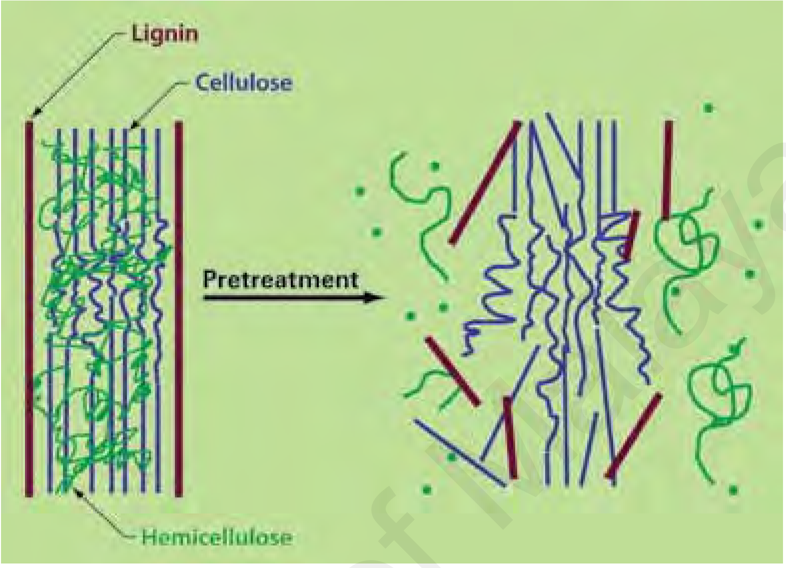


Figure 2.8: Break down the structure of lignocellulosic biomass upon pretreatment (Hsu et al., 1980; Mosier et al., 2005)

Effective pretreatment of biomass is a must process to break down the recalcitrance of lignocellulosic structure and increase digestibility of lignin, hemicellulose and cellulose as shown in Figure 2.8 (Hsu et al., 1980, Pielhop et al., 2016). The concentrated of lignin between the outer layers of the fibers lead to the rigidity of structure and it holds the polymers together about 27 % (Farran et al., 2015). Thus, it makes lignocellulosic biomass become resistant to the chemical and biological pretreatments. According to Tan and co-workers, the glass transition temperature of lignin is around 150 °C, thus high temperature and high pressure are needed during pretreatment process (Tan et al., 2009). Industrial pretreatments; such as steam pretreatment, lime pretreatment, liquid hot water pretreatments and ammonia based pretreatments, are known to use harsh solvents and harsh conditions that contribute to environmental pollutions (Farrán et al., 2015). These techniques for separation lignocellulosic biomass are mostly destructive ways, and the obtained lignin can only be used as low value products or burnt as a low grade fuel (Zhang, 2008; Zakrzewska et al., 2010).

High pressure and temperature conditions cause the cellulose structure to degrade and affect the production of fermentable sugar (glucose) (Vila et al., 2003; Baptista et al., 2008). Delignification of wood techniques, such as Kraft and sulfite processes is the oldest and most common technologies, which involves high energy inputs, uneconomical and potential pollutants due to sulfur containing reagents (Rashid et al., 2016). Most pretreatment processes fractionate raw biomass into cellulose, hemicellulose and lignin components. However, to define which pretreatment method is the best, it depends on the type of biomass and the desired components/products. The conventional pretreatment methods to extract lignin and cellulose from biomass are summarized in Table 2.1 and 2.2.

Table 2.1: Pretreatment methods to process cellulose

Pretreament methods	Definition	Examples	Advantages	Disadvantages	References
Physical	A technique using pulverizer to reduce the size of biomass	Chipping, milling, grinding or shredding	Reduce cellulose crystallinity, reduce the degree of polymerization (DP) and improve hydrolysis	High energy demands	Hendriks & Zeeman, 2009; Brodeur et al., 2011
Physiochemical	Involves high pressure	Steam explosion	Degradation of hemicellulose and transformation of lignin; cost effective	Destruction of xylan region, incomplete dissolution of biomass matrix	Bals et al., 2011
		Ammonia fiber explosion (AFEX)	Increase surface area, delignification and remove hemicellulose	Unable dissolve lignocellulosic biomass with high content of lignin	Kumar et al., 2009
Biology	Employs microorganisms	Soft, brown or white rot fungi	Requires low energy, mild process condition; removal of lignin and hemicellulose feedstock	Rate of saccharafication is lower and time consuming	Sun & Cheng, 2002
Chemical	Involves use of highly concentrated acid and alkaline	Using concentrated acid, like HCl, H_2SO_4, H_2PO_4	Alter lignin structure, hydrolyzes hemicellulose into xylose and other sugars	Corrosion, formation of toxic substance, high cost and cause environmental pollutions	McMillan, 1994; Brodeur et al., 2009
		Use alkaline like lime, calcium or sodium hydroxide and anhydrous ammonia	Delignification process and increase accessibility of enzyme	Long incubation time, formation of irrecoverable salts and cause environmental pollutions	Galbe & Zacchi, 2007

Table 2.2: Pretreatment methods in delignification process of lignin

Pretreatment methods	Examples	Definition	Advantages	Disadvantages	References
Physical	Milling, irradiation, microwave	Involves breakdown of biomass size and crystallinity	Increase the accessible surface area & pore size, reduce cellulose crystallinity	High operational cost, require high energy, low yield fermentable sugars	Brodeur et al., 2011; Hamsen & Huijgen, 2010.
Biology	Fungi	Employs microorganisms and lignolytic enzymes to degrade lignin	Helps in delignification, reduce degree of polymerization (DP), require low energy and chemicals use.	Not suitable for industrial applications, long incubation time.	Sun & Cheng, 2002; Tengerdy & Szakacs, 2003; Cardona & Sanchez, 2007
Chemical	Alkaline pretreatment	Involves the use of bases, such as sodium, potassium, calcium, and ammonium hydroxide	Removal lignin from the biomass, improve the reactivity of the remaining polysaccharides.	Difficulty in recovering hydroxide salts, safety issue raise as ammonium is used and stored in large amount.	Baral, Li, & Jha, 2016; Silva & Ferreira Filho, 2017
	Oxidative delignification	Treatment with an oxidizing agent such as hydrogen peroxide, ozone, oxygen or air	High yield of enzyme hydrolysis, reduce DP, partially or completely hydrolysis of hemicellulose	Harsh condition, affect environment	Taherzadeh & Karimi,2008; Sun & Cheng, 2002
	Dilute and concentrated acid hydrolyses	Employs concentrated acids (H_2SO_4 and HCl) to treat lignocellulosic materials	Flexibility in terms of feedstock choice, high monomeric sugar yield and mild temperature conditions	Require high energy, strong acid cause corrosion, hazardous and toxicity	Jurgens et al. 2012; Sun & Cheng 2002

Table 2.2: continued

	Organosolv process	Use organic solvent or mixtures of organic solvents with water for removal of lignin before enzymatic hydrolysis of the cellulose fraction.	Produce relatively high quality lignin, recover the solvent by distillation, and improve accessibility of the cellulose fibres.	Cause corrosion, cellulose acetylation during pretreatment and high operational cost	Sun & Cheng 2002; Zhao et al.,2009

2.4 Ionic liquids

Ionic liquids have been known for many years and become a major topic of research in chemistry. It exhibits many interesting properties which make them suitable for industrial and medical applications. Ionic liquids (ILs) are generally defined as a salt with melting point below 100 °C and contain organic cation and organic/inorganic anion (Welton, 1999; Sheldon et al., 2002; Wasserscheid & Welton, 2008). It also recognizes as room temperature ionic liquids (RTIL), non-aqueous ionic liquid, molten salt, liquid organic salt and fused salt (Keskin et al., 2007). Unlike molecular solvents, ILs shows distinctive solvation effects under certain circumstances as it contains entirely cation and anion (Mao et al., 2016).

Some distinctive features include a negligible vapour pressure, non-flammability, a low melting point, and they are found in liquid form at ambient atmosphere (Baranyai et al., 2004; Dorn et al., 2008). ILs have lower melting points due to their large ions and delocalized of charges (Greaves & Drummond, 2015). ILs are considered to be green solvents compared with inorganic acids (sulfuric acid, hydrochloric acid, and nitric acid). ILs tends not to give off vapors in contrast to traditional organic solvents such as benzene, acetone, and toluene. Unlike the volatile organic compounds (VOCs), ILs are not explosive due to low or negligible vapour pressure and feasibility to be reused and recycled up to four times, while it reduces the health risks (Li et al., 2011; Liebmann et al., 2012).

Ionic liquids have been used in many applications of chemical industries, for instance, reaction media, lubricants, catalysts and extraction media (Keskin et al., 2007; Farran et al., 2015). In addition, ILs are able to dissolve biomass by disrupting the strong intermolecular and intramolecular hydrogen bonds that keep cellulose, hemicellulose, and lignin in close association (Silva & Ferreira Filho, 2017). ILs also possesses excellent capacity to dissolve many different organic, inorganic and organometallic compounds (Xie & Gathergood, 2013; da Costa Lopes et al., 2013). It could dissolved many compounds including salts, keratin, fats, proteins, amino acids, surfactants, sugars and polysaccharides. Therefore, ILs have been chosen as solvents compared to inorganic acids (Sriram & Shahidehpour, 2005).

Ionic liquids (ILs) are extensively employed in various fields, for instances, bio-catalyst, polymer chemistry and synthesis. Slight modification or combination of organic cation and organic/inorganic of anions, the ILs can be synthesized and used for various specific applications (Farran et al., 2015). Moreover, several studies (Sriram & Shahidehpour, 2005; Mohtar et al., 2017) have reported that the dissolution process to extract lignin and cellulose from lignocellulosic biomass occurs due to destruction of cell wall structure, cellulose crystallinity and cellulose sheathing with hemicelluloses-lignin network. Therefore, it seems that lignocellulosic biomass can be accesibled to dissolve in ILs and fractionate the regenerated lignin, cellulose and hemicellulose.

2.4.1 Types of ionic liquids

Ionic liquids have two types, which are protic and aprotic ionic liquids.

2.4.1.1 Protic ionic liquids

Protic Ionic Liquids (PILs) are a subset of ionic liquids formed by an equimolar combination of a Brösted acid, AH, and a Brösted base, B (Fumino et al., 2009; Greaves & Drummond, 2008). The donation of proton from AH to B will yield a $[BH^+][A^-]$ type. The cation part of PILs able for being hydrogen bond donor, while anion part functions to accept the hydrogen bond.

$$AH + B \rightleftharpoons BH^+ + A^-$$

Several PILs are distillable media where their boiling point and thermal stability occurs at a lower temperature. Due to their unique characteristics, many papers have been published especially in the area of catalysis, physiochemical studies and reaction media (Janus et al., 2006; Iglesias et al., 2010; Anouti et al., 2012). The PILs are cheaper and easier to be prepared as compare to AILs (Greaves & Drummond, 2015; Idris et al., 2014; Rashid et al., 2016). Moreover, it can be distilled from a reaction mixture (Idris et al., 2014). However, AILs are more preferred as a solvent to dissolve biomass because it is stable in high temperature rather than PILs. The solubilisation process of lignocellulosic biomass mostly take place at lower than 100 °C, while AILs can be up to 150–200 °C**.** Although the majority of the published works chose AILs, the interest in PILs has grown in recent years, due to its capacity to establish strong hydrogen bonds.

Achinivu and co-workers (Archinivu et al., 2014) reported that protic acetate (PILs) were studied for delignification of biomass (corn stover) and the lignin extraction was found to be > 50 % w/w. Unfortunately, protic acetates were found to be thermally unstable because of lower degree of protonation (less ionicity) of amines by acetic acid. They also initially demonstrated the solubility of [Pyr][Ace], [Mim][Ace] and [Pyrr][Ace] in commercially available model biopolymers; Kraft lignin, microcrystalline cellulose (MCC) and hemicellulose (xylan). The results showed that Kraft lignin was soluble, while xylan and MCC were insoluble in [Pyr][Ace].

Rashid et al., (2016) synthesized a series pyridinium based protic ionic liquids (pyridinium formate ([Pyr][HCOO]), pyridinium acetate ([Pyr][Ace]), and pyridinium propionate ([Pyr][Pro]). The results showed that [Pyr][HCOO] dissolved up to 70 % (w/w) Kraft lignin compared to [Pyr][Ace] and [Pyr][Pro]. The increase of alkyl chain length of anion and the unstable of thermal stability of PILs influence the solubility of lignin.

2.4.1.2 Aprotic ionic liquids

Aprotic ionic liquids (AILs) are salts consisting solely of cations (which are not protonated) and anions (Freemantle, 2010). Most AILs are generally the combination of alkylated organic cations (imidazolium, pyridinium) and various anions (chloride, bromide, dicyanamide, etc.), typically formed through ion exchange (King et al., 2009). Introduction of aprotic ionic liquid into lignocellulosic biomass dissolution is a great deal to a foundation of sustainable chemical industry by offering varieties of valuable chemical feedstocks.

Imidazolium-based ionic liquids (ILs) with short side alkyl chains have been widely used for the dissolution and delignification of raw lignocellulose materials (Pu et al., 2007; King et al., 2009).). Among the ILs investigated, imidazolium chloride was the most suitable for cellulose dissolution (Dadi et al., 2006; Kilpeläinen et al., 2007; Vitz et al., 2009), whereas imidazolium acetate was the best IL for lignin dissolution (Zakrzewska et al., 2010). Despite their usefulness, AILs possess certain drawbacks namely high viscosity and high operating temperature and recoverability. Apart from these issues, extended dissolution times are required for dissolution of lignocellulosic biomass (generally >12 h), AILs have high thermal stability up to 250 °C compared to PILs.

2.5 Dissolution of lignocellulosic biomass in ionic liquids

In order to utilize the lignocellulosic biomass and convert them into usable materials, there is a need for alternative solvents that efficient in dissolving lignocellulosic biomass. The traditional lignin separation and analysis processes only distrupt the structural information of lignin after hydrolysis of carbohydrate under strong acidic condition (Xie & Gathergood, 2013). Therefore, the main objective of our study is to investigate the use of ionic liquids (ILs) in the dissolution and regeneration of lignin and cellulose from coconut shell, especially in utilizing the unique solvency characteristics and high temperature properties of ILs.

Recently, imidazolium-based ionic liquids (ILs) with short side alkyl chains have been used extensively for the dissolution and delignification of lignocellulosic biomass (Pu et al., 2007; King et al., 2009). Thus, several of ionic liquids demonstrate the ability to selectively dissolve lignocellulosic biomass either partially or completely (Reddy, 2015).

Different ILs shows different levels of the dissolution process because lignocellulosic biomass have two categories; woody and non-woody. Non-woody lignocellulosic biomass demonstrates to be easier to dissolve in ILs compared to woody biomass under the same condition. Solubilisation of lignocellulosic biomass in ILs revealed that it reduces the recalcitrance structure of biomass in order to extract the lignin, cellulose and hemicellulose. During the pretreatment process, the components (cellulose, lignin and hemicellulose) of biomass become accessible to external reagents and catalysts (chemical and biological). This lignocellulosic biomass are dissolved or dispersed in the same medium for conversion processes (Zhang, 2013; Reddy, 2015). The ability of ionic liquids to dissolve lignocellulosic biomass depends on hydrogen basicity, β of anion, hydrogen bonds between cation and anion parts of IL with the chain of lignocellulosic biomass, therefore, each of individual strands can be separated (O'sullivan, 1997; Nishiyama et al., 2002; Qian et al., 2005). Several studies have reported that ionic liquids incorporated with halides, dialkylphosphate/dialkylphosphate, and carboxylate anions shows as a promising candidate for dissolution of lignocellulosic biomass (Swatloski et al., 2002; Fukaya et al., 2008; Xu et al., 2010; King et al., 2011; Ohira et al., 2012).

Previous papers reported that [Amim]Cl and [Bmim]Cl capable to dissolve biopolymer effectively (Swatroski et al., 2002; Pu et al., 2004; Kilpeläinen et al., 2007). [EMIM][Ace] is commonly known to be effective in the dissolution of cellulose (Doherty et al., 2010; Brandt et al., 2013). The solubility of cellulose in ILs are dependent on hydrogen-bond basicity, requiring $\beta > 0.8$ for dissolution to occur (Clough et al., 2015). When the temperature is higher above 150 °C, parts of lignocellulose started to solubilize the hemicellulose and followed by lignin (Bobleter, 1994; Garrote et al., 1999). The ILs that can dissolve various types of biomass are shown in Table 2.3.

Table 2.3: Dissolution of biomass in ionic liquids

Biomass	Ionic Liquids	Conditions	Dissolution (wt %)	References
Norway spruce sawdust	[Amim]Cl [Bmim]Cl	110 °C, 8 h	8	Kilpelainen et al., 2007
Southern pine powder		80 °C, 8 h		
Southern yellow pine	[Bmim]Cl	110 °C, 16 h	5	Sun et al., 2009
Sugarcane	[Bmim][ABS]	190 °C, 2 h	10	Tan et al., 2009
Bamboo	[EMIM][Gly]	120 °C, 8h	5	Muhammad et al., 2011
Pine Sapwood, Debarked willow, *Miscanthus giganteus*	[Bmim][HSO_4] [Bmim][$MeSO_3$] [Bmim][Ace]	120 °C, 22 h	10	Brandt et al., 2011
Bamboo	[Amim]Cl	100 °C, 2 h	5	Yang et al., 2012
Rice hulls	[Emim][Ace]	110 °C, 8 h	1	Lynam et al., 2012
Corncob & rice straw	[Emim][Ace]/ DMA	120 °C, 24 h	5	Weerachanchai & Lee, 2013
Rubberwood	[Bmim]Ac	130 °C, 8 h	5	Darji et al., 2013
Southern Yellow Pine	[Emim]Ac	110 °C, 6 h	5	Cheng et al., 2014
Eucalyptus (stalk)	[Bmim]Br [Emim]Ac [Amim]Cl [Bmim]Cl [Emim]Cl	120 °C, 3 h	5	Xu et al. 2014
Switchgrass	[Bmim]Cl	130 °C, 12 h	10	Lomboy & Grewell, 2014
Macadamia nut	[Emim][Ace]	110 °C, 18 h	5.5	Teh et al., 2015

Table 2.3: continued

Pinus radiate	[Emim][Ace] [Emim]Cl	80 °C, 3 h	5	Torr et al., 2016
Peanut and chestnut shell	[Emim][Ace]	70 °C, 15 h	7	Carneiro et al. 2017

CHAPTER 3 : MATERIALS AND METHODOLOGY

This chapter will discuss the usage of lignocellulosic biomass, protic and aprotic ionic liquids in the current research, their purity and sources. The details of the instruments and equipments are described further below.

3.1 Materials

All chemicals are commercially available and analytical grade, unless otherwise specified. The chemicals were used without further purification, unless otherwise stated. Ionic liquids of 1-ethyl-3-methylimidazolium acetate [Emim][Ace], 1-ethyl-3-methylimidazolium chloide [Emim]Cl, 1-butyl-3-methylimidazolium acetate [Bmim][Ace], and 1-butyl-3-methylimidazolium chloride [Bmim]Cl were purchased from Sigma Aldrich. The other chemicals used in this work were 3,5-dinitrosalicylic acid (>98%), citric acid monohydrate, hydrochloric acid (37%), potassium sodium tartrate tetrahydrate, sodium bisulfite (99%) were purchased from Sigma Aldrich (United States) and sodium hydroxide (Merck Sdn Bhd). The organic solvent such as acetone (ACS Grade, ≥99.5%, Riendenann Schmidr Chemical, Germany), acetonitrile (HPLC grade, 99.8%, Merck, Germany), deuterated dimethyl sulfoxide (DMSO- d_6, 99.8%, Merck) and ethanol (for analysis, ≥99.5%, J.Kollin Chemicals) and methanol (for analysis, ≥99.5%, Merck, Germany) were used without purification.

For synthesizing of protic ionic liquids, *N*,*N*-dimethyletaholamine (99.5 %), pyridine, formic acid (99 %), hydrochloric acid (37 %), glacial acetic acid (99.8 %), sulfuric acid (72 %) were purchased from Sigma-Aldrich and used as received. For NMR analysis, deuterated chloroform ($CDCl_3$) and deuterated dimethyl sulphoxide acid (DMSO-d6) were purchased from Merck Pty., Ltd. unless otherwise stated, all other organic solvents and reagents were used as received from commercial suppliers.

3.1.1 Biomass preparation

Lignocellulosic biomass from coconut shell was purchased in the market and initially washed with water to remove the flesh and impurities. It was dried in an oven at 60 °C for 24 hours to remove the excess water and moisture. The dried coconut shells were ground into small particle sizes. Then the small particle sizes were sieved with Laboratory Test Sieve (BS1377:1990 standard). 200 g of the ground coconut shell was placed into a set of sieves arranged in descending order of fineness and was shaken for 30 minutes. The size of sieves were 10-63 µm, 63-125 µm, 125-250 µm, and 250-500 µm.

3.1.2 Determination of moisture content in coconut shell

The moisture content was determined following the TAPPI method (TAPPI T264 cm-97, 1997). Approximately 1 g of coconut shell was dried overnight in an oven at 105 °C. The sample was cooled in a desiccator containing anhydrous silica (weight of dry sample), until achieving the final weight of the dry sample constant (weight did not change by more than 0.001 g). This measurement was conducted at an interval time 1 to 2 hours.

3.1.3 Determination of ash content in coconut shell

Determination of ash content was carried out according to National Renewable Energy Labratory (NREL) standard method in Determination of Ash in Biomass (NREL/TP-510-42622) (TAPPI T211 om-93, 2002). Sample in the crucible with the lid was ignited to constant weight in a furnace at temperature of 550 °C for 1 hour. It was then cooled and kept in the desiccator before weighing.

3.1.4 Preparation of protic ionic liquids (PILs)

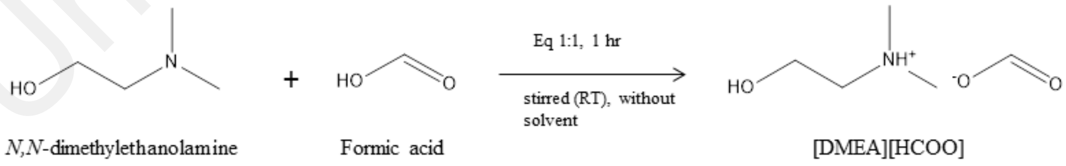
Protic ionic liquids were prepared by an equimolar combination of a Brösted acid, AH, and a Brösted base, B.

$$AH + B \rightleftharpoons BH^+ + A^-$$

The PILs were prepared by simple neutralization reaction. The base was placed in a three-necked flask and equipped with dropping funnel, the acid was dropped wisely into the flask. It was stirred rapidly for 1 hour in an ice bath due to exothermic reaction. Colorless liquid was obtained as a final product. Two bases were chosen (*N*,*N*-dimethylethanolamine and pyridine), while four acids were selected (formic acid, acetic acid, hydrochloric acid and sulfuric acid) and prepared according to Belieres and Angell (2007).

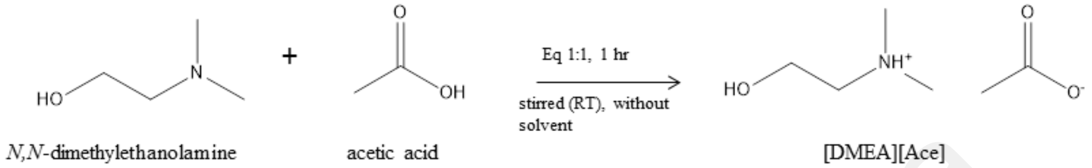
The prepared PILs were dried under vacuum to remove water and excess moisture, which were formed during the reaction. Structural confirmation of the PILs obtained was carried out by ^{1}H NMR (Bruker Advance 400).

3.1.4.1 Preparation of [DMEA][HCOO]



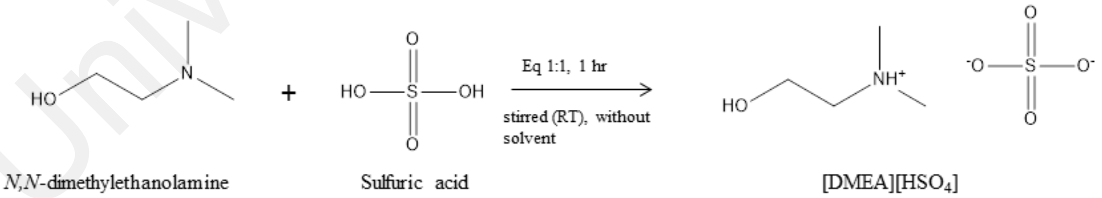
The base was initially placed in a three-necked flask and equipped a dropping funnel. An equimolar amount of formic acid (34.0 g, 0.74 mol) was then added dropwise to the *N*,*N*-dimethyethanolamine (65.96 g, 0.74 mol) while stirring rapidly in an ice bath. The mixture was stirred for 1 h and yielded the colorless liquid as final product: (99.5 g, 99.5%). ^{1}H NMR (ppm, 400 MHz, $CDCl_3$) δH: 8.85 (1H,s, HCOO-), 8.39 (1H, s, $^+$NH), 3.77 (2H, q, CH_2O), 3.35 (1H,s, OH), 3.02 (2H, t, CH_2N), 2.67 (6H, s, CH_3).

3.1.4.2 Preparation [DMEA][Ace]



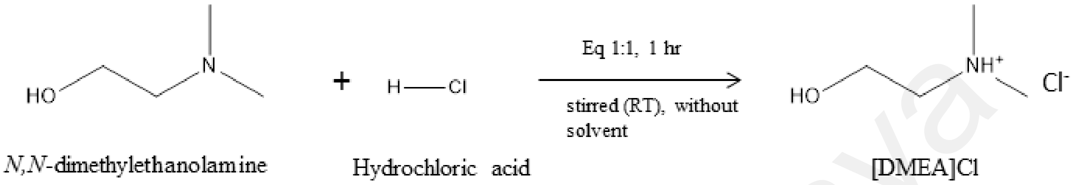
The base was initially placed in a three-necked flask and equipped a dropping funnel. An equimolar amount of acetic acid (51.96 g, 0.74 mol) was then added dropwise to the *N*,*N*-dimethyethanolamine (65.96 g, 0.74 mol) while stirring rapidly in an ice bath. The mixture was stirred for 1 h and yielded the colorless liquid as final product: (99.0 g, 99.0 %). ^{1}H NMR (ppm, 400 MHz, $CDCl_3$) δH: 8.55 (1H, s, $^+$NH), 5.82 (1H,s, OH), 3.77 (2H, q, CH_2), 2.87 (2H, t, CH_2), 2.58 (6H, s, CH_3), 1.92 (2H, s, CH_3).

3.1.4.3 Preparation of [DMEA][HSO4]



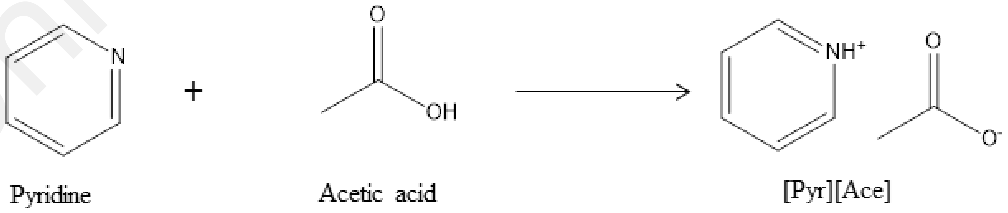
The base was initially placed in a three-necked flask and equipped a dropping funnel. An equimolar amount of sulfuric acid (100.82 g, 0.74 mol) was then added dropwise to the *N*,*N*-dimethyethanolamine (65.96 g, 0.74 mol) while stirring rapidly in an ice bath. The mixture was stirred for 1 h and yielded the colorless liquid as final product: (99.4 g, 99.4%). ^{1}H NMR (ppm, 400 MHz, DMSO-d_6) δH: 7.19 (1H, s,$^+$NH), 4.29 (2H, q, CH_2), 3.73 (1H,s,OH), 3.15 (2H, t, CH_2), 2.76 (6H, s, CH_3).

3.1.4.4 Preparation of [DMEA]Cl



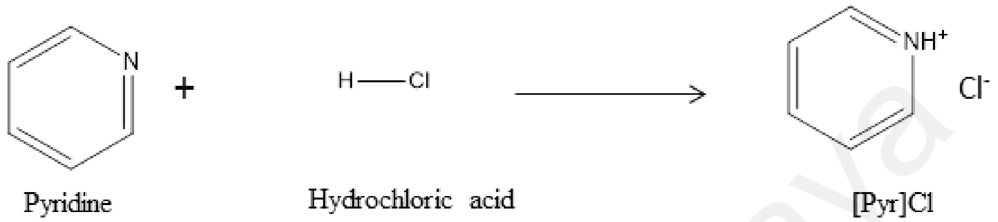
The base was initially placed in a three-necked flask and equipped a dropping funnel. An equimolar amount of hydrochloric acid (74.0 g, 0.74 mol) was then added dropwise to the *N*,*N*-dimethyethanolamine (65.96 g, 0.74 mol) while stirring rapidly in an ice bath. The mixture was stirred for 1 h and yielded the colorless liquid as final product: (99.3 g, 99.3%). ^{1}H NMR (ppm, 400 MHz, DMSO-d_6) δH: 10.35 (1H, s,$^+$NH), 4.27 (2H, q, CH_2), 3.73 (1H,s,OH), 3.15 (2H, t, CH_2), 2.76 (6H, s, CH_3).

3.1.4.5 Preparation of [Pyr][Ace]



The base was initially placed in a three-necked flask and equipped a dropping funnel. An equimolar amount of acetic acid (51.95 g, 0.74 mol) was then added dropwise to the pyridine (5.87 g, 0.74 mol) while stirring rapidly in an ice bath. The mixture was stirred for 1 h and yielded the colorless liquid as final product: (99.2 g, 99.2%). ^{1}H NMR (ppm, 400 MHz, DMSO-d_6) δH: 8.58 (2H, d, CH), 7.8 (1H, t, CH), 7.4 (2H, t, CH), 1.92 (1H,s, CH_3).

3.1.4.6 Preparation of [Pyr]Cl



The base was initially placed in a three-necked flask and equipped a dropping funnel. An equimolar amount of hydrochloric acid (74.0 g, 0.74 mol) was then added dropwise to the pyridine (5.87 g, 0.74 mol) while stirring rapidly in an ice bath. The mixture was stirred for 1 h and yielded the colorless liquid as final product: (99.4 g, 99.4 %). ^{1}H NMR (ppm, 400 MHz, DMSO-d_6) δH: 8.85 (2H, d, CH), 8.64 (1H, t, CH), 8.09 (2H, t, CH).

3.2 Purification and drying of ionic liquids

Ionic liquids were purified and dried using Schlenk line technique to remove the excess water content. This is necessary due to the highly hygroscopic behaviour of ionic liquid. The ionic liquid was dried through continuous stirring under vacuum on a standard Schlenk line. Water evaporation from the ionic liquid was collected in cooling trap. Karl Fischer Coulometric (831 Coulometric Karl Fischer Titrators, Metrohm USA) with ethanol-based hydranal reagents was used to measure the water content of ionic liquids prior to use.

3.3 Dissolution of coconut shell in ionic liquids

The dissolution of coconut shell in ionic liquids was carried out and followed by fractionation of lignin and cellulose according to the method reported by Sun *et al*. (2009) with slight modification. The dissolution of coconut shell in ILs was investigated with various particle sizes. The dissolution process was carried out in glass vials and placed into a heating block, while stirring under a nitrogen (N_2) atmosphere as shown in Figure 3.1. The temperature range of 80-150 °C was used in this study to investigate the dissolution rate in ILs (Tan et al., 2009).

Figure 3.1: The dissolution process of coconut shell in ionic liquids under a N_2 atmosphere

The brownish solution formed was gradually added into the mixture of acetone: water (6:4) and rapidly stirred until resulted in precipitation of regenerated cellulose rich materials. The regenerated cellulose was separated by centrifugation (4000 rpm, 10 min), then dry under vacuum at 60 °C. The regenerated cellulose was fawn-colored solid. The supernatant was transferred to a beaker and allowed the acetone to evaporate at room temperature. The precipitated lignin was separated by vacuum filtration using 0.8 µm nylon filter membrane due to the smaller particle size of lignin. Then the regenerated lignin was dried in the vacuum oven at 60 °C for 4 hour. The regenerated lignin material was a black soft solid.

3.3.1 Solubility test of coconut shell

In order to determine the solubility of the coconut shell, 10 mg of coconut shell was added to 1 g of ionic liquid under stirring condition until it dissolved completely. The complete dissolution process occurred when the particle coconut shell could not be detected by the naked eye. Besides, the microscope was used to detect the small particle. Dissolution was observed rapidly in the first three hours, then the dissolution rate decreased as viscosity of the coconut shell solution increased.

3.4 Recycle of ionic liquids

The ionic liquid was examined for its recyclability as a pretreatment solvent for coconut shell. The remaining liquid fraction from the lignin extraction contain a mixture of IL and water. The recovered ionic liquid was obtained after evaporation of water using a rotary evaporator. The moisture content in ionic liquid was measured using Karl Fischer coulometric (KFC). The recovered ILs was used up to four cycles without any addition of fresh ionic liquid. Prior to use, the recycled ionic liquids are characterized using ^{1}H NMR and TGA.

3.5 Characterization methods

3.5.1 Field emission scanning electron microscope (FESEM)

The morphology of untreated and regenerated coconut shell from various sizes were observed with FESEM (Supra 35 VP-24-58) (Carl Zeiss, Germany) at an acceleration voltage of 5.0 kV.

3.5.2 Fourier transform infrared (FTIR)

The untreated and regenerated cellulose from coconut shell spectra were measured using an attenuated total reflection FTIR Spectrometer (Thermo Nicolet 6700, Waltham, United States). While, the spectra of untreated coconut shell, Kraft lignin and regenerated lignin were obtained by using a Perkin-Elmer Spectrum RX1 FT-IR spectrophotometer, with KBr pellets made up of 1% sample. The FTIR was performed in the wavenumber range of 800 cm $^{-1}$ to 4000 cm^{-1}. The spectra were recorded with a resolution of 4 cm^{-1} with 32 scans. The baseline of spectra were corrected.

3.5.3 Solid state nuclear magnetic resonance (CP-MS NMR)

^{13}C CP-MAS NMR was performed using a Bruker AM300 (Rheinstetten, Germany) instrument equipped with a Bruker 4 mm solid-state probe operating at 75.5MHz. The spectra were collected using a magic angle spinning speed of 5 KHz.

3.5.4 Proton nuclear magnetic resonance (^{1}H NMR)

Purified and recycled ionic liquids were dissolved in deuterated dimethyl sulfoxide (99.8%) and chloroform (99.8%) (Sigma Aldrich) solvents. The proton (^{1}H) spectra of the dissolved sample were recorded using Bruker Spectrometer operating at 400 MHz (Rheinstetten, Germany). For each sample was accumulated at 32 scans. Chemical shifts are reported in ppm on the δ scale. Chemical shifts were calibrated on the solvent peak unless otherwise specified.

3.5.5 Thermogravimetric analysis (TGA)

Thermal stability of the coconut shell and regenerated cellulose and lignin were carried out by using Perkin Elmer Pyris 400 TGA (Waltham, United States). The average weight of a sample (~5 mg) was placed in a ceramic pan and heated from 40 °C to 900 °C at a rate of 20 °C min^{-1} in a flowing nitrogen atmosphere. The instrument was calibrated using nickel as a reference material.

3.5.6 Powder x-ray diffraction (XRD)

Powder x-ray diffraction (XRD) patterns were obtained to measure the coconut shell crystallinity by calculating the area under the peaks. The XRD spectra obtained from Bruker D8 Discover X-ray diffractometer (XRD) (Madison, United States) using CuKα1 as radiation source. For each experiment, approximately 1-2 mg of finely ground sample was placed on a locally designed flat brass sample holder fitted with an O-ring sealed Mylar sheet providing an airtight atmosphere. The sample was scanned and recorded with 2θ, from 5 to 50° and with a step size of 0.02°.

The crystallinity index (CrI) for native cellulose was calculated (Eq 1) by Segal et al.,(1959) using peak height method.

$$\mathrm{CrI}\ (\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \qquad (1)$$

Where I_{002} was the maximum intensity of the 002 crystalline portion at 22° and Iam the height between the 002 and 101 peaks, amorphous portion sample at $2\theta = \sim 15$.

3.5.7 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was conducted on a TA Instruments DSC Q200 (New Castle, Delaware) with 5–10 mg of sample in closed aluminium pans, at a ramp rate of 10 ℃ min^{-1}. The untreated coconut shell and regenerated lignin samples were heated from room temperature to 200 ℃. The transition temperature is reported using the peak maximum of the thermal transition, while glass transition temperature (T_g) was defined as the midpoint of the temperature range at which the change in heat capacity occurred.

3.5.8 Elemental analysis

Carbon, hydrogen, nitrogen and sulfur analysis were performed on Perkin Elmer Series II 2400 CHN/S Analyzer (Waltham, USA). The sample was weighted around 1.5-2.0 mg weight averages.

CHAPTER 4 : RESULTS AND DISCUSSION

Recent years, the utilization of lignin as the potential feedstock for chemical production attracts more attention due to its outstanding characteristics as renewable, low-cost and high availability. The bioconversion of lignocellulosic biomass to glucose is well-known part for second generation of biofuel production. Therefore, a pretreatment process is a first stage to disrupt the holocellulosic components of biomass and to fractionate the lignin and cellulose. It is an important process before converted into valuable products. The aim of this study is to explore the efficiency of protic and aprotic ionic liquids as pretreament solvents in dissolving coconut shell and fractionate into the lignin and cellulose. Section 4.1 shows the protic and aprotic ionic liquids underwent solubilisation process to determine which ionic liquids have good solvency characteristics to dissolve coconut shell. Section 4.2 explores the aprotic ionic liquids under variety of conditions including temperature, duration of time, particle sizes, and the cations and anions of ionic liquids. The successful extraction of regenerated lignin and cellulose will be discussed in Section 4.3 and Section 4.4, followed by determination of recyclability of reused ionic liquids in dissolution of coconut shell in Section 4.5.

4.1 Dissolution of coconut shell in ionic liquids

Prior to starting the pretreatment process, selecting the types of ionic liquids are the most crucial parameter that need to be considered. Ionic liquids have been shown to be capable of dissolving lignocellulosic biomass and other biopolymers (Freire et al., 2011; Montalbo-Lomboy & Grewell, 2014; Sun et al., 2011). There are a few general characteristics of the cation and anion likely to lead on dissolution process (Greaves & Drummond, 2015). Although imidazolium-based aprotic ionic liquids (AILs) have predominantly used in dissolution of lignocellulosic biomass, however these ILs cannot easily removed from substrate. In order to address this issue, protic ILs recently gain interest as they are relatively are less expensive, easy to synthesize and are potentially distillable. Hence, in this study, the dissolution of coconut shell was conducted in two types of ionic liquids, which were protic and aprotic. To our knowledge, ionic liquids have not been investigated yet with coconut shell and it is not been used commercially. Therefore, protic and aprotic ionic liquids were screened to determine their ability to dissolve the coconut shell.

4.1.1 Dissolution of coconut shell in protic ionic liquids (PILs)

4.1.1.1 Synthesis of PILs

Six types of protic ionic liquids were successfully synthesized using simple neutralization reaction between bases (*N*,*N*-dimethylethanolamine and pyridine) and acids (formic acid, acetic acid, sulphuric acid and hydrochloric acid). A series of distillable PILs were prepared as a pretreatment solvent for coconut shell. The synthesized protic ionic liquids are *N*,*N*-dimethylethanolammonium formate ([DMEA][HCOO]), *N*,*N*-dimethylethanolammonium acetate ([DMEA][Ace]), *N*,*N*-dimethylethanolammonium sulfate ([DMEA][HSO_4]), *N*,*N*-dimethylethanolammonium chloride ([DMEA]Cl), pyridinium acetate ([Pyr][Ace]), and pyridinium chloride ([Pyr]Cl). Figure 4.1 shows the neutralization reaction to synthesize dimethylethanolammonium formate ([DMEA] [HCOO]). Prior to use, the water content of PILs was determined by Karl Fischer coulometer and recorded to be less than 0.001%.

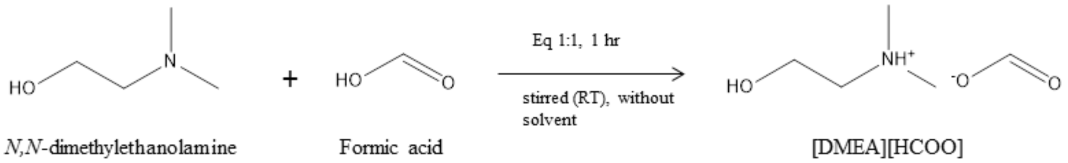


Figure 4.1: Synthesis of [DMEA][HCOO]

The structure of protic ionic liquids were confirmed by ^{1}H NMR spectroscopy. Figure 4.2 represents the ^{1}H NMR spectra of *N*,*N*-dimethylethanolammonium formate ([DMEA][HCOO]). It was prepared by neutralization of *N*,*N*-dimethylethanolamine with formic acid and yield colorless liquid as final product. The mixture was stirred for 1 h and yielded the colorless liquid as final product: (99.5 g, 99.5%). ^{1}H NMR (ppm, 400 MHz, $CDCl_3$) δH: 8.85 (1H,s, HCOO-), 8.39 (1H, s, $^+$NH), 3.77 (2H, q, CH_2O), 3.35 (1H,s, OH), 3.02 (2H, t, CH_2N), 2.67 (6H, s, CH_3).

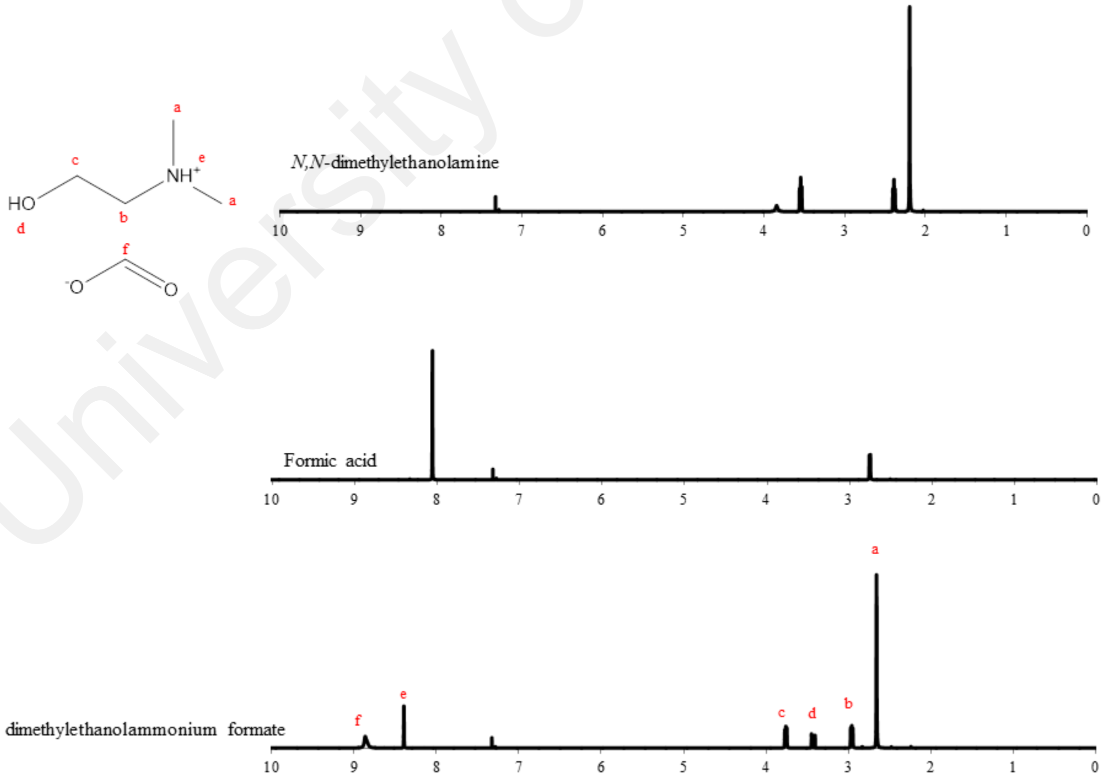


Figure 4.2: ^{1}H NMR spectroscopy of [DMEA][HCOO]

^{1}H NMR spectra to confirm the structure of synthesized PILs are shown in Appendix A.

4.1.1.2 Solubility of coconut shell in synthesized PILs

The powdered of coconut shell was dissolved in a series of synthesized PILs. The solubilisation process was done by adding small incremental amounts of coconut shell (10 mg) to the PILs (1 g). The dissolution process was taken place at room temperature, 80 and 90 °C, however, no dissolution was observed. Then, the temperature was increased to 100 °C, the changes of color were observed. The complete dissolution was only recorded in [DMEA]Cl (1 wt %) at 100 °C as shown in Table 4.1. This temperature was chosen in this study due to the lignocellulosic structure at some level becoming unfolded at the elevated temperature, hence permitting more interaction between coconut shell and the PILs (Idris et al., 2014).

Table 4.1: Solubility experiment of coconut shell in protic ionic liquids at 100°C (6h)

Protic Ionic Liquids (PILs)	Coconut shell (mg) / IL (g) dissolved
[DMEA][HCOO]	Not dissolved
[DMEA][Ace]	Not dissolved
[DMEA]Cl	10
[DMEA][HSO_4]	Not dissolved
[Pyr][Ace]	Not dissolved
[Pyr]Cl	Not dissolved

The results show that PILs gave poor ability to dissolve coconut shell. The solubility exhibit only [DMEA]Cl dissolved coconut shell (1 wt %) compared to other PILs. [DMEA]Cl displayed good solubility of coconut shell compared to [Pyr]Cl. Increase temperature affects the dissolution process of coconut shell in PILs, where the solubility was observed at 100 °C. According to Idris et al. reported the thermally unstable of PILs caused the lower degree of protonation and make them less ‘ionic’ to dissolve the solute (Horvath, 2009; Idris et al., 2014). This suggests that the solubility of biopolymer and biomass in PILs may originate from interaction with salt ions.

Previously, the PILs were tested their ability to dissolve in commercial available biomass components (microcrystalline cellulose, Kraft lignin and xylan) and showed good solubility (Achinivu et al., 2014; Rashid et al., 2016). But, when PILs were further investigated using real biomass (coconut shell), they seemed to have very poor performance. This shows that the lignocellusic structure of biomass difficult to dissolve in PILs.

4.1.2 Dissolution of coconut shell in aprotic ionic liquids (AILs)

The powdered coconut shell was dissolved with a series of AILs to determine their ability to dissolve the coconut shell.

4.1.2.1 Solubility of coconut shell in AILs

Initially, the dissolution of coconut shell were attempted at room temperature, 80, 90 and 100 °C, however, no dissolution was observed. This could have been due to the highly crystalline structure of the lignocellulosic biomass (Stöcker, 2008). At 110 °C, the coconut shell was completely dissolved in the ILs, which due to the network of hydrogen bonds was destabilized during the solubility of the coconut shell (Kilpeläinen et al., 2007; Xu et al., 2010). Table 4.2 shows the solubility of coconut shell in several AILs with the sequential addition of 10 mg of coconut shell in 1 g of AILs. The process was carried out at 110 °C for 6 hours with mechanical stirring until the point where the powdered coconut shell could not be visually seen. If none were present, further amounts were added stepwise until the material was observed to not properly dissolve further.

Table 4.2: Solubility testing of coconut shell in AILs

Ionic Liquids (IL)	**Coconut shell (mg)/ IL(g) dissolved**
[Emim][DEP]	<10
[Bmim][OS]	<10
[Emim][ESO$_4$]	<10
[Bmim]Br	<10
[Bmim][Ace]	70
[Bmim]Cl	70
[Emim][Ace]	70
[Emim]Cl	70

The solubility results showed low dissolution of coconut shell in [Emim][DEP], [Bmim][OS], [Emim][ESO$_4$], and [Bmim]Br, which was likely due to the low viscosities and thermal stabilities of those ILs (Swatloski et al., 2002). The reason for this can be related to the weak hydrogen bond basicity of those ILs as well as their low dipolarity. Although, Brandt and co-workers reported the high solubility of lignin was observed in the ionic liquid that based on the sulfate anion (Brandt et al., 2013). On the contrary, in this study, the lower solubility of coconut shell in sulfate salt was obtained.

The highest solubility of coconut shell was found in [Bmim][Ace], [Bmim]Cl, [Emim][Ace] and [Emim]Cl; which were up to 70 mg (coconut shell) g^{-1} (IL). The complete dissolution was confirmed by using microscope and a laser beam via scattering to detect any presence of small particles. Since, [Bmim][Ace], [Bmim]Cl, [Emim][Ace] and [Emim]Cl showed good solubility, therefore, these AILS were selected to determine the extraction efficiency of lignin and cellulose from coconut shell.

Thermal properties and decompositions of AILs; [Bmim][Ace], [Bmim]Cl, [Emim][Ace] and [Emim]Cl were conducted by using thermogravimetric analysis (TGA). The plot of weight percent loss temperature in the Figure 4.3 represents the thermal decomposition of four AILs. The temperature near ~100 °C corresponds to the drying period where evaporation of water occurred. The stability of [Bmim]Cl and [Emim]Cl were stable up to 260 °C, while the [Bmim][Ace] and [Emim][Ace] being slightly lower up to 220 °C. Thus, [Bmim][Ace], [Bmim]Cl, [Emim][Ace] and [Emim]Cl were the best candidate for further study in this work.

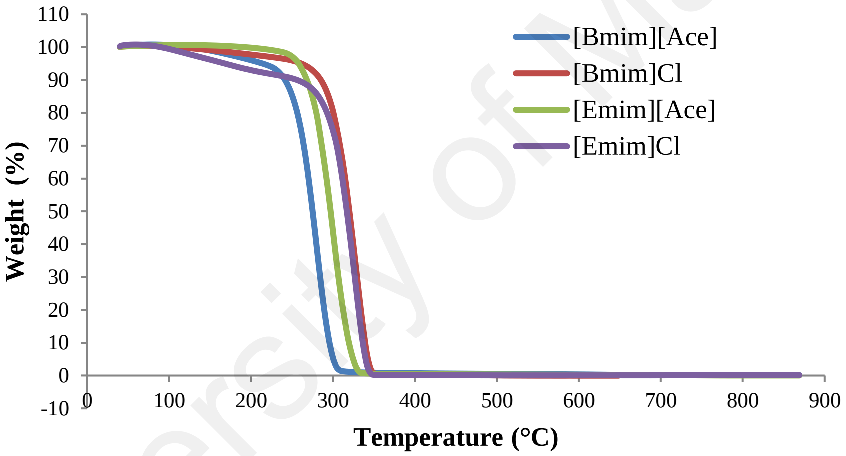


Figure 4.3: TGA curve of fresh aprotic ionic liquids

4.1.3 Summary of solubility experiments

From the solubility experiment, it can be concluded that AILs have good solvency characteristics than PILs. It was observed that [Bmim][Ace], [Bmim]Cl, [Emim][Ace], and [Emim]Cl displayed better efficiency compared with PILs, where the highest dissolution of coconut shell was recorded up to 7 wt %. Complete dissolution of powdered coconut shell was achieved in aprotic ionic liquids at 110 °C for 6 hours with the smallest particle size (10-63 µm). Imidazolium-based ionic liquids have high polarity due to their ionic characters, resulting in enhanced lignocellulosic biomass dissolving capacity (Pinkert et al., 2009). Therefore, the dissolution effects of coconut shell in [Bmim][Ace], [Bmim]Cl, [Emim][Ace] and [Emim]Cl were investigated. The ionic liquids for dissolution of coconut shell under a variety of conditions, including temperature, duration of time, particle sizes, cation and anion of ionic liquids were also studied.

4.2 Dissolution of coconut shell in aprotic ionic liquids

In earlier study (section 4.1), AILs was proved to have good solvency characteristics during the dissolution process. Therefore, the ionic liquids were based on imidazolium-salt of various anions were conducted under variety of conditions including various particle sizes, temperature, duration of time, and efficiency of recycled ionic liquids. The variety of conditions of pretreatment process will be discussed in details below.

4.2.1 Effect of particle size

In order to increase the dissolution of lignocellulosic biomass, milling or grinding is important step to obtain smaller particle size. Small particle size of solutes provides a larger surface area, resulting higher rate of dissolution compared to large particle size of solutes. Coconut shell is hard lignocellulosic biomass that has thick cell wall, thus, reduction on particle size is a crucial step before undergo pretreatment process.

The surface morphology of coconut shell at different sizes were analyzed through field emission scanning electron micrograph (FESEM). Figure 4.4 shows the FESEM images of coconut shell at different particle sizes (a) 250-500 µm, (b) 125-250 µm, (c) 63-125 µm and (d) 10-63 µm. Long and large sizes of rod shaped materials are clearly seen in Figure 4.6 (a) and (b). While tiny rod shaped fiber and size reduction were observed at smaller particle size in Figure 4.6 (c) and (d). These various sizes of coconut shell were further dissolved in aprotic ionic liquids to identify their dissolution rate at 110 °C.

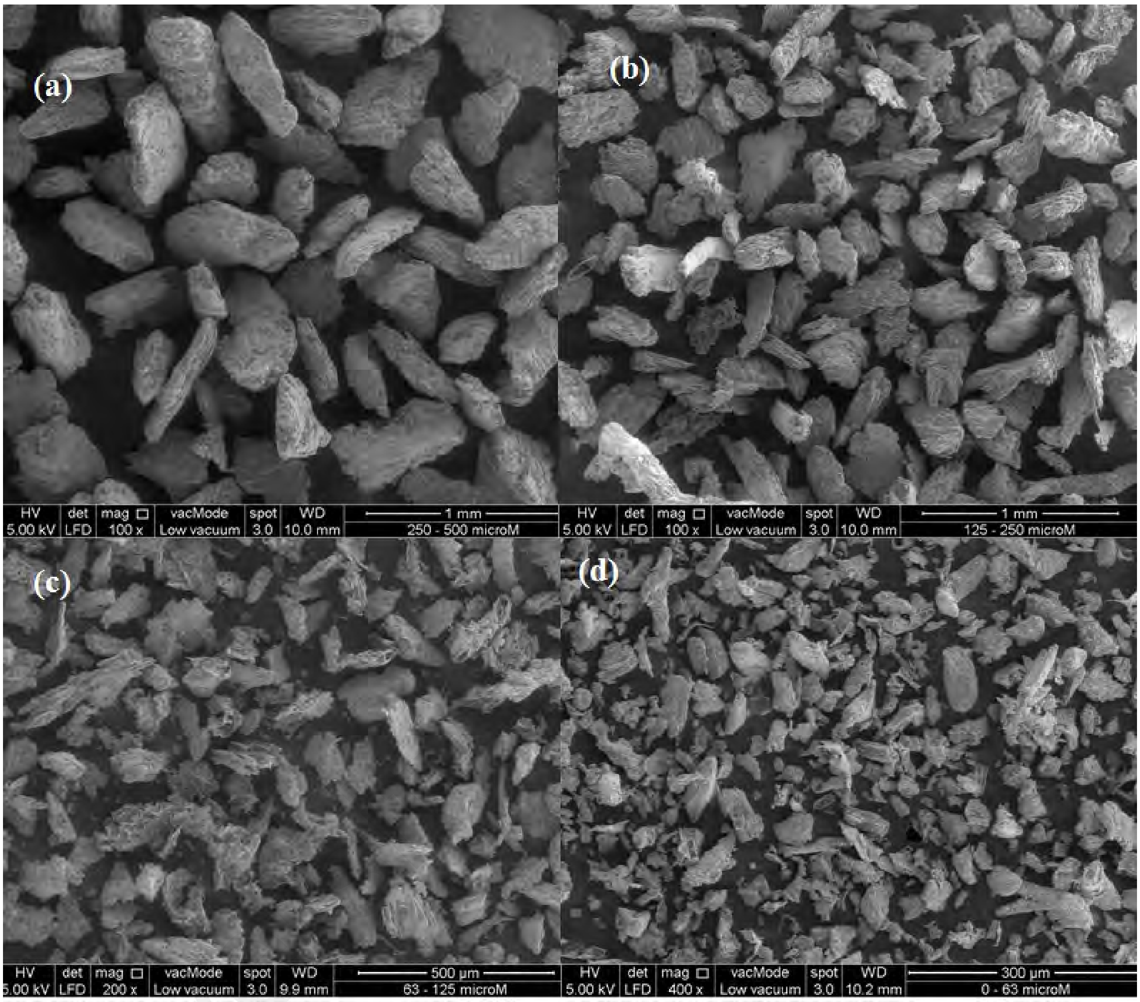


Figure 4.4: FESEM images of coconut shell at different particle sizes (a) 250 – 500 µm, (b) 125 – 250 µm, (c) 63- 125 µm and (d) 10-63 µm

Initially, different particle sizes of coconut shell (70 mg) were dissolved in 1 g of [Emim][Ace], [Emim]Cl, [Bmim][Ace] and [Bmim]Cl to determine the mass regenerated of coconut shell within 10 hours as shown in Table 4.3. It is important to select the right particle size of biomass in dissolving with ionic liquids.

Table 4.3: The dissolution of coconut shell with various particle sizes at 110 °C

Ionic liquids	**Particle size (μm)**	**Dissolution time (h)**	**Mass of biomass dissolved (mg)**	**Mass of regenerated biomass (mg)**	**Percentage of regenerated yield (%±2)**
[Emim][Ace]	10-63	10	70	68.2	97.4
	63- 125	10	70	58.4	83.4
	125-250	10	70	45.0	64.3
	250-500	10	70	33.1	47.3
[Emim]Cl	10-63	10	70	65.6	93.7
	63- 125	10	70	54.7	78.1
	125-250	10	70	40.9	58.4
	250-500	10	70	30.9	44.1
[Bmim][Ace]	10-63	10	70	66.6	95.1
	63- 125	10	70	56.8	81.1
	125-250	10	70	43.5	62.1
	250-500	10	70	31.9	45.6
[Bmim]Cl	10-63	10	70	63.9	91.3
	63- 125	10	70	50.1	71.6
	125-250	10	70	39.3	56.1
	250-500	10	70	28.1	40.1

The mixture of biomass and ionic liquids caused the increase of transparency and viscosity. During pretreatment process, once the coconut shell was added into AILs and started to dissolve, the color started to change (brown to black color) after 30 min. The color indicated the presence of the soluble lignin fraction in the ILs (Sun & Cheng, 2002; Kilpeläinen et al., 2007). It was crucial to choose the right particle size for dissolving the lignocellulosic biomass in ILs. According to Leskinen et al. (2013) indicated that the particle sizes and milling types affect the dissolution of sawdust in ILs. In addition, Padmanabhan et al., (2011) reported that the reduction of particle size of Miscanthus wood also reduced the dissolution time. Therefore, the percentage of regenerated material of coconut shell was affected by particle sizes of lignocellulosic biomass.

Ionic liquids exhibit interesting properties where it dissolved coconut shell even at larger particle size (250-500 μm). However, a better and efficient solubility of coconut shell in AILs were obtained for smaller particle size (10-63 μm); where [Emim][Ace]

(97.4 %), [Emim]Cl (93.7 %), [Bmim][Ace] (95.1 %) and [Bmim]Cl (91.3 %). This was due to the larger surface area, which allowed the IL to easily penetrate and break the lignocellulosic network (Sun et al., 2009).

4.2.2 Effect of temperature and duration of time

There are several factors to be explored to improve the solubilisation of coconut shell including the effect of various temperature and duration of time. Initially, the dissolutions of coconut shell were attempted at room temperature, 80, 90 and 100 °C, however, no dissolution was observed (as mentioned in 4.1.2.1). According to Espinoza-Acosta et al., (2014) high temperature and long incubation time influence the yield of regenerated materials from lignocellulosic biomass. In this study, 70 mg of coconut shell in 1 g of AIL, the dissolution process was carried out at different temperature (110, 130 and 150 °C) and duration of time.

Table 4.4 shows the percentage of the regenerated lignin and cellulose from aprotic ionic liquids at 110 °C (6 h), 130 °C (4 h) and 150 °C (2 h). At high temperature, the swollen of coconut shell structure permits further interaction between coconut shell an ionic liquids. The aim of this section is to investigate the percentage of regenerated lignin and cellulose from coconut shell in various temperature. No precipitate was observed when complete dissolution occurred at 110, 130 and 150 °C. The mixture of coconut shell in [Bmim][Ace] and [Bmim]Cl were detected to have slightly higher viscosities compared to [Emim][Ace] and [Emim]Cl. This was regarded to the fact that the viscosity of [Bmim][Ace] and [Bmim]Cl were higher compared to [Emim][Ace] and [Emim]Cl.

Table 4.4: Percentage of regenerated lignin and cellulose from AILs at various temperature and time

Ionic Liquid	Temperature (°C)	Time (h)	Percentage of regenerated lignin (%)	Percentage of regenerated cellulose (%)
[Bmim][Ace]	110	6	4.1	82.5
	130	4	5.6	80.4
	150	2	8.6	78.0
[Bmim]Cl	110	6	2.8	84.6
	130	4	3.1	82.7
	150	2	3.5	80.0
[Emim][Ace]	110	6	5.3	78.5
	130	4	7.2	74.8
	150	2	10.3	70.0
[Emim]Cl	110	6	2.8	85.1
	130	4	4.6	83.6
	150	2	4.3	81.1

The results illustrate that percentage of lignin improved, while the percentage of cellulose decreased when the temperature increased to 150 °C. This could be due to the breaking of cellulose-lignin network at high temperature. Li and co-workers also stated that the yield of regenerated lignin increases from 160 °C to 190 °C (Li et al., 2011). It indicates a high temperature accelerate the separation of cellulose and lignin. This lead to increase the precipitation of free lignin and decrease the regenerated cellulose. From the results, at 150 °C, the regenerated lignin from AILs increased, while the regenerated cellulose decreased. This also agreed with Tan and co-workers, where they found the delignification of biomass occurred by increasing the temperature above glass transition (T_g) of lignin (170-190 °C) (Tan et al., 2009).

According to the findings from Table 4.4, high temperature showed increase of the regenerated lignin from [Emim][Ace] and [Bmim][Ace], which were 10.3 % and 8.6 %, compared to the regenerated of lignin from [Emim]Cl and [Bmim]Cl (4.5 % and 3.6 %). While the regenerated of cellulose from AILs were completely decrease when increase of temperature from 110 °C to 150 °C. This could be due to the breaking of cellulose-lignin network at high temperature. Among AILs, [Emim][Ace] displayed good performance to fractionate 10.3 % of regenerated lignin from coconut shell. [Emim][Ace] also shows good solubility in macadamia nut shell, rice hull and other wood-based biomass (Lynam et al., 2012; Sun et al., 2009; Teh et al., 2015).

4.2.3 The effect of cation and anion of ionic liquids in the dissolution process

Certain lignocellulosic biomass such as cellulose, lignin, and wood are difficult to dissolve and have very limited solubility in water and organic solvents. However, these lignocellulosic biomass can be dissolved in ionic liquids. Swelling and dissolution of the biomass depend on the types of cation and anion in the ILs (George et al., 2011). Figure 4.5 and 4.6 represents the percentage of regenerated lignin and cellulose in AILs at different particle sizes at 110 °C, respectively.

Imidazolium-based ILs have high polarities because of their ionic characteristics, resulting in enhanced biopolymer dissolving capacities (Pinkert et al., 2009). Previous studies demonstrate that, imidazolium chloride was discovered to be more suitable for cellulose dissolution, whereas imidazolium acetate was considered to be fit for lignin dissolution (Kilpeläinen et al., 2007; Vitz et al., 2009; Zakrzewska et al., 2010; Rashid et al., 2016). Along with other researchers, the results depict that [Bmim][Ace] and [Emim][Ace] produced higher percentage of regenerated lignin, while [Bmim]Cl and [Emim]Cl yield a high percentage of regenerated cellulose from dissolution of coconut shell.

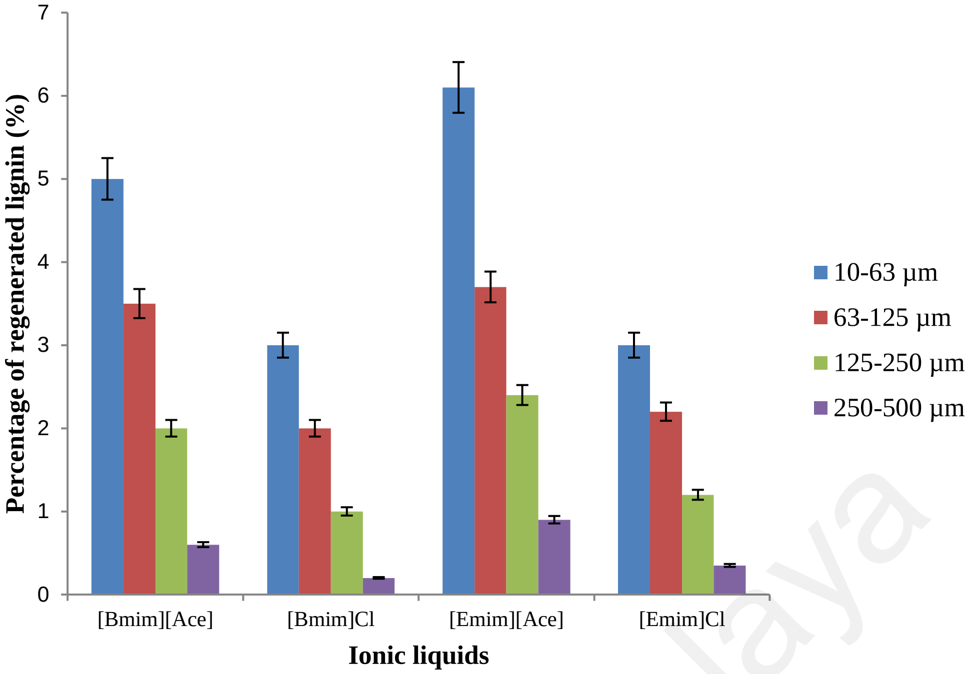


Figure 4.5: The percentage of regenerated lignin in AILs with different particle sizes at 110 °C

Acetate-based ILs have been found to have low viscosities, low melting points, low toxicity, and less corrosive than chloride-based ILs (Fendt et al., 2011). Previous studies also used acetate ions as a choice for the IL anion to dissolve lignocellulosic biomass, especially lignin (Swatloski et al., 2002; Stöcker 2008; Cobb et al., 2011; Li et al., 2011). The strong hydrogen bond acceptance of the acetate anion enables the destruction of the hydrogen network of the polymer chain in the coconut shell. As a result, the high hydrogen basicity of acetate anion allows it to attack free hydroxyl groups and cleave intra and intermolecular hydrogen bonds, which lead to increase the dissolution of lignocellulosic biomass (Sun et al., 2009; Brandt et al., 2012; Luo et al., 2013; Zhang et al., 2014).

Hence, anions influence the degree of lignin structural modifications, which leads to the cleavage of different linkages within lignin, and also control the solubility of lignin (George et al., 2011; Sun et al., 2011). The interaction of ILs with terminal hydroxyl groups of lignin, resulting disruption of lignin-cellulose network of lignocellulosic biomass, thus increasing the release of the regenerated lignin. Lateef et al., (2009) also reported the disruption of the internal network within lignin molecule would affect the dissolution of lignin. Although, chloride anion showed good lignin extraction, but it has high liquid viscosity and high melting temperature compared to acetate anion. Therefore, acetate-based ILs are recognized as the best ILs for lignin dissolution. Moreover, ILs containing large, non-coordinating anions, such as PF_6, OS, and ESO_4, were unsuitable as solvents for lignin (Pu et al., 2007). Recently, it has been demonstrated that anions mostly affect the lignin reactivity in the order: alkylsulphonates > lactates > acetates > chlorides > phosphates. This is explained by the nucleophilicity of the electronegative part of the anion (Xu et al., 2014).

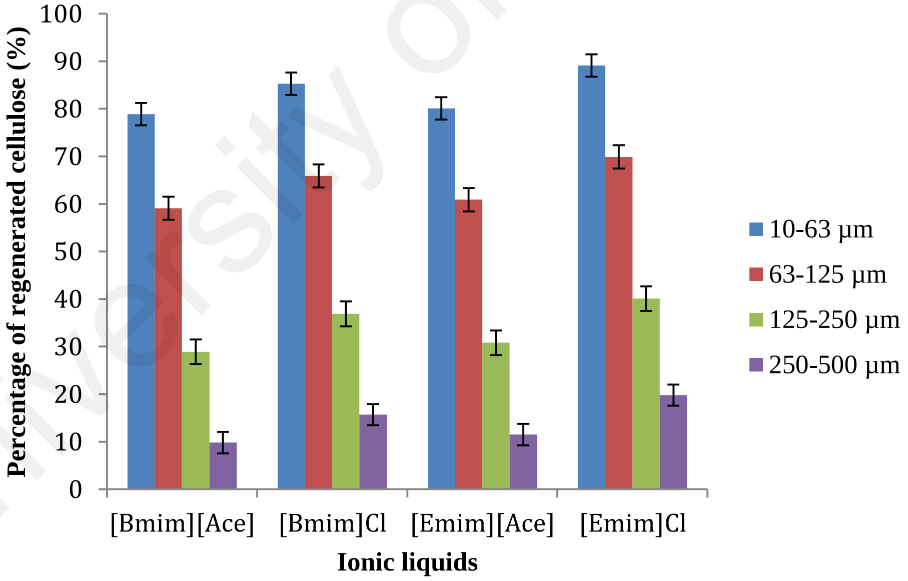


Figure 4.6: The percentage of regenerated cellulose in aprotic ionic liquids with different particle sizes at 110 °C

Figure 4.6 exhibits the percentage of regenerated cellulose from coconut shell in AILs. The regenerated of cellulose from [Emim]Cl and [Bmim]Cl were obtained up to

89% compared to [Emim][Ace] and [Bmim][Ace], which only 79% obtained. It was observed that [Emim]Cl and [Bmim]Cl have higher viscosity compared to [Emim][Ace] and [Bmim][Ace]. Kilpeläinen and co-workers discovered that imidazolium chloride have good capability for cellulose dissolution (Kilpeläinen et al., 2007; Vitz et al., 2009; Montalbo-Lomboy & Grewell, 2014). It has been found that the ionic liquid needs to contain anions with high hydrogen-bond basicity such as chloride, phosphates, phosphonates and carboxylates in order to solubilise cellulose (Pinkert et al., 2009). These correlations between hydrogen basicity anion of ionic liquids will swell and dissolve the cellulose and other lignocellulosic biomass.

Although the role of the anion seems clear, however the cation has not yet been shown to have any great effect on the reactivity of the ionic liquid with biomass dissolution. By comparing cation-based ILs, [Emim]-based ILs produced higher percentage of lignin and lignin compared with the [Bmim]-based ILs. This was due to the shorter alkyl side chain length on the imidazolium cation, which decreases the viscosity of the ILs (Pinkert et al., 2009; Yu et al., 2009; Pinkert et al., 2011). [Emim][Ace] has lower viscosity than [Bmim][Ace], which led to an increase in the ion mobility during the pretreatment process. According to Teh et al. (2015), [Emim][Ace] was also shown to dissolve macadamia nut shells.

4.3 Characterization of regenerated lignin from coconut shell

The regenerated lignin was obtained after evaporation of acetone as described in Section 3.4. The precipitated lignin (in supernatant) was separated by vacuum filtration due to the smaller particle size of lignin as displayed in Figure 4.7.

Figure 4.7: The supernatant contained precipitate lignin, water and ionic liquid

The structural and chemical changes of untreated coconut shell and regenerated lignin were characterized by elemental analysis (CHNS), solid state nuclear magnetic resonance spectroscopy (CP MAS NMR), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD).

4.3.1 Elemental analysis (CHNS)

Elemental composition materials of untreated coconut shell, Kraft lignin and regenerated lignin from AILs were determined through CHNS analysis. The elemental analysis is a technique for the determination of the weight percent of chemical elements in organic components such as carbon (C), hydrogen (H), Nitrogen (N) and Sulfur (S)

(Mainka et al., 2015). Table 4.5 shows the CHNS elements of untreated coconut shell, Kraft lignin and regenerated lignin from AILs.

Table 4.5: The CHNS elements of untreated coconut shell, Kraft lignin and regenerated lignin from AILs

	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)
Untreated coconut shell	64.33	6.34	0.77	0.06
Kraft lignin	44.53	4.61	1.71	3.33
Lignin from [Bmim][Ace]	59.58	6.14	0.43	0.04
Lignin from [Bmim]Cl	58.06	5.85	0.61	0.05
Lignin from [Emim][Ace]	58.73	5.53	0.19	0.03
Lignin from [Emim]Cl	56.52	5.34	0.54	0.02

From Table 4.5, it can be observed that the carbon percentage of untreated coconut shell was higher compared to regenerated lignin from AILs. This could be due to the broken of carbon fragments from untreated coconut shell into regenerated lignin and cellulose during dissolution process. The highest of sulfur content was observed in Kraft lignin compared to regenerated lignin and untreated coconut shell. The increased of sulfur content was contributed during the sulfite process (pretreatment method) (Tan & Macfarlane, 2009; Sahoo et al., 2011; Manara et al., 2014).

4.3.2 Solid state nuclear magnetic resonance (CP MS NMR)

Solid state NMR provides chemical information of Kraft lignin and regenerated lignin from AILs. The comparison of the ^{13}C CP MAS NMR spectra of Kraft lignin (standard) and regenerated lignin from [Emim][Ace], [Emim]Cl, [Bmim][Ace], and [Bmim]Cl are shown in Figure 4.8. The NMR spectra of the regenerated lignin is slightly similar to the Kraft lignin (standard), with a small difference of the intensity peak. In the upfield region, a peak between 10-40 ppm were assigned to methylene group ($-CH_2/-CH$) (Katahira et al., 2013). The intensity peak assigned to a methylene group of regenerated lignin from coconut shell was greatly increased after pretreatment process. The sharp peak that attributed to methoxy group was observed between 55-57 ppm for all spectra.

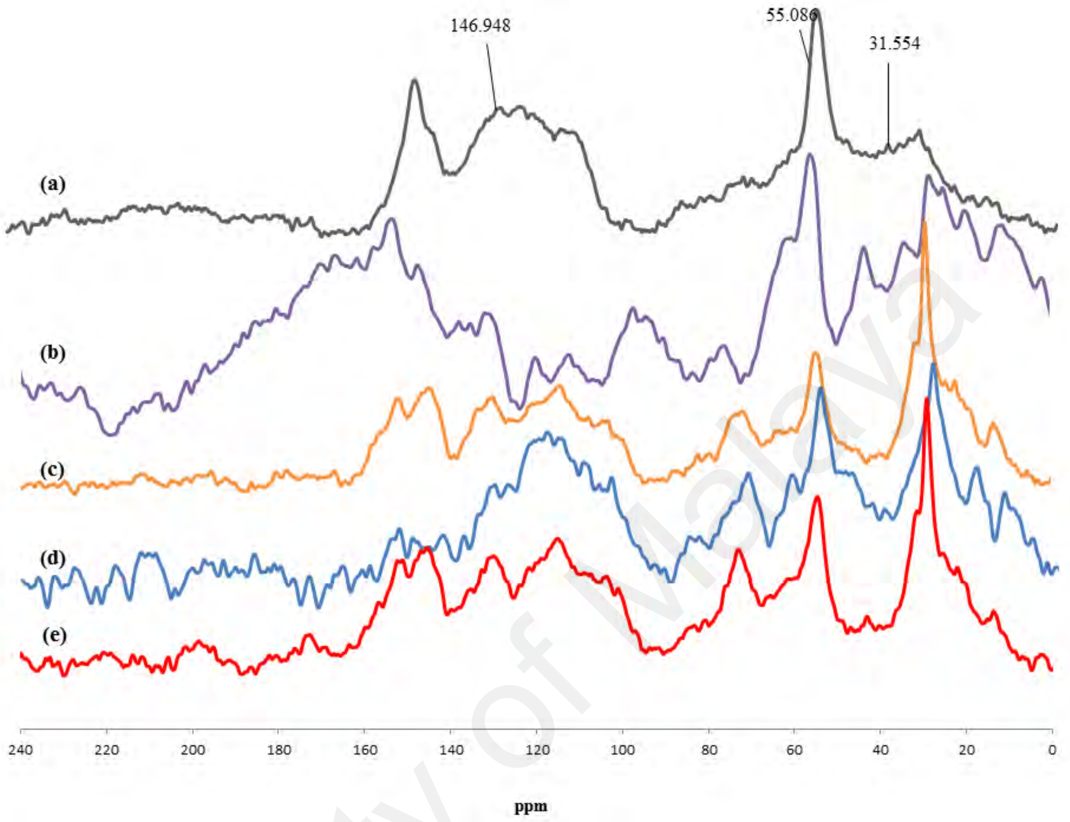


Figure 4.8: ^{13}C CP MAS NMR spectra of (a) Kraft lignin, and regenerated lignin from (b)[Bmim][Ace], (c)[Bmim]Cl, (d)[Emim][Ace], and (e) [Emim]Cl

The 110-160 ppm peaks were assigned to lignin aromatic ring structure. It was observed that the intensity peaks of aromatic ring and methoxy group gradually decreased on regenerated lignin from AILs. In hardwood, the presence of monomers of lignin (syringyl and guaiacyl) can be identified at peak 153.6 ppm (β-O-4 structures). This peak is correspond to C-3 and C-5 of syringyl units (Pu et al., 2013; Wen et al., 2013; Mohtar et al., 2017). While, in softwood, less obvious peak of β-O-4 structures of guaiacyl was observed (Melkior et al. 2017).

4.3.3 Fourier transform infrared (FTIR) analysis

To further understand the structural differences in the untreated coconut shell and regenerated lignin from the AILs, FTIR measurements were performed. Figure 4.9 displays the absorption spectra of the untreated coconut shell, kraft lignin (standard), and regenerated lignin from the AILs. The absorption bands of the regenerated lignin from [Bmim][Ace], [Bmim]Cl, [Emim][Ace], [Emim]Cl were found to be similar to the commercial kraft lignin (standard) and were in agreement with the literature (Sun et al. 2009; Tan et al. 2009; Hsu et al. 2010; Pinkert et al. 2011; Cesarino et al. 2012; Financie et al. 2016).

It also showed the presence of functional groups in lignin, as reported in previous studies, such as hydroxyl, methyl, carbonyl, methoxyl, and carboxyl groups. The spectra showed a broad absorption band at 3500 to 3200 cm^{-1} that represents the stretching hydroxyl groups in phenolic and aliphatic structure. There was also C-H stretching in the methyl and methylene groups (2936 to 2938 cm^{-1}), C-H stretching in the methoxy groups (2842 to 2849 cm^{-1}), C=O stretching (1706 to 1653 cm^{-1}), C=C stretching (1680 to 1640 cm^{-1}), and C-O stretching (1300 to 1000cm^{-1}) (Pinkert et al. 2011). The regenerated lignin from AILs displayed a significant increase absorption for -OH groups (3300 cm^{-1}) stretching and increase in C-H groups (2850 cm^{-1}) stretching in methoxy groups compared to kraft lignin.

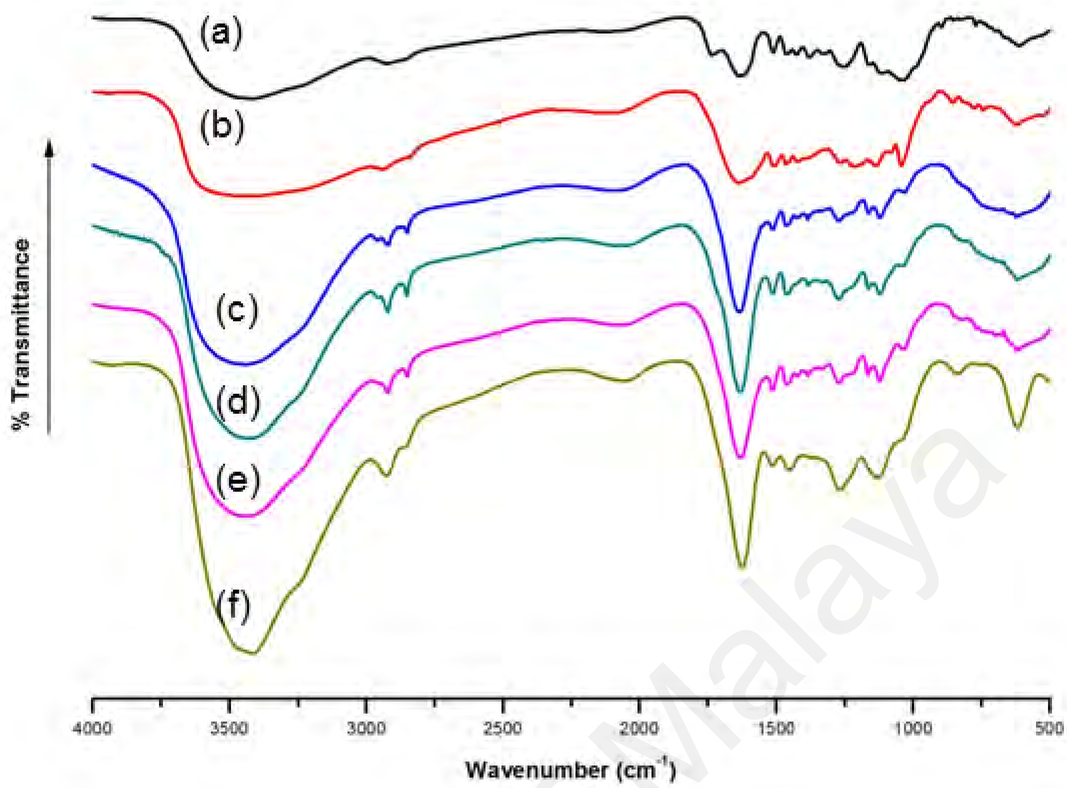


Figure 4.9: FTIR spectra of (a)untreated coconut shell, (b)Kraft lignin, regenerated lignin from ionic liquids; (c)[Bmim][Ace], (d)[Bmim]Cl, (e)[Emim][Ace], (f)[Emim]Cl

From the spectra, typical lignin structures were identified: aromatic skeletal vibrations (1597 to 1456 cm^{-1}), syringyl ring breathing with C-O stretching (1120 cm^{-1}), C-H in plane deformation in the guaiacyl ring (1113 cm^{-1}), C-H in-plane deformation in the guaiacyl ring and C-O deformation in the primary alcohol (1033 cm^{-1}), and aromatic C-H out-of-plane deformation (823 cm^{-1}) (Prado et al. 2016). The bands located at 1270, 1033 cm^{-1} are corresponding to guaiacyl units of lignin, while 1250 and 1120 cm^{-1} can be attributed to syringyl units of lignin (Boeriu et al., 2004; Qu et al., 2015). The regenerated lignin from [Emim]Cl showed enhancement of absorption at 1250 and 1170 cm^{-1} , indicating the increase of syringyl units compared to the others.

4.3.4 Powder x-ray diffraction (XRD) analysis

The untreated coconut shell and the regenerated lignin from AILs were characterized by XRD analysis to study the crystallinity of the materials. The XRD patterns were compared between untreated coconut shell and regenerated lignin from [Bmim][Ace], [Bmim]Cl, [Emim][Ace] and [Emim]Cl. The XRD results are presented in Figure 4.9. Two peaks for the crystal structure in the untreated coconut shell were observed, which typically observed in biomass (Darji et al., 2013). Figure 4.10 shows two peaks were appeared at 13° and 18.9°. The XRD patterns of the regenerated lignin showed a disappearance of the peaks at approximately 13° and 18.9° when compared with the untreated coconut shell. The dissolution and regeneration process reduced the crystalline structure of the regenerated materials (lignin). The formation of amorphous materials was observed.

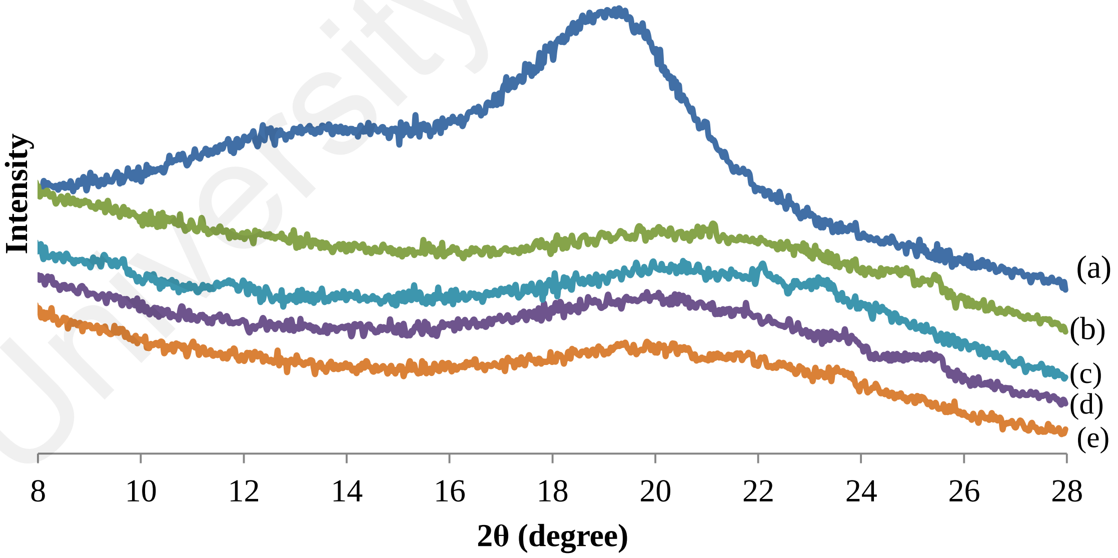


Figure 4.10: XRD patterns of (a)untreated coconut shell and regenerated lignin from aprotic ionic liquids; (b)[Bmim][Ace], (c)[Bmim]Cl, (d)[Emim][Ace], (e)[Emim]Cl

4.3.5 Thermogravitational Analysis (TGA)

The thermal decomposition of the untreated coconut shell and regenerated lignin from AILs were studied by TGA. The thermal stability of all of the samples were evaluated by their weight loss as the temperature increased from 50 to 900 °C. The TGA curves showed the thermal decomposition of the untreated coconut shell and regenerated lignin from [Bmim][Ace], [Bmim]Cl, [Emim][Ace], and [Emim]Cl after the dissolution process and are displayed in Fig. 4.11. The thermal stability of the untreated coconut shell showed a higher stability compared with the regenerated lignin from the ILs, as it started to decompose at 250 °C. This was due to the high crystallinity of the untreated coconut shell, which contained high amounts of hydrogen bonds and led to an increase in the thermal decomposition temperature (Kim et al. 2010).

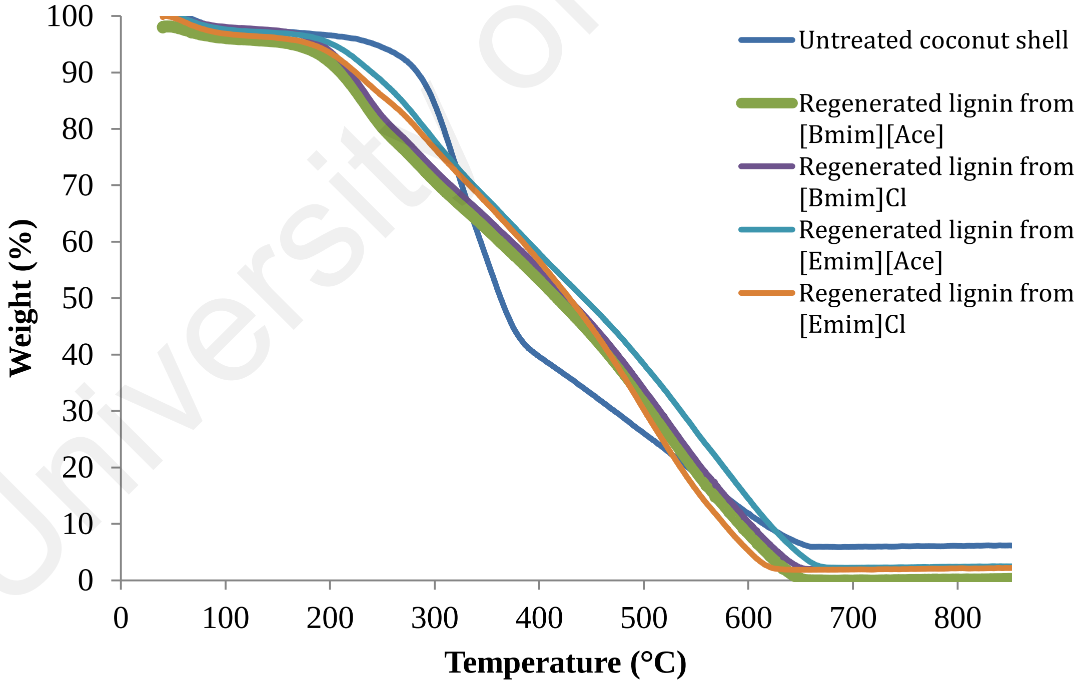


Figure 4.11: TGA plots of untreated coconut shell and regenerated lignin from aprotic ionic liquids

In contrast, the regenerated lignin from [Bmim][Ace], [Bmim]Cl, [Emim][Ace], and [Emim]Cl showed lower thermal decomposition temperatures (190 °C) compared with the untreated coconut shell. These materials have lower crystallinities compared with the untreated biomass. This corresponded to a noticeable drop in weight for all of the samples, which was due to the liberation of volatile hydrocarbons by thermal decomposition of the lignocellulosic biomass (Yang & Wu, 2009). The regenerated lignin from AILs also displayed lower thermal decomposition compared with Kraft lignin, which around 260 °C. This might be due to the cross-linked network of hydrogen bonding in the regenerated lignin from AILs were disrupted, which led to lower stabilities.

Previous studies also reported that the acid-insoluble lignin from alkaline extraction of bagasse started to decompose at 186 °C (Sun et al., 2003; Tan et al., 2009). Heat and chemical reactions also influence the decomposition rate, product yields, and composition of lignin (Burhenne et al., 2013). The thermal analysis was important for understanding the properties of the regenerated materials to determine if they can meet the standards for industrial applications.

4.3.6 Differential scanning calorimetry (DSC) analysis

The phase behaviour of the Kraft lignin and regenerated lignin from the ILs were studied using differential scanning calorimetry. The samples were subjected to three consecutive heating and cooling cycles in order to obtain reproducible results, and the third cycles are reported. The DSC can be used to measure a polymer’s glass transition temperature (T_g), where changes in heat capacity occur. Additionally, the T_g of the regenerated lignin was measured to understand the behaviour of the lignin, so that it can be used in current industrial applications, especially in making carbon fiber (Kubo & Kadla, 2004). The T_g of the Kraft lignin and regenerated lignin from different AILs are presented in Figure 4.12.

The Kraft lignin showed same T_g (165 °C) with the regenerated lignin from the AILs (165 and 185 °C). This could have been due to the interaction of the intermolecular hydrogen bonding, and decomposition temperature during the pretreatment process (Popescu et al., 2006). Previous literature reported the T_g of lignin to be between 80 and 180 °C (Popescu et al., 2006; Tejado et al., 2007). Meanwhile, Tan and coworker reported that the T_g of dried lignin from [Emim] alkylbenzenesulfonate was 144 °C (Tan et al., 2009).

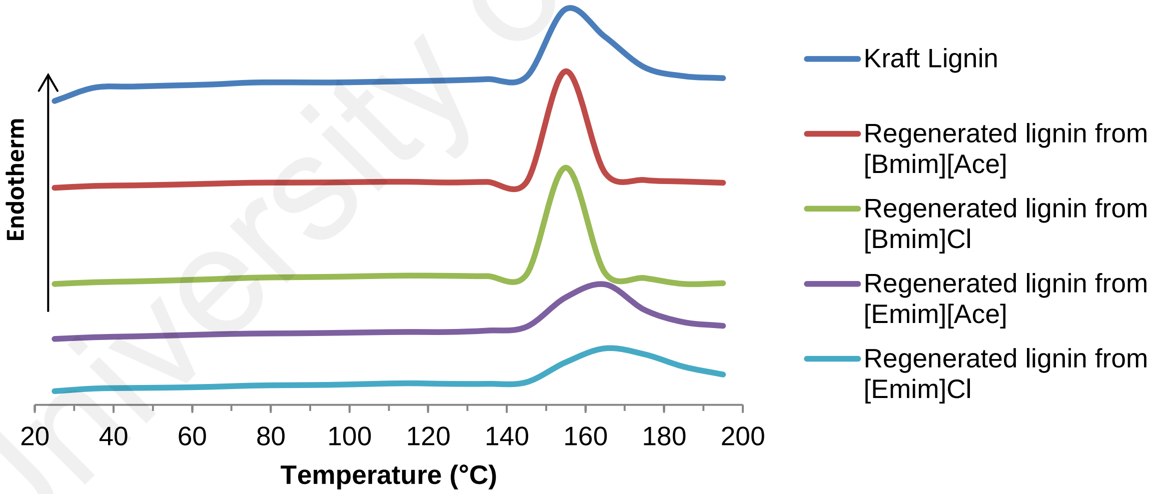


Figure 4.12: DSC curves of (a)kraft lignin and regenerated lignin from aprotic ionic liquids; (b)[Bmim][Ace], (c)[Bmim]Cl, (d)[Emim][Ace], (e)[Emim]Cl

4.4 Characterization of regenerated cellulose from coconut shell

The precipitation of regenerated cellulose rich materials was obtained after addition of anti-solvent. Then, it was centrifuged and dried in the oven at 60 °C after washing three times with distilled water. Figure 4.13 shows the regenerated cellulose from coconut shell after pretreatment process. The structural and chemical changes of untreated coconut shell and regenerated cellulose from AILs were investigated by using FESEM, FTIR, and XRD.

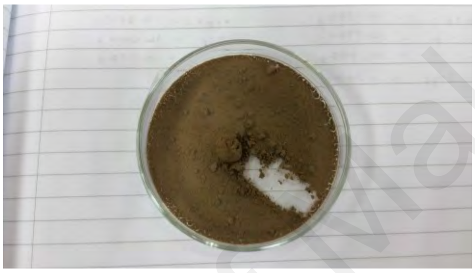


Figure 4.13: The regenerated cellulose from coconut shell

4.4.1 FESEM analysis

After the pretreatment process, FESEM analysis was conducted to observe the morphology of untreated coconut shell and regenerated cellulose. Figure 4.14 represents the FESEM images for untreated coconut shell and regenerated cellulose. The FESEM analysis clearly shows the difference in the morphology of the untreated coconut shell and regenerated cellulose. In the untreated coconut shell, the fibrous structure and individual arrangement was observed. After pretreatment process, the changes was occurred in regenerated cellulose where it exhibits amorphous structure. The cell wall of lignocellulosic biomass collapse as the cellulose crystallinity decreased.These changes of the structure of cellulose into amorphous make it easier to penetrate for enzymatic hydrolysis (Farran et al., 2015).

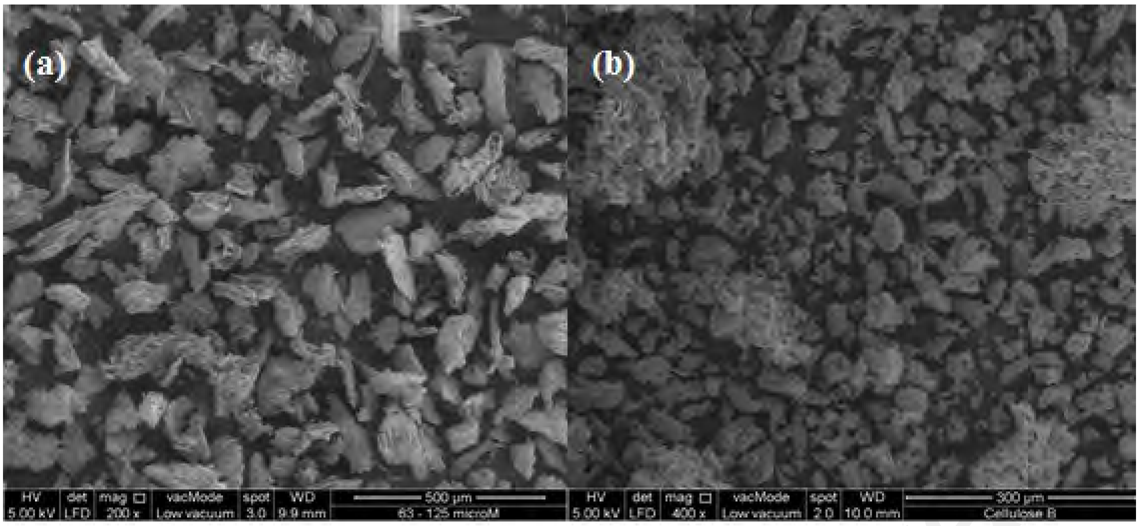


Figure 4.14: FESEM images of (a) untreated coconut shell, (b) regenerated cellulose

4.4.2 FTIR analysis

The FTIR analysis was carried out to characterize the present of functional groups in untreated coconut shell, microcrystalline cellulose (MCC) as a standard and regenerated cellulose from AILs as presented in Figure 4.15. The broad band between 3300 and 3900 cm^{-1} for all patterns is due to the strong O-H strectching. The peak at 2800-3000 cm^{-1} is correspond to C-H stretching in methyl and methylene groups (Liu et al., 2005; Oh et al., 2005; Leskinen et al., 2011). The sharp peak at 1160 cm^{-1} is attributed to C-O-C stretching in cellulose (Labbe et al., 2005; Muller et al., 2008).

The reduced peak at 1644 to 1638 cm^{-1} is due to the O-H bending of absorbed water (Hahary et al., 2015). The intensity of 1376 cm^{-1} increased because of the C-H bending vibration in regenerated cellulose from AILs compared to MCC standard. It showed that untreated coconut shell biomass contain high amount of cellulose. Higher intensity was observed at 2900-3100 cm^{-1} for regenerated cellulose from [Emim]Cl and [Bmim]Cl compared to [Bmim][Ace] and [Emim][Ace]. It indicates that the higher disorder cellulose structure was present. This is due to deformation on the glycosidic linkages and hydrogen bond rearrangement (Proniewicz et al., 2001; Oh et al., 2005). The shifted peak positions is due to arrangement of hydrogen bonds, this could be due to functional group contents was cleaved during dissolution process. The missing peak indicates that the regenerated cellulose is more amorphous (Darji et al., 2013).

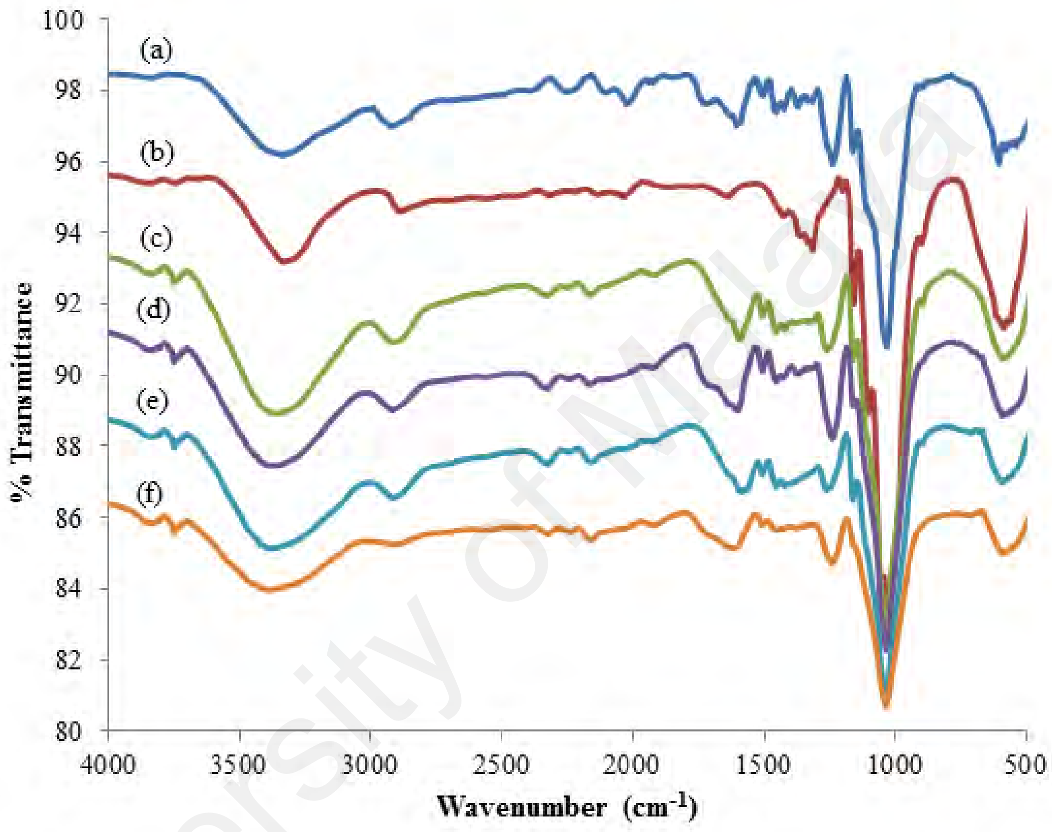


Figure 4.15: The FTIR analysis of (a)untreated coconut shell, (b)microcrystalline cellulose (MCC) and regenerated cellulose from (c)[Bmim][Ace], (d)[Bmim]Cl, (e)[Emim][Ace], (f)[Emim]Cl

In biomass, the rigid structure of cellulose prevents the enzymatic hydrolysis and the fermentation of sugar (glucose). According to Nelson & O'Connor (1964), the crystallinity structure of untreated biomass and regenerated cellulose can be calculated through lateral order index (LOI) and total crystallinity index (TCI). The LOI is measured by the infrared ratio of absorbance at peaks α 1437 cm^{-1} (band for CH_2 symmentry mode) / α 899 cm^{-1} (peak for vibrational mode involving C_1 and four atoms attached to it which is characteristic of beta-linked glucose polymer). Each value of the peak reflects the percentage of crystalline cellulose in biomass and the regenerated cellulose (Spirido et al., 2011; Tan & Lee, 2012). At peak 1437 cm^{-1}, it is also known as crystallinity band, while 899 cm^{-1} is assigned to amorphous band. On the other hand, the TCI is the ratio of absorbance at peak α 1378 cm^{-1} (band for C-H bending mode) /α 2900 cm^{-1} (band for CH and CH_2 stretching). Thus, the higher the value of LOI and TCI of biomass represent the higher crytallinity and more ordered structure of cellulose.

Table 4.6 represents the LOI and TCI of untreated coconut shell biomass and regenerated cellulose from AILs. It was calculated that all regenerated cellulose from AILs gave a lower value compared to untreated coconut shell. The crystallinity structure of regenerated cellulose from coconut shell were altered after pretreatment process.

Table 4.6: Lateral Order Index (LOI) and Total Crystallinity Index (TCI) of untreated coconut shell and regenerated cellulose from AILs

Fractionated	LOI (α 1437 cm^{-1} /α 899 cm^{-1})	TCI (α 1378 cm^{-1} /α 2900 cm^{-1})
Untreated coconut shell	1.83	1.1
Regenerated cellulose from [Bmim][Ace]	0.61	0.15
Regenerated cellulose from [Bmim]Cl	0.42	0.09
Regenerated cellulose from [Emim][Ace]	0.58	0.12
Regenerated cellulose from [Emim]Cl	0.35	0.04

The LOI and TCI of regenerated cellulose from AILs were greatly reduced compared to untreated coconut shell. From Table 4.14, it showed that the regenerated cellulose become disordered and less crystallinity after pretreatment process. This will improve the enzymatic hydrolysis as it increases the accessibility for fermentation of sugar (Sun et al., 2008; Spiridon et al., 2010). The LOI and TCI of regenerated cellulose from [Emim]Cl and [Bmim]Cl showed the lower value and more disordered form of structure compared to [Emim][Ace] and [Bmim][Ace]. This is consistent with the XRD results and proved that the ionic liquid is powerful solvent to dissolve coconut shell.

4.4.3 XRD analysis

The XRD patterns of the untreated coconut shell and regenerated cellulose from AILs; [Bmim][Ace], [Bmim]Cl, [Emim][Ace], and [Emim]Cl are compared in Figure 4.16. The diffractogram of the untreated coconut shell reveals that the two major peaks are 15° and 23°, which corresponds to the (110) and (002) lattice planes of crystalline cellulose (Segal et al., 1959; Cheng et al., 2011). After the pretreatment process, the intensity peak of regenerated cellulose from AILs became flat and weaker. This could be due to the changes of transition in the crystalline form of untreated coconut shell towards an amorphous structure of regenerated cellulose from AILs.

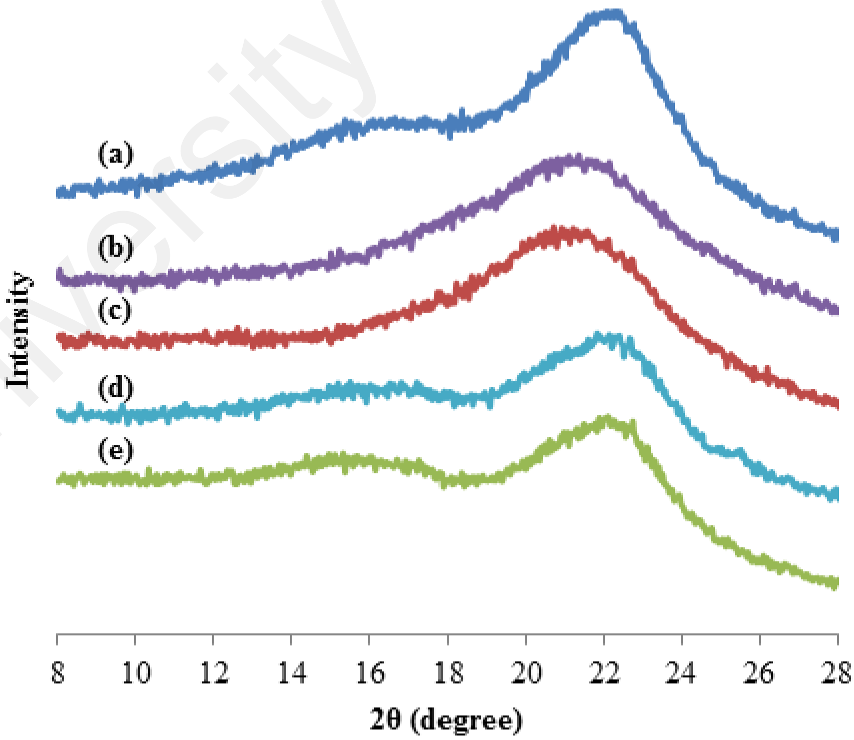


Figure 4.16: XRD patterns of (a)untreated coconut shell and regenerated cellulose from aprotic ionic liquids; (b)[Emim][Ace], (c)[Bmim][Ace], (d)[Emim]Cl, (e)[Bmim]Cl

The peak (002) became broader and weaker, while the peak (101) disappeared for regenerated cellulose from [Emim]Cl and [Bmim]Cl because the loss of crystalline structure. This showed that [Emim]Cl and [Bmim]Cl have good efficiency to alter the crystalline structure of cellulose from biomass compared to [Emim][Ace] and [Bmim][Ace]. Previous literature also mentioned the good solvency characteristics of [Emim]Cl and [Bmim]Cl for cellulose dissolution (Kilpeläinen et al., 2007; Vitz et al., 2009; Iguchi et al., 2013; Moltalbo-Lomboy & Grewell, 2014; Liu et al., 2016).

Table 4.7 shows the crystallinity index (CrI) of untreated coconut shell and regenerated cellulose from AILs. As mentioned in Section 3.5.6, crystallinity index can be calculated from XRD patterns of untreated coconut shell and regenerated cellulose from AILs. The CrI was determined from the height of crystalline peak minus with the height of amorphous peak and divided by the height of crystalline peak according to the equation by Segal et al., (1959). The regenerated cellulose from AILs showed lower CrI compared to untreated coconut shell due to the breakage of hydrogen bonds in lignocellulosic biomass during the dissolution process (Zhang et al., 2014).

Table 4.7: The crystallinity index (CrI) of untreated coconut shell and regenerated cellulose from AILs

Materials	Crystallinity Index- CrI (%)
Untreated coconut shell	35
Regenerated cellulose from [Emim][Ace]	32
Regenerated cellulose from [Bmim][Ace]	31
Regenerated cellulose from [Emim][Cl]	23
Regenerated cellulose from [Bmim][Cl]	16

The results displayed that [Bmim]Cl and [Emim]Cl showed a lowest crystallinity index (16% and 23%) compared to [Bmim][Ace] and [Emim][Ace] which were 31% and 32%, respectively. The anion of the IL forms hydrogen bonds with cellulose (sugar hydroxyl protons) in a 1:1 ratio and breaks up the cellulose crystalline hydrogen bonded structure, thus making it more amorphous and accessible to enzymatic hydrolysis (Brodeur et al., 2011).

4.5 Recyclability of ionic liquids for dissolution of lignocellulosic biomass

Ionic liquids (ILs) capable to dissolve lignocellulosic biomass by disrupting the intermolecular and intramolecular hydrogen bonds that fractionate it into lignin, cellulose, and hemicellulose without promoting significant depolymerization or degradation reactions (Oliveira et al., 2017). One of the challenges of ionic liquid pretreatment is that the ILs are expensive. However, many researchers have demonstrated the reusability and recyclability of ionic liquids, allowing them to be reused up to four times (Lee et al. 2009; Nguyen et al. 2010). The objective of this study is to investigate the recyclability of ionic liquids for dissolution of coconut shell.

In this study, the ILs [Bmim]Cl, [Bmim][Ace], [Emim][Ace], and [Emim]Cl were recycled up to four times. Badgujar and Bhanage (2015) reported that the impurities in recycled imidazolium-based ILs in their study affect the dissolution results. Therefore, it was necessary to ensure the purity or stability for the recycled ILs. Additionally, Karl Fischer coulometer was used to evaluate the water content in the ILs. ^{1}H NMR was conducted on the fresh and recycled ILs to confirm the similarity in term of chemical structure. The recycled ILs were used to dissolve coconut shell in pretreatment process. The regenerated lignin and cellulose were characterized with FTIR and discuss in details below. These results demonstrate the feasibility to recover and reuse AILs up to fourth times for the efficient pretreatment of coconut shell biomass.

4.5.1 Dissolution coconut shell in recycled ionic liquids

Ionic liquids are well-known as green solvents as it can be easily recovered and reused for multiple times (Auxefans et al., 2014; Prado et al., 2016). This is a good opportunity to ensure the sustainability and environmental protection. The potential to recyce ILs make them perfect alternatives solvent due to the low vapour pressure of ILs (Anstas et al., 2010, Dharaskar et al., 2015). The experimental results discovered the good performance of recycled AILs to extract the regenerated lignin and cellulose from coconut shell.

The mass compositions of regenerated lignin and cellulose, and recovery of [Emim][Ace] are summarized in Figure 4.17. The rest of mass composition from [Emim]Cl, [Bmim][Ace] and [Bmim]Cl have been included in Appendix B. The results showed the recovery of aprotic ionic liquids is above 90 %, even after four recycle. The percentage yield of lignin and cellulose were recorded to be similar up to four times of recycled of AILs. This reveals the successful used of recycled AILs in dissolution of coconut shell.

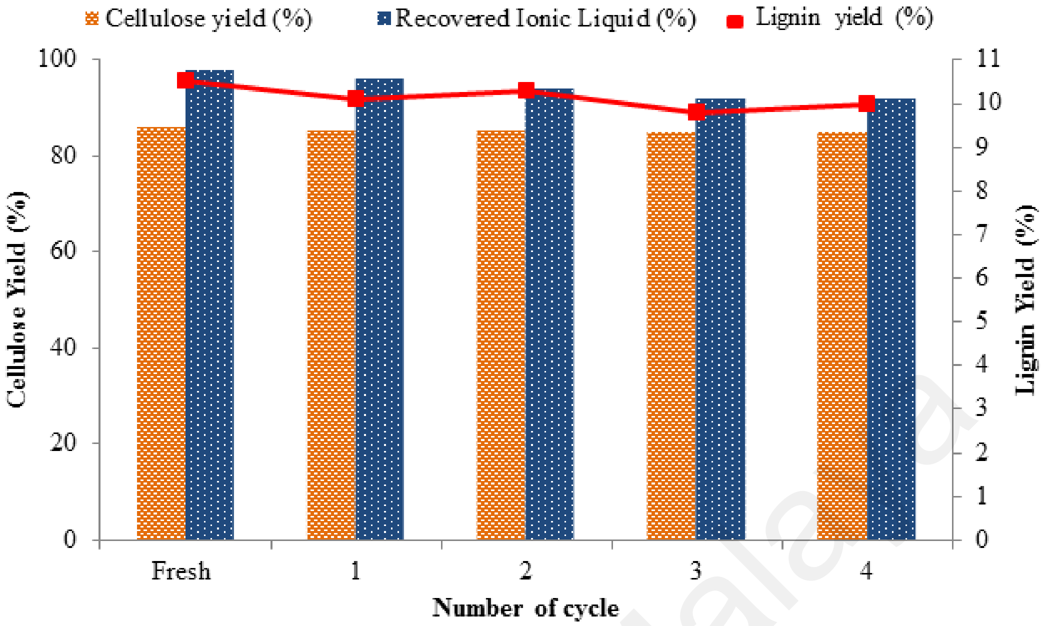


Figure 4.17: Yield of lignin, cellulose and recovery of [Emim][Ace] obtained after pretreatment process (1 = first, 2 = second, 3 = third and 4 = fourth cycle)

4.5.2 Characterizations of regenerated lignin from recycled ionic liquids

The regenerated lignin from recycled aprotic ionic liquids were analyzed using FTIR spectroscopy to determine their absorption bands and compared with regenerated lignin from fresh AILs and commercial lignin. The comparison of regenerated lignin and cellulose will be compared with the standard (Kraft lignin and MCC).

4.5.2.1 Fourier transform infrared (FTIR) analysis

FTIR analysis was performed for the untreated coconut shell, Kraft lignin (standard) and regenerated lignin from recycled [Emim][Ace] and presented in Figure 4.18. The regenerated lignin from recycled AILs were compared with standard lignin. All of the spectra showed a broad absorption band at 3500 to 3200 cm^{-1} because of the phenolic and aliphatic O-H groups. There was also C-H stretching in the methyl and methylene groups (2936 to 2938 cm^{-1}), C-H stretching in the methoxy groups (2842 to 2849 cm^{-1}), C=O stretching (1706 to 1653 cm^{-1}), C=C stretching (1680 to 1640 cm^{-1}), and C-O stretching (1300 to 1000cm^{-1}) (Pinkert et al. 2011). The FTIR results showed that the obtained regenerated lignins were similar until the fourth cycle. The rest of FTIR analysis of regenerated lignin from [Emim]Cl, [Bmim][Ace] and [Bmim]Cl have been included in Appendix C.

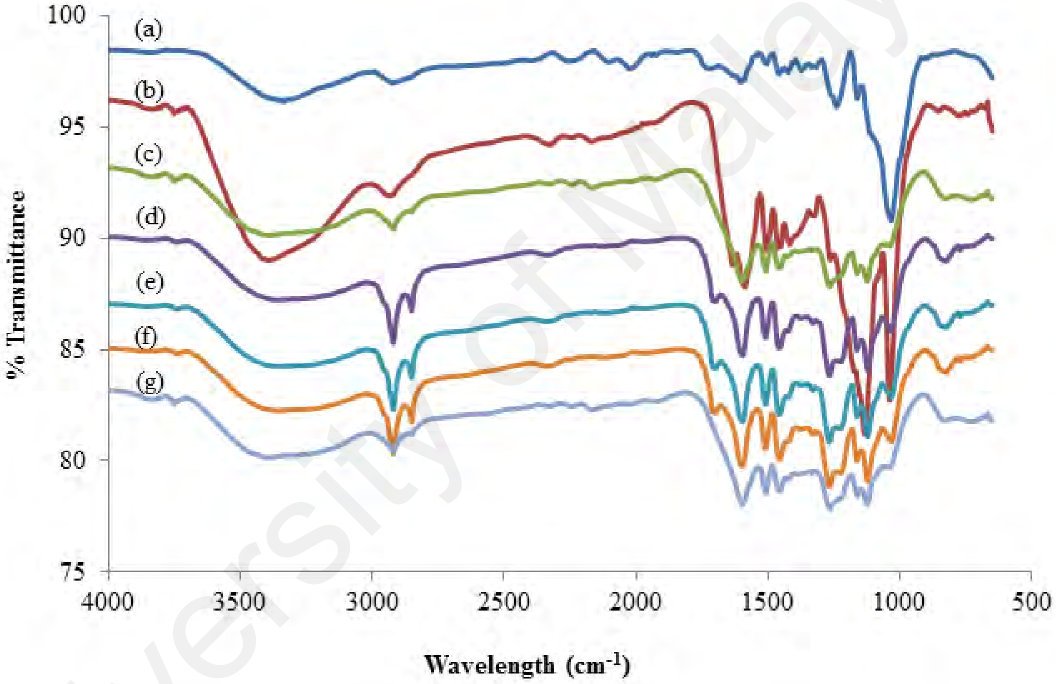


Figure 4.18: FTIR analysis of (a)untreated coconut shell, (b)Kraft lignin and regenerated lignin by (c)fresh IL, (d)first recycle, (e)second, (f)third and (g)fourth cycle of [Emim][Ace]

4.5.3 Characterization of regenerated cellulose from recycled ionic liquids

The regenerated cellulose from recycled AILs were analyzed using FTIR spectroscopy to determine their absorption bands and compared with commercial cellulose.

4.5.3.1 Fourier transform infrared (FTIR) analysis

The FTIR analysis was carried out to detect functional groups in regenerated cellulose from AILs and compared with microcrystalline cellulose (MCC) as a standard. The FTIR spectra of the untreated coconut shell, MCC and regenerated cellulose from recycled AILs are presented in Figure 4.19. The rest of FTIR analysis of regenerated cellulosed from [Emim]Cl, [Bmim][Ace] and [Bmim]Cl have been included in Appendix D. It was observed that regenerated cellulose from recycled AILs show the similar characteristics as a standard. The FTIR spectra were analyzed the presence of hydroxyl, carbonyl, methoxyl and carboxyl functional groups respectively according to previous literature reviews. At 3300-4000 cm^{-1}, O-H stretching was observed. While C-H stretching in methyl and methylene groups (2800-3000 cm^{-1}) and discrete absoprtions in the region from 1000 to 1750 cm^{-1} were recorded in the spectra (Liu et al., 2005; Myllymaki & Aksela, 2005; Leskinen et al., 2011). The FTIR results showed that the obtained regenerated cellulose were similar until the fourth cycle.

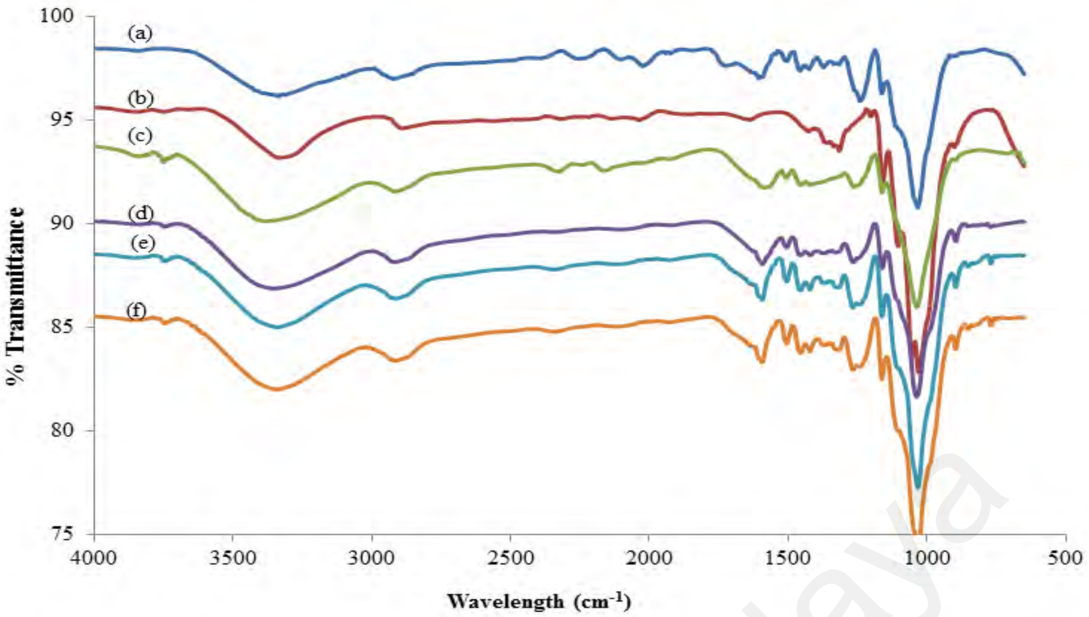


Figure 4.19: FTIR analysis of (a) untreated coconut shell and regenerated cellulose by (b)fresh IL, (c)first recycle, (d)second, (e)third and (f)fourth cycle of [Emim][Ace]

4.5.4 Characterization of recycled ionic liquids

It is compulsory to maintain the stability and purity of ionic liquids as to preserve the recyclability of the ILs without losing its efficiency during pretreatment process. Before using the recycle AILs for pretreatment process, they were analyzed using TGA and ^{1}H NMR to determine their purity and stability. The chemical informations and properties of AILs from each cycled were compared with fresh AILs.

4.5.4.1 Thermogravimetric analysis (TGA)

TGA analysis was investigated to determine the thermal decomposition (stability) of fresh and recycled AILs. Table 4.8 represent the thermal properties of the fresh and recycled [Emim][Ace], [Emim]Cl, [Bmim][Ace] and [Bmim]Cl, respectively. The thermal stability of recycled AILs showed to be slightly lower compared to fresh AILs. As the reaction goes up, the thermal stability of AILSs decrease during dissolution process of coconut shell. However, the recycled AILs still can be used as they have same efficiency as fresh AILs (able to dissolve 70 mg of coconut shell in 1 g of recycled AILs). The rest of TGA analysis of fresh and recycled AILs have been included in Appendix E.

Table 4.8: TGA properties of the fresh and recycled AILs

Cycle	**Degradation Temperature (°C)**			
	[Emim][Ace]	[Bmim][Ace]	[Emim]Cl	[Bmim]Cl
Fresh	220	210	260	260
1	203	192	239	229
2	198	192	200	205
3	194	190	190	196
4	189	185	188	191

4.5.4.2 Proton Nuclear Magnetic resonance analysis (^{1}H NMR)

^{1}H NMR analysis was studied to determine chemical changes on AILs before and after recycling for several times. No differences between the spectra of the fresh and recycled AILs were observed. Furthermore, no additional or impurities peaks were detected, except for a water solvent peak was detected in NMR (chemical shift 3.53 ppm). This showed that properties of the recycled AILs remain the same as the fresh AILs. Although, water was detected in the NMR, the value is less than 1 %, as detected by Karl Fischer coulometer, which was acceptable for the dissolution process. Figure 4.20 shows the ^{1}H NMR spectra of the fresh and recycled [Emim][Ace]. The ^{1}H NMR spectra for [Bmim]Cl, [Bmim][Ace] and [Emim]Cl are presented at the Appendix F.

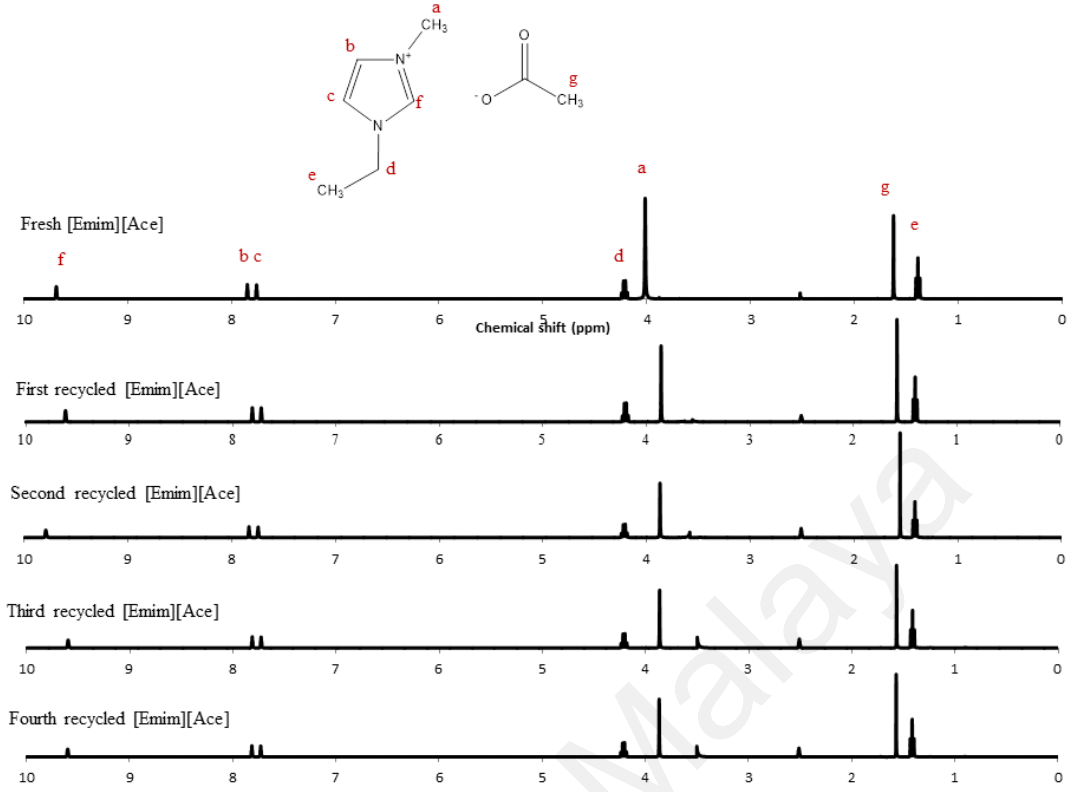


Figure 4.20: ^{1}H NMR of fresh and recycled [Emim][Ace] up to four times

4.5.5 Summary of recyclability of ionic liquids

In this study, the results showed that the AILs, [Bmim]Cl, [Bmim][Ace], [Emim][Ace], and [Emim] Cl can be recovered (90 %) and reused up to four times. The regenerated cellulose and lignin from coconut shell also displayed similar results as fresh aprotic ionic liquids. No changes to the properties of recycled AILs were detected from TGA and ^{1}H NMR analysis. This clearly showed that recycled [Emim][Ace], [Emim]Cl, [Bmim][Ace] and [Bmim]Cl can be potentially used as pretreatment solvent for extraction of lignin and cellulose from lignocellulosic biomass.

CHAPTER 5 : CONCLUSION AND FUTURE WORKS

5.1 Conclusion

In recent years, the dissolution of lignocellulosic biomass in ionic liquids have been studied extensively, for instance oil palm fronds, rubber tree, and bamboo. None of the studies of lignocellulosic biomass reported has ustilized the coconut shell. For that reason, coconut shell was chosen in this study to dissolve in ionic liquids and fractionate into lignin and cellulose. These study successfully confirm that certain ionic liquids; namely [Bmim][Ace], [Bmim]Cl, [Emim][Ace], and [Emim]Cl have good potential to be applied as solvent for coconut shell dissolution.

The highest dissolution of coconut shell was found in aprotic ionic liquids; [Bmim][Ace], [Bmim]Cl, [Emim][Ace], and [Emim]Cl, which up to 7 wt % compared to protic ionic liquids. Imidazolium-based ILs with various anions have high polarities and different degree of biopolymer's solubility because of their ionic characteristics, resulting in enhanced different biopolymer dissolving capacities. The results demonstrated that at temperature of 110 °C, the coconut shell was completely dissolved in the ILs due to good solubility and higher regenerated yield obtained (90 %). No dissolution of coconut shell was observed at lower temperature (<110 °C). The percentage of regenerated cellulose started to decrease when the temperature increases due to the improvement of linkage between lignin-cellulose networks. [Emim][Ace] was better than the other ionic liquids such as [Emim]Cl, [Bmim][Ace] and [Bmim]Cl, because of good solubility and higher regenerated yield obtained (97.4%). Among of the AILs explored, imidazolium acetate was the best for lignin extraction, while imidazolium chloride was discovered to suit for cellulose extraction. The effect of particle sizes ranging from 10-500 µm for coconut shell during pretreatment process were investigated. The highest dissolution yields and regenerated materials were recorded at smaller particle size (10-63 µm).

The most important consideration to achieve economical and environmentally friendly, biomass processing is the ease of extraction of lignin and cellulose from lignocellulosic biomass. In addition, the ease recovery of these AILs without losing its extraction efficiency also provide great potential for recycling. In this study, [Bmim]Cl, [Bmim][Ace], [Emim][Ace], and [Emim]Cl can be recycled up to four times (90 %). The pretreatment process of coconut shell with recycled AILs showed similar extraction efficiency as fresh aprotic ILs. Besides, TGA and ^{1}H NMR analysis also demonstrated no changes to the properties of recycled AILs.

5.2 Future works

Extraction of lignin and cellulose from coconut shell was successfully achieved using aprotic ionic liquids. Ionic liquids can potentially open up a new route to coconut shell processing. It also illustrates a useful feature of ionic liquids in providing a reaction medium for pretreatment process. Overall, the use of ionic liquids to extract lignin from lignocellulosic biomass has been successfully demonstrated, although a number of issues remain, such as simplification of ionic liquid recovery and tailoring an ionic liquid to fractionate lignin with desirable products. Currently, lignin has a high potential for use in more valuable applications than its current use as fuel in pulp mills and integrated pulp and paper mills. Lignin has grabbed interest for its conversion into carbon fiber with more than 60 % of carbon content. Therefore, the development for manufacturing of carbon fibres could also be explored. Another component that successfully extracted from coconut shell was cellulose. This shows that ionic liquids also reduce the crystallinity and disrupt the lignocellulosic network of coconut shell.

Following are some suggestion for future works:

i. Study the degradation and conversion of lignin into monomers, such as conniferyl, sinapyl and gualciyl through bioconversion.
ii. Study the possibility of using lignin (from coconut shell) as a precursor for the manufacturing of carbon fibre and compare with the commercial lignin.
iii. Study the chemical designs for efficient lignin conversion into vanillin, ferullic acid and other interesting phenolic components.
iv. Study the lignin depolymerization and development of lignin valorization by microbial conversions.
v. Study the enzymatic hydrolysis of cellulose to glucose and optimization of conditions.

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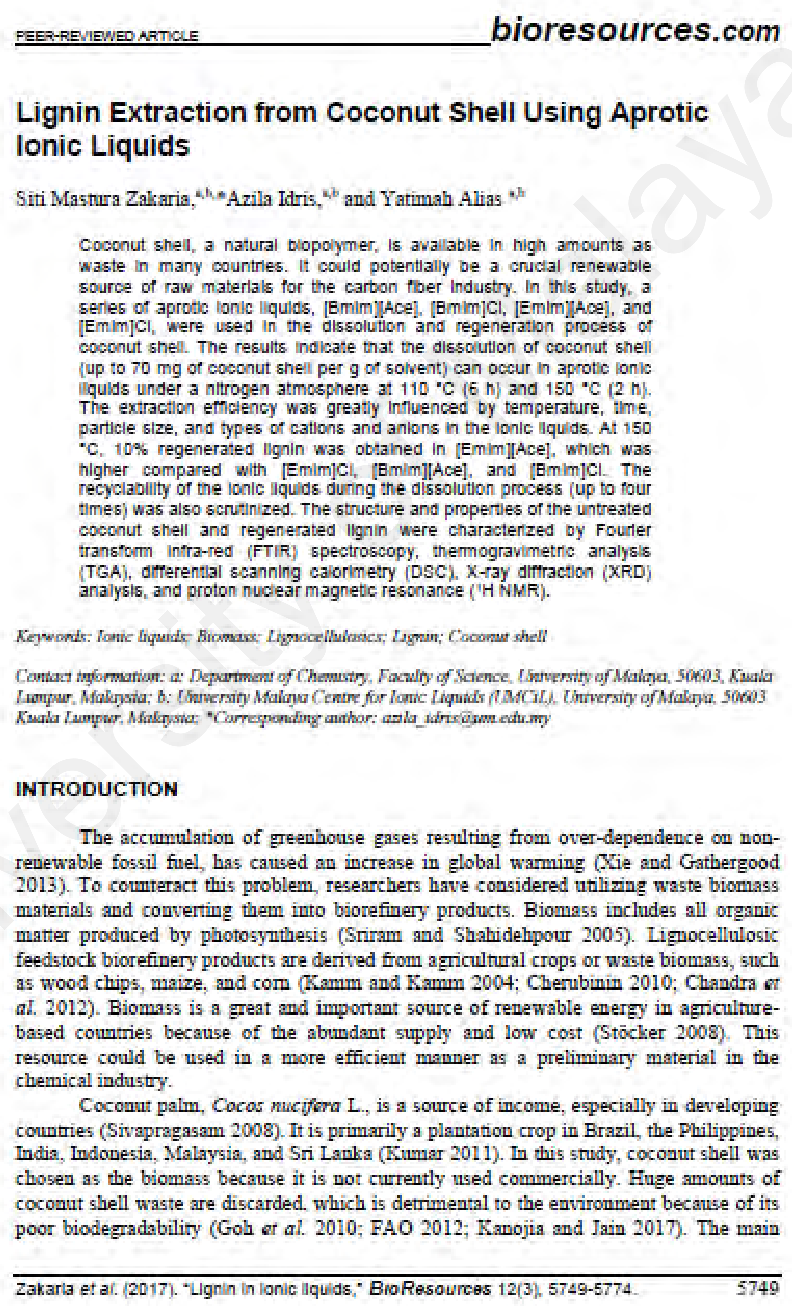
SUPPLEMENTARY

LIST OF PUBLICATION AND PAPER PRESENTED

1. Zakaria, S. M., Idris, A., & Alias, Y. (2017). Lignin Extraction from Coconut Shell Using Aprotic Ionic Liquids. *BioResources*, *12*(3), 5749-5774.



PEER-REVIEWED ARTICLE **bioresources.com**

Lignin Extraction from Coconut Shell Using Aprotic Ionic Liquids

Siti Mastura Zakaria,[a,b,]*Azila Idris,[a,b] and Yatimah Alias [a,b]

Coconut shell, a natural biopolymer, is available in high amounts as waste in many countries. It could potentially be a crucial renewable source of raw materials for the carbon fiber industry. In this study, a series of aprotic ionic liquids, [Bmim][Ace], [Bmim]Cl, [Emim][Ace], and [Emim]Cl, were used in the dissolution and regeneration process of coconut shell. The results indicate that the dissolution of coconut shell (up to 70 mg of coconut shell per g of solvent) can occur in aprotic ionic liquids under a nitrogen atmosphere at 110 °C (6 h) and 150 °C (2 h). The extraction efficiency was greatly influenced by temperature, time, particle size, and types of cations and anions in the ionic liquids. At 150 °C, 10% regenerated lignin was obtained in [Emim][Ace], which was higher compared with [Emim]Cl, [Bmim][Ace], and [Bmim]Cl. The recyclability of the ionic liquids during the dissolution process (up to four times) was also scrutinized. The structure and properties of the untreated coconut shell and regenerated lignin were characterized by Fourier transform infra-red (FTIR) spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction (XRD) analysis, and proton nuclear magnetic resonance (^{1}H NMR).

Keywords: Ionic liquids; Biomass; Lignocellulosics; Lignin; Coconut shell

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INTRODUCTION

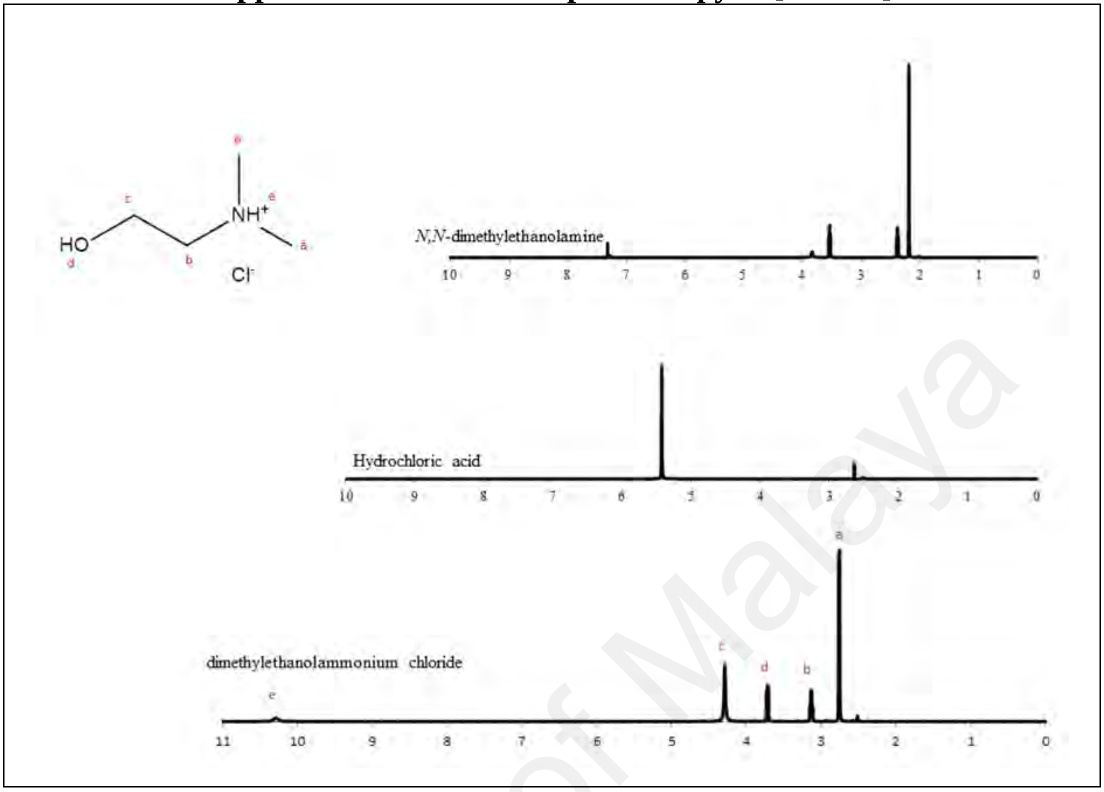
The accumulation of greenhouse gases resulting from over-dependence on non-renewable fossil fuel, has caused an increase in global warming (Xie and Gathergood 2013). To counteract this problem, researchers have considered utilizing waste biomass materials and converting them into biorefinery products. Biomass includes all organic matter produced by photosynthesis (Sriram and Shahidehpour 2005). Lignocellulosic feedstock biorefinery products are derived from agricultural crops or waste biomass, such as wood chips, maize, and corn (Kamm and Kamm 2004; Cherubinin 2010; Chandra *et al.* 2012). Biomass is a great and important source of renewable energy in agriculture-based countries because of the abundant supply and low cost (Stöcker 2008). This resource could be used in a more efficient manner as a preliminary material in the chemical industry.

Coconut palm, *Cocos nucifera* L., is a source of income, especially in developing countries (Sivapragasam 2008). It is primarily a plantation crop in Brazil, the Philippines, India, Indonesia, Malaysia, and Sri Lanka (Kumar 2011). In this study, coconut shell was chosen as the biomass because it is not currently used commercially. Huge amounts of coconut shell waste are discarded, which is detrimental to the environment because of its poor biodegradability (Goh *et al.* 2010; FAO 2012; Kanojia and Jain 2017). The main

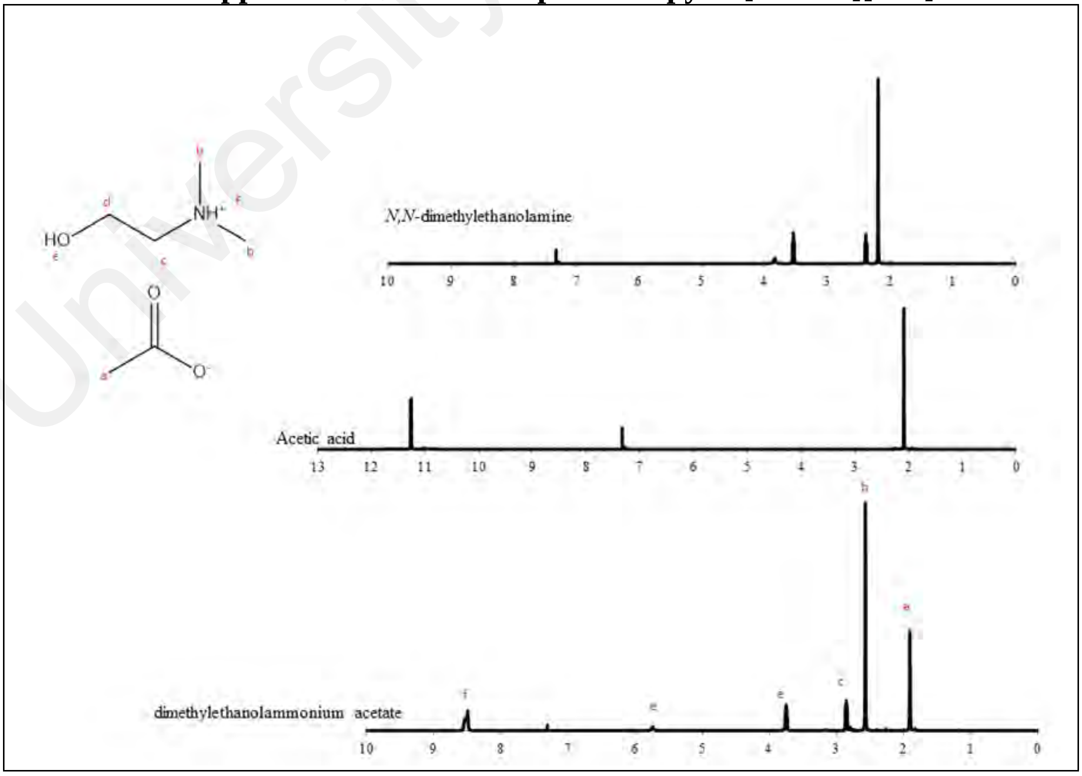
Zakaria *et al.* (2017). "Lignin in ionic liquids," *BioResources* 12(3), 5749-5774. 5749

APPENDICES

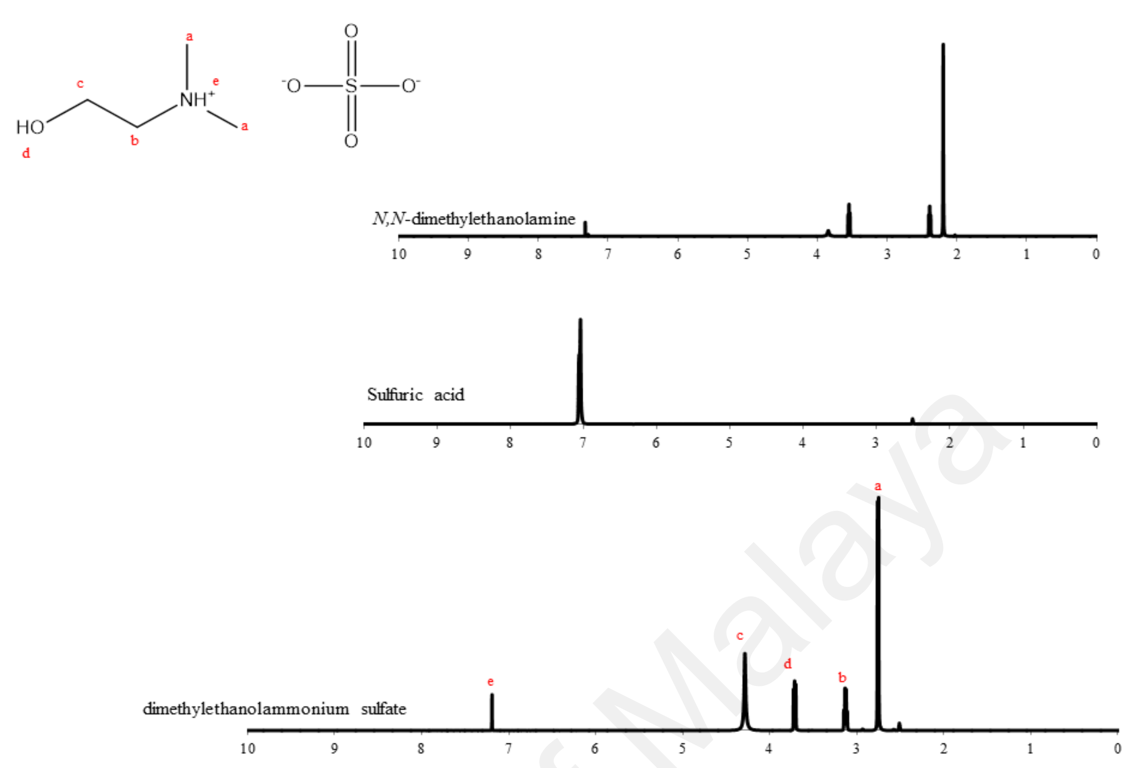
Appendix A 1– ^{1}H NMR spectroscopy of [DMEA]Cl



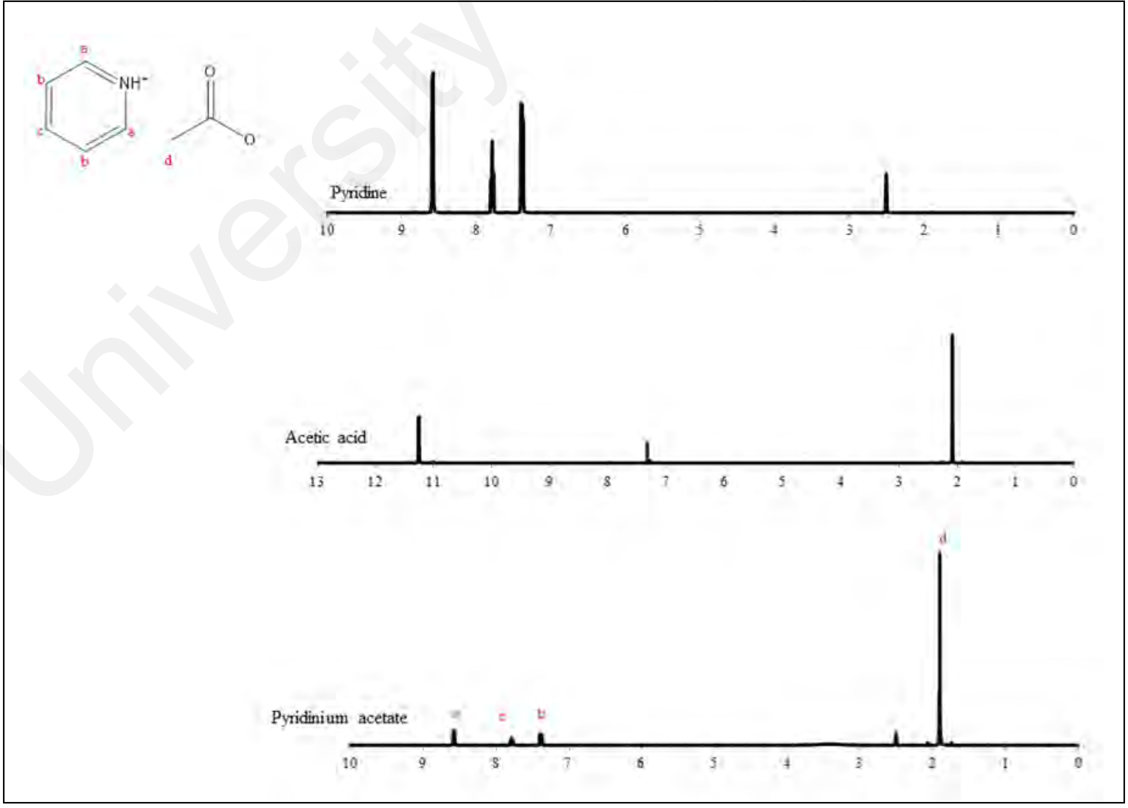
Appendix A 2-^{1}H NMR spectroscopy of [DMEA][Ace]



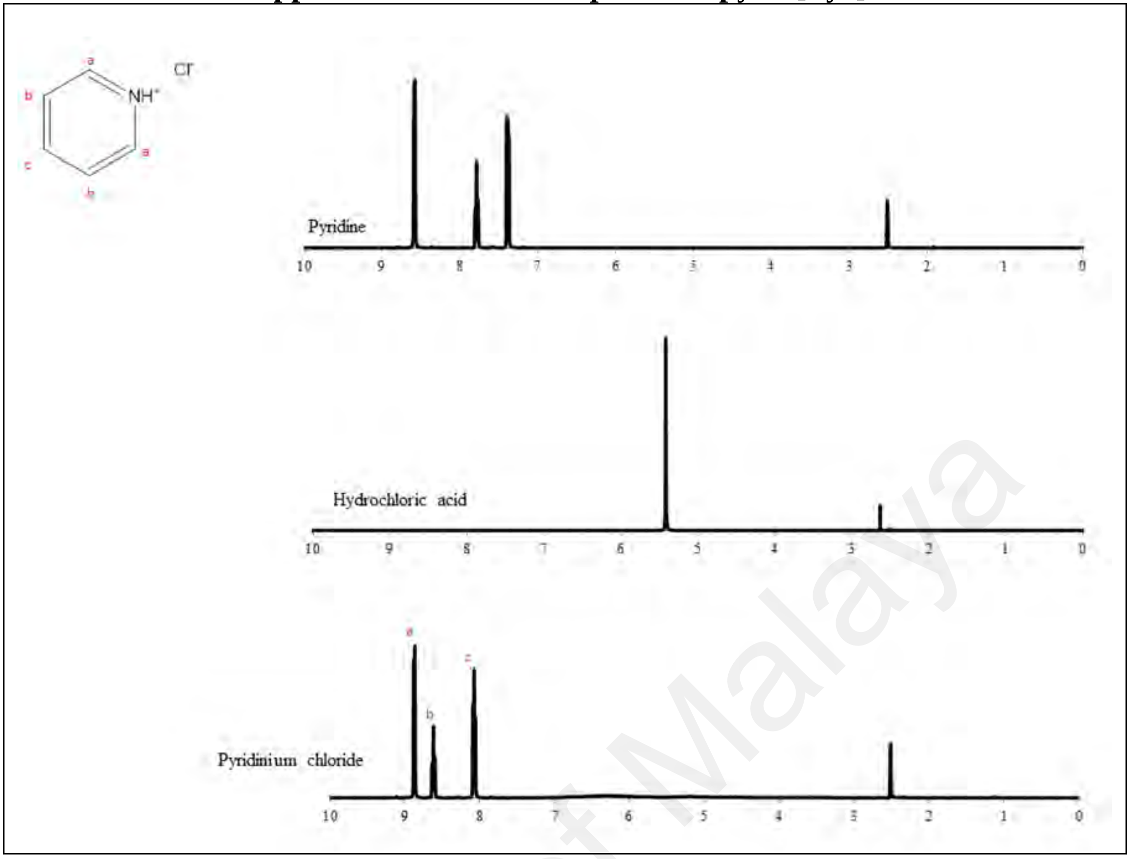
Appendix A 3-^{1}H NMR spectroscopy of [DMEA][HSO$_4$]



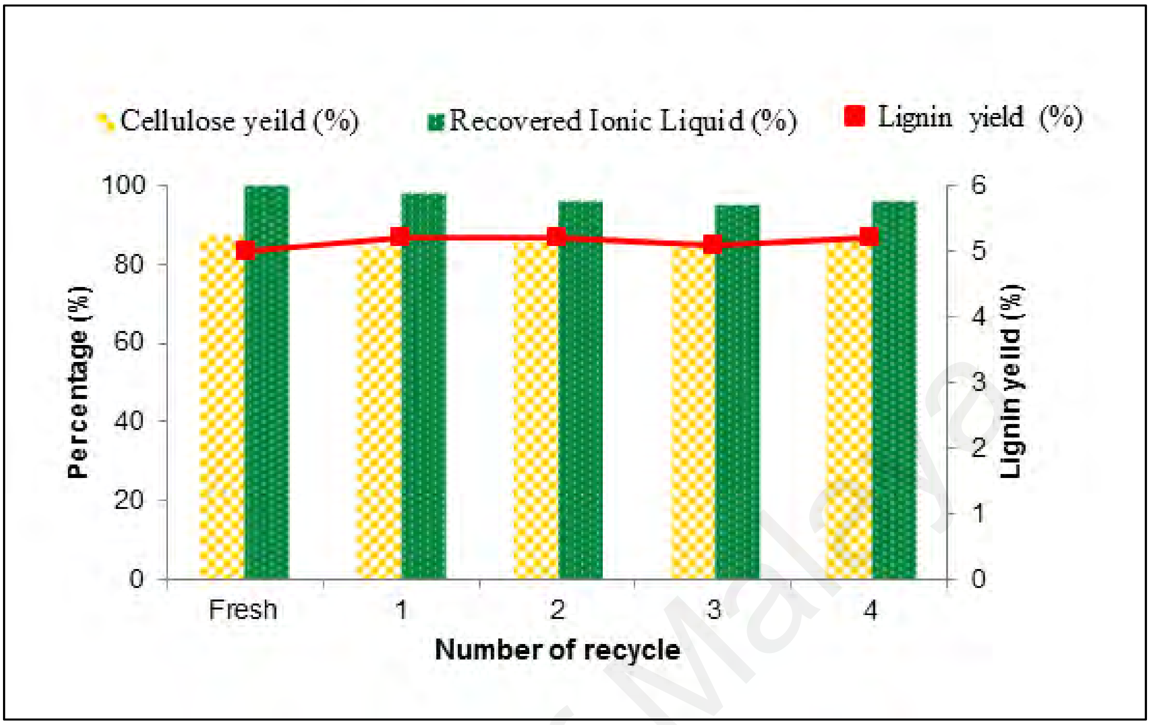
Appendix A 4-^{1}H NMR spectroscopy of [Pyr][Ace]



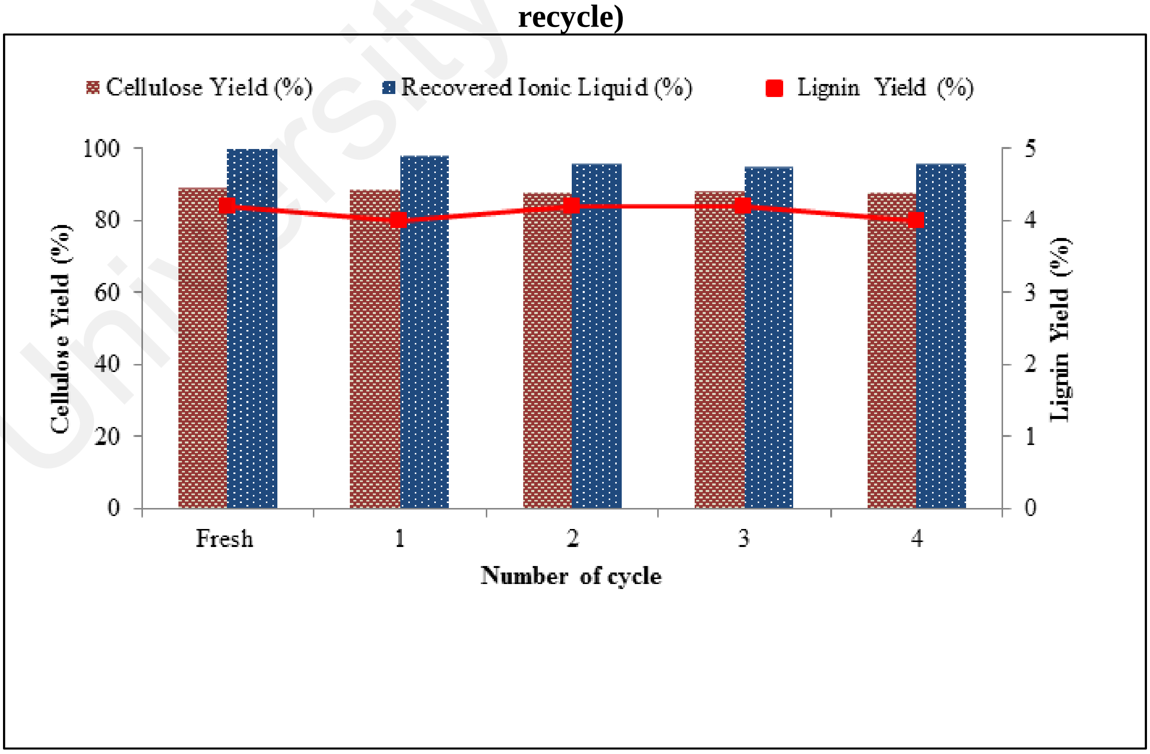
Appendix A 5-^{1}H NMR spectroscopy of [Pyr]Cl



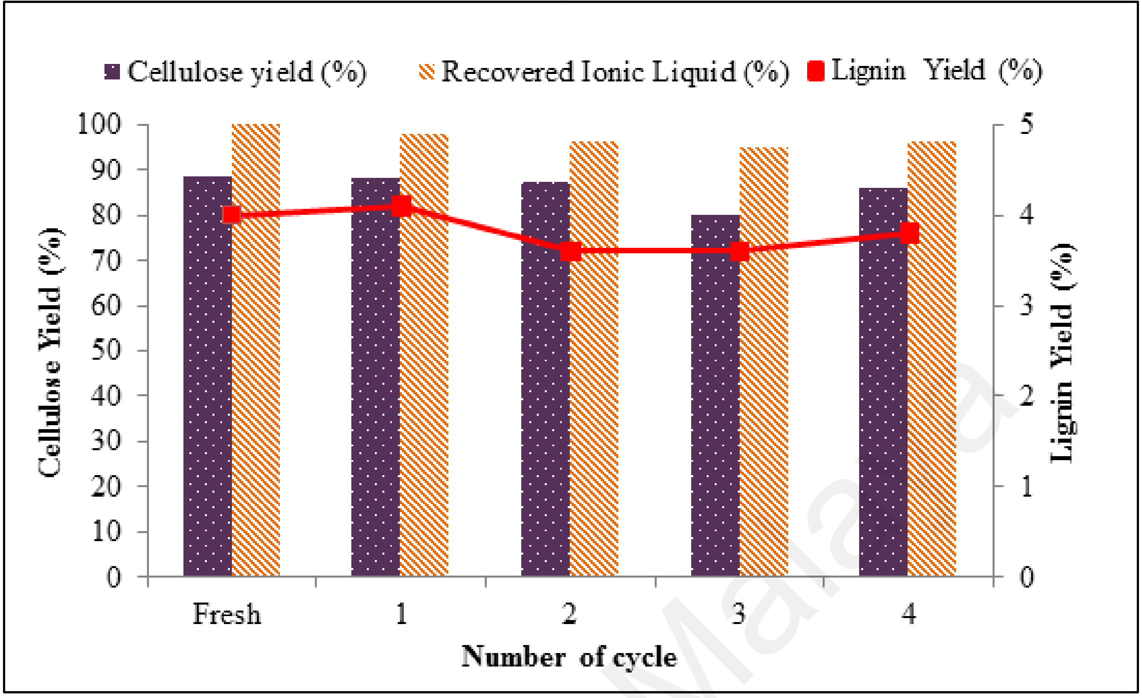
Appendix B 1- Regenerated cellulose, lignin yield and recovery of [Bmim][Ace] obtained after pretreatment process (1 = first, 2 = second, 3 = third and 4 = fourth recycle)



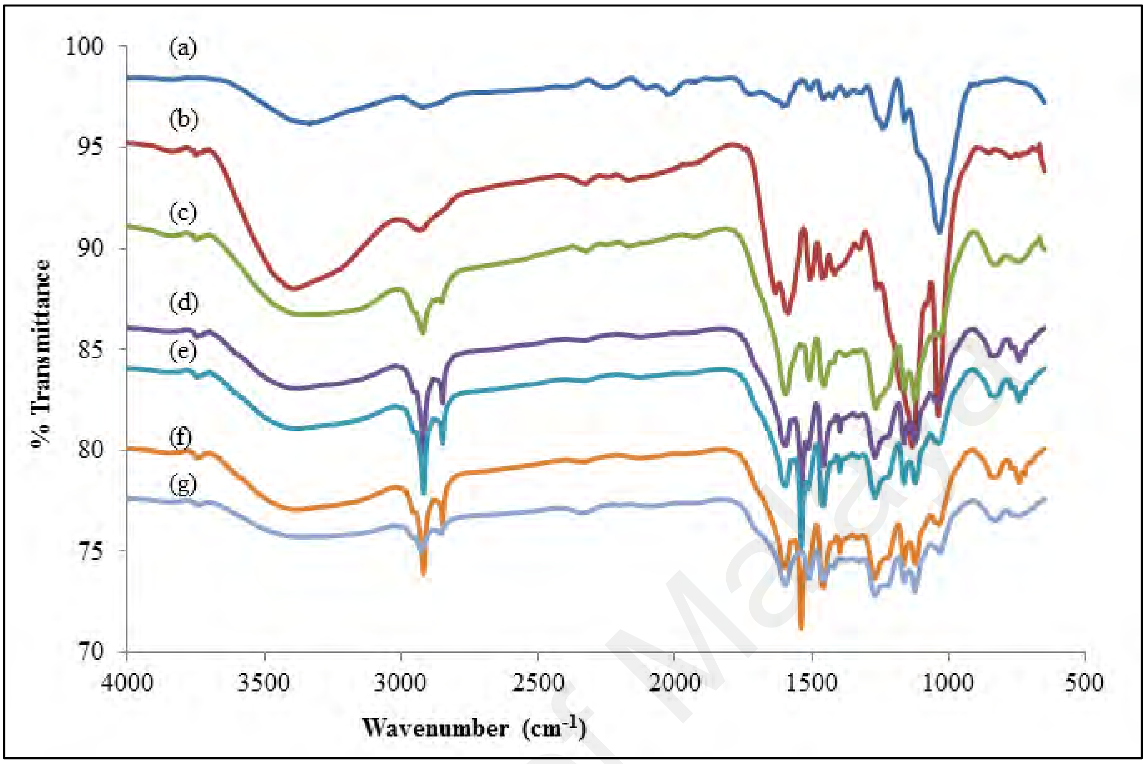
Appendix B 2- Regenerated cellulose, lignin yield and recovery of [Emim]Cl obtained after pretreatment process (1 = first, 2 = second, 3 = third and 4 = fourth recycle)



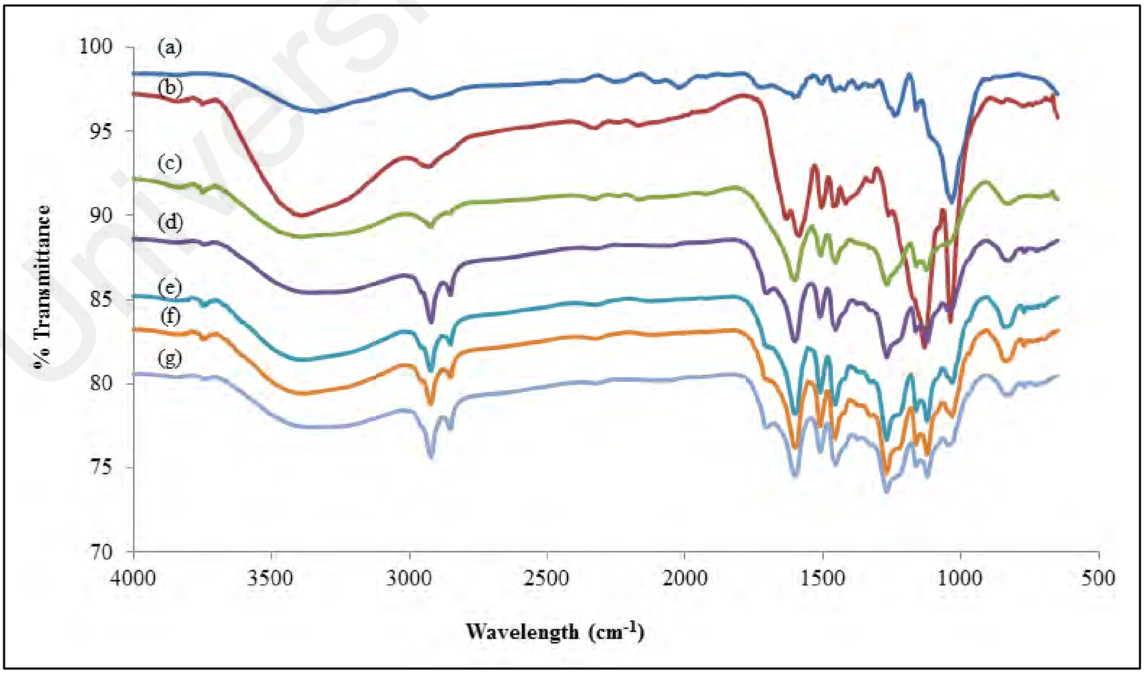
Appendix B 3- Regenerated cellulose, lignin yield and recovery of [Bmim]Cl obtained after pretreatment process (1 = first, 2 = second, 3 = third and 4 = fourth recycle)



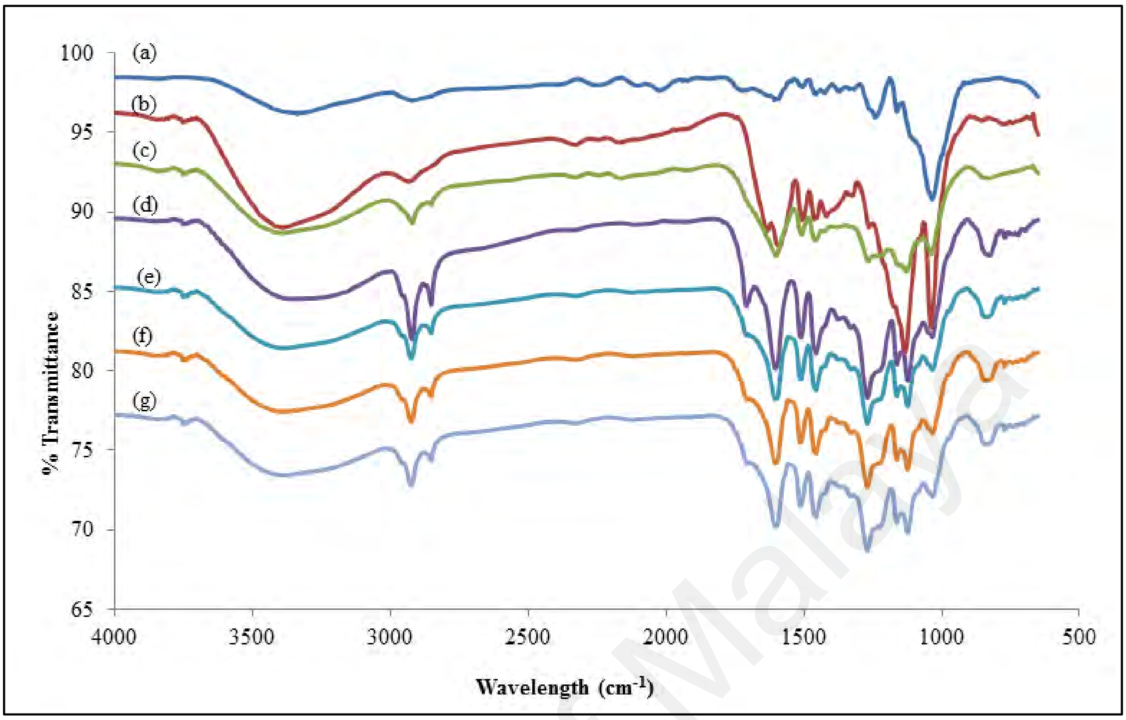
APPENDIX C 1- FTIR analysis of (a) untreated coconut shell, (b) Kraft lignin and regenerated lignin by (c) fresh IL, (d) first recycle, (e) second, (f) third and (g) fourth recycled [Bmim][Ace]



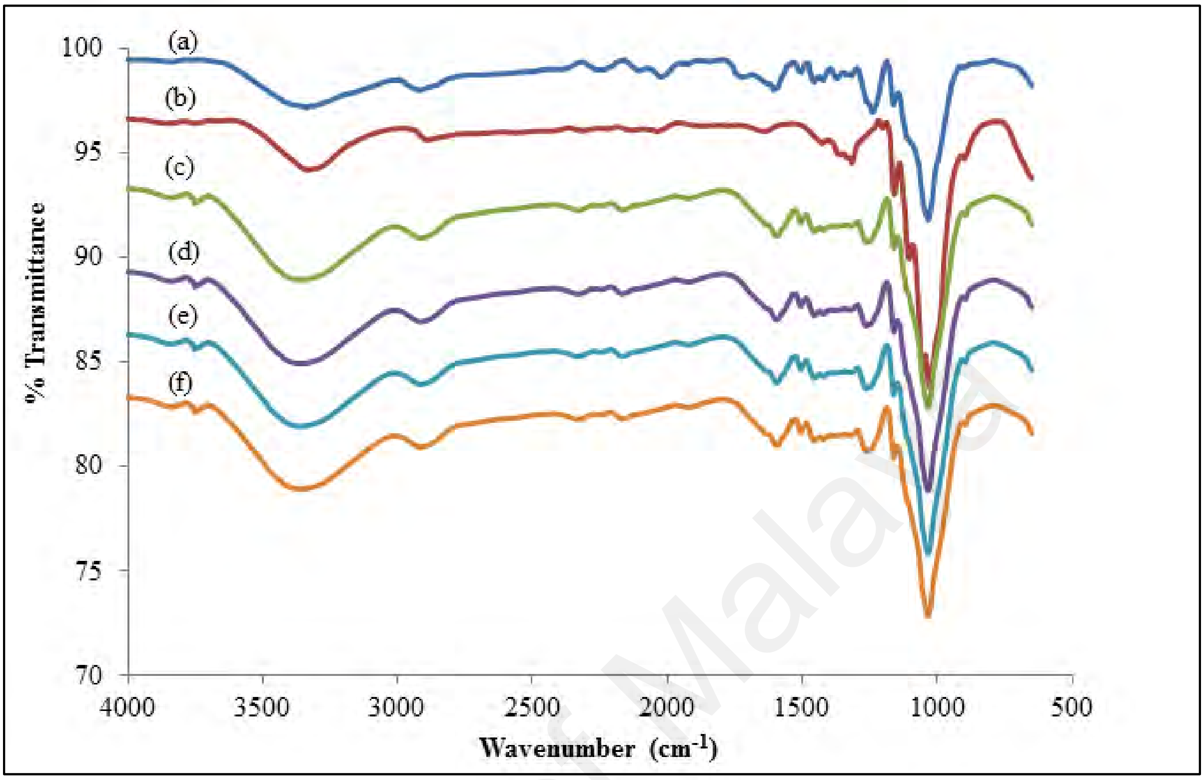
APPENDIX C 2- FTIR analysis of (a) untreated coconut shell, (b) Kraft lignin and regenerated lignin by (c) fresh IL, (d) first recycle, (e) second, (f) third and (g) fourth recycled [Emim]Cl



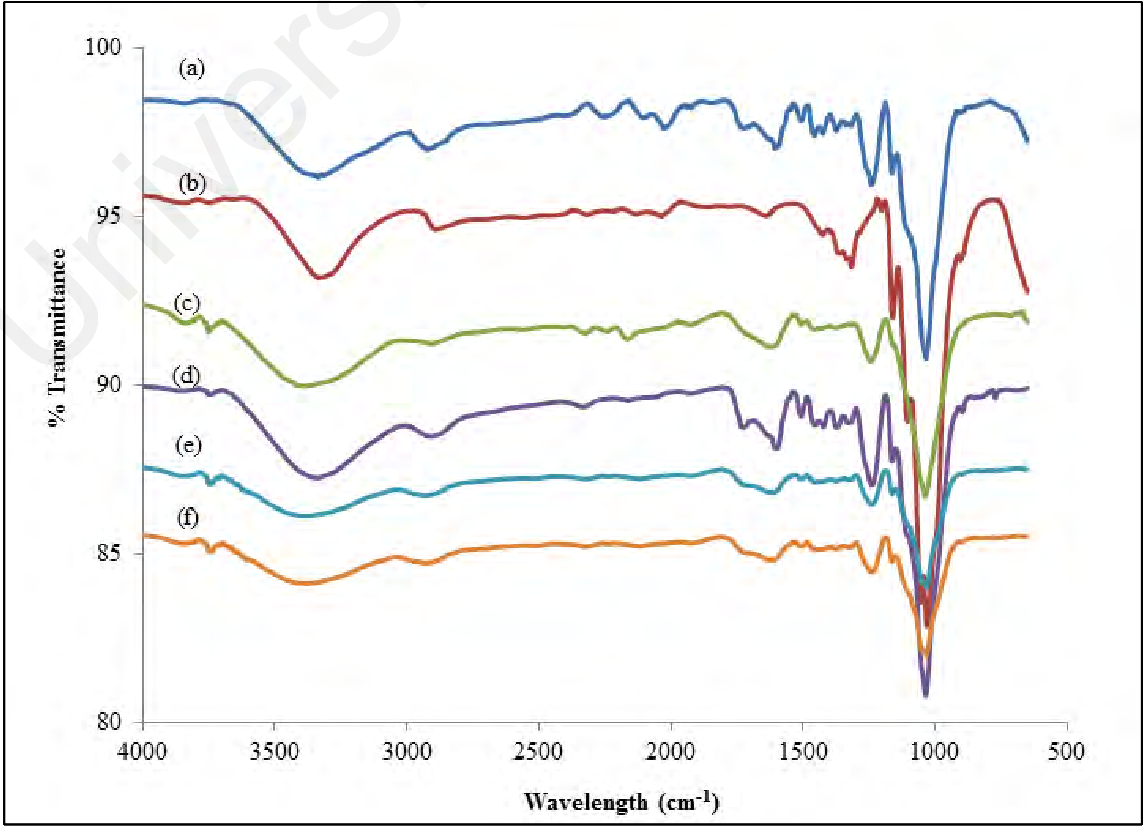
APPENDIX C 3- FTIR analysis of (a) untreated coconut shell, (b) Kraft lignin and regenerated lignin by (c) fresh IL, (d) first recycle, (e) second, (f) third and (g) fourth recycled [Bmim]Cl



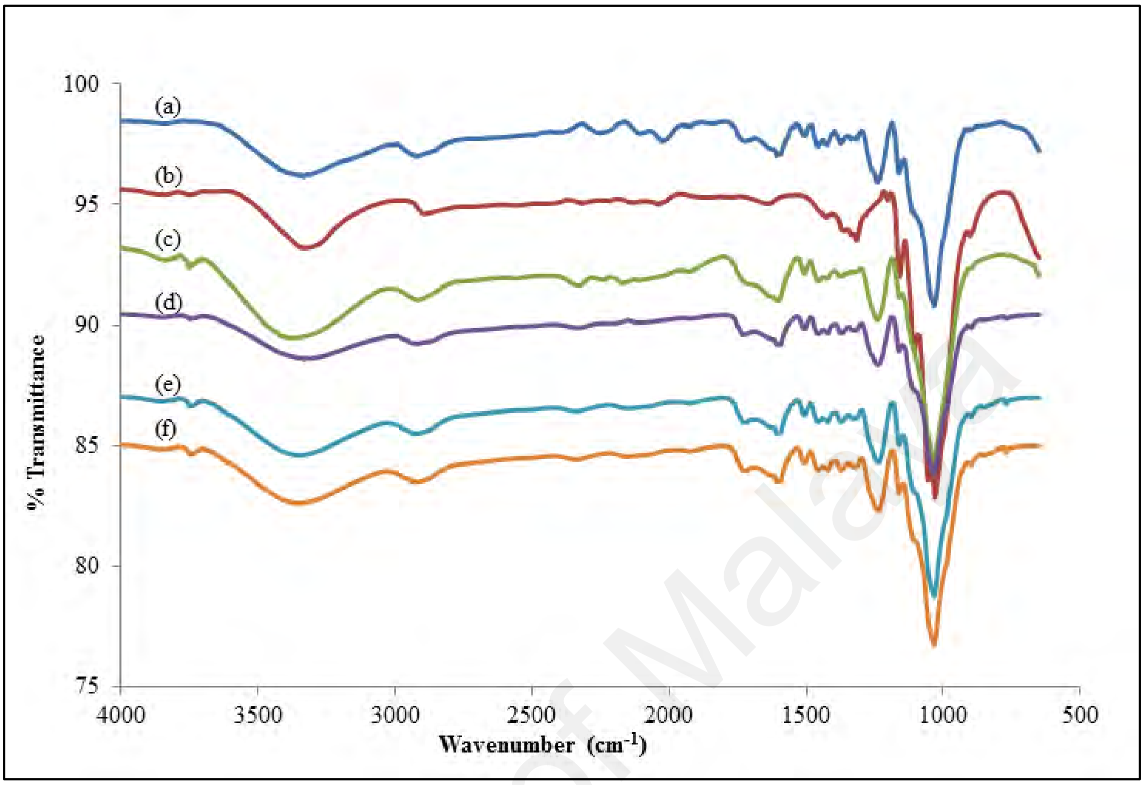
APPENDIX D 1- FTIR analysis of (a) untreated coconut shell, (b) microcrystalline cellulose and regenerated cellulose from (c) first recycle, (d) second, (e) third and (f) fourth cycle of [Bmim][Ace]



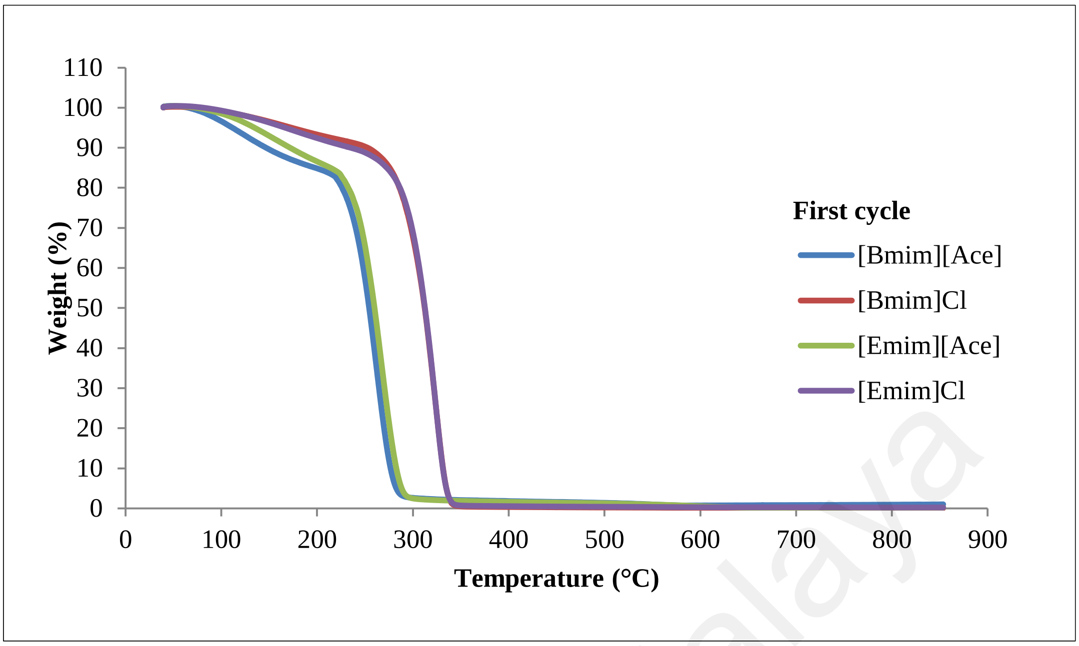
APPENDIX D 2- FTIR analysis of (a) untreated coconut shell, (b) microcrystalline cellulose and regenerated cellulose from (c) first recycle, (d) second, (e) third and (f) fourth cycle of [Emim]Cl



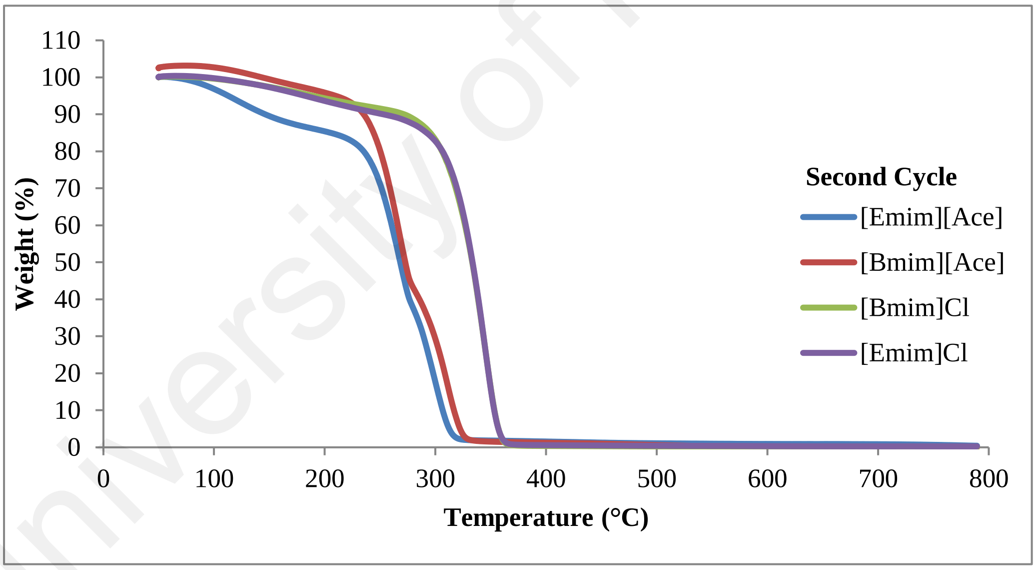
APPENDIX D 3- FTIR analysis of (a) untreated coconut shell, (b) microcrystalline cellulose and regenerated cellulose from (c) first recycle, (d) second, (e) third and (f) fourth cycle of [Bmim]Cl



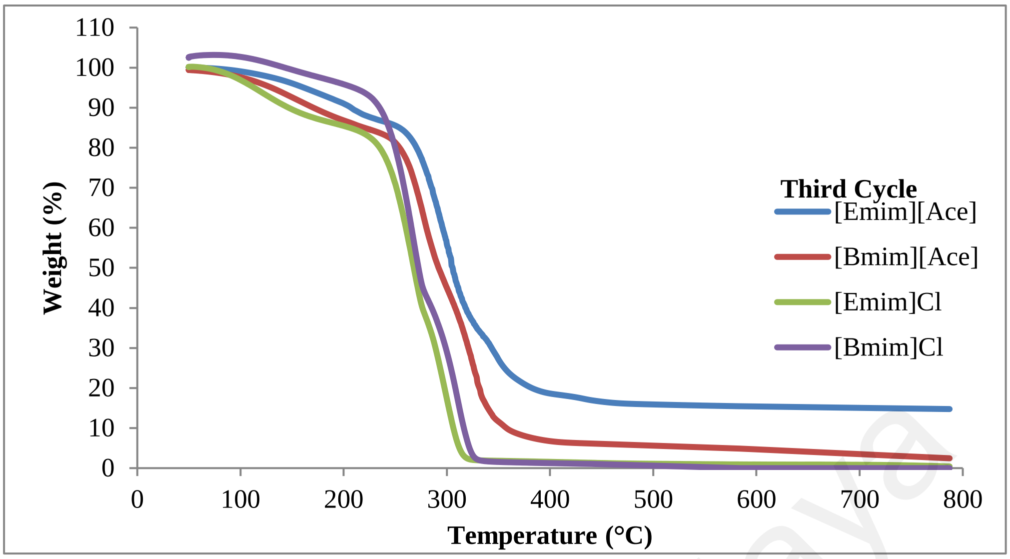
Appendix E 1- TGA curve of first cycle of AIL



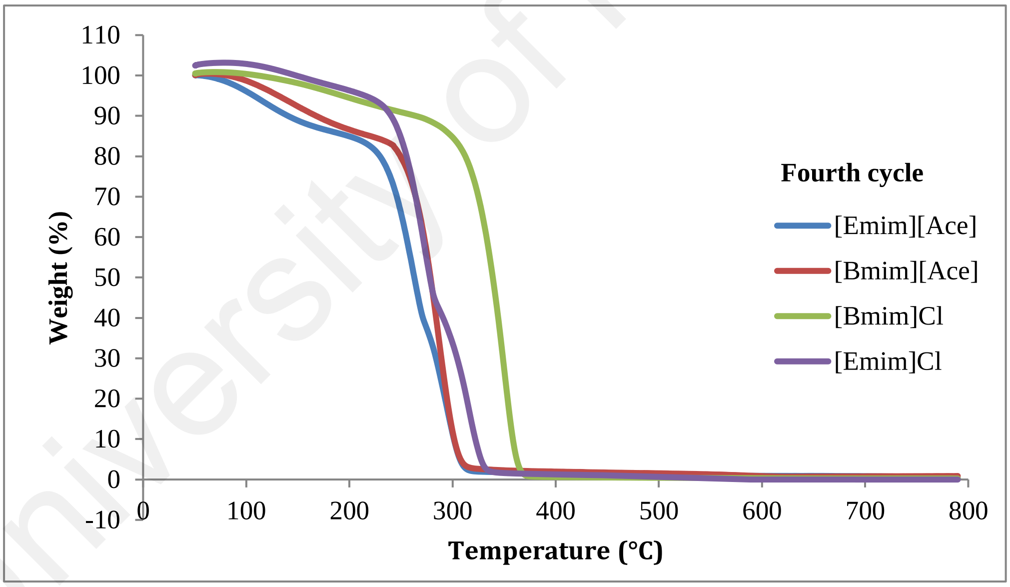
Appendix E 2- TGA curve of second cycle of AILs



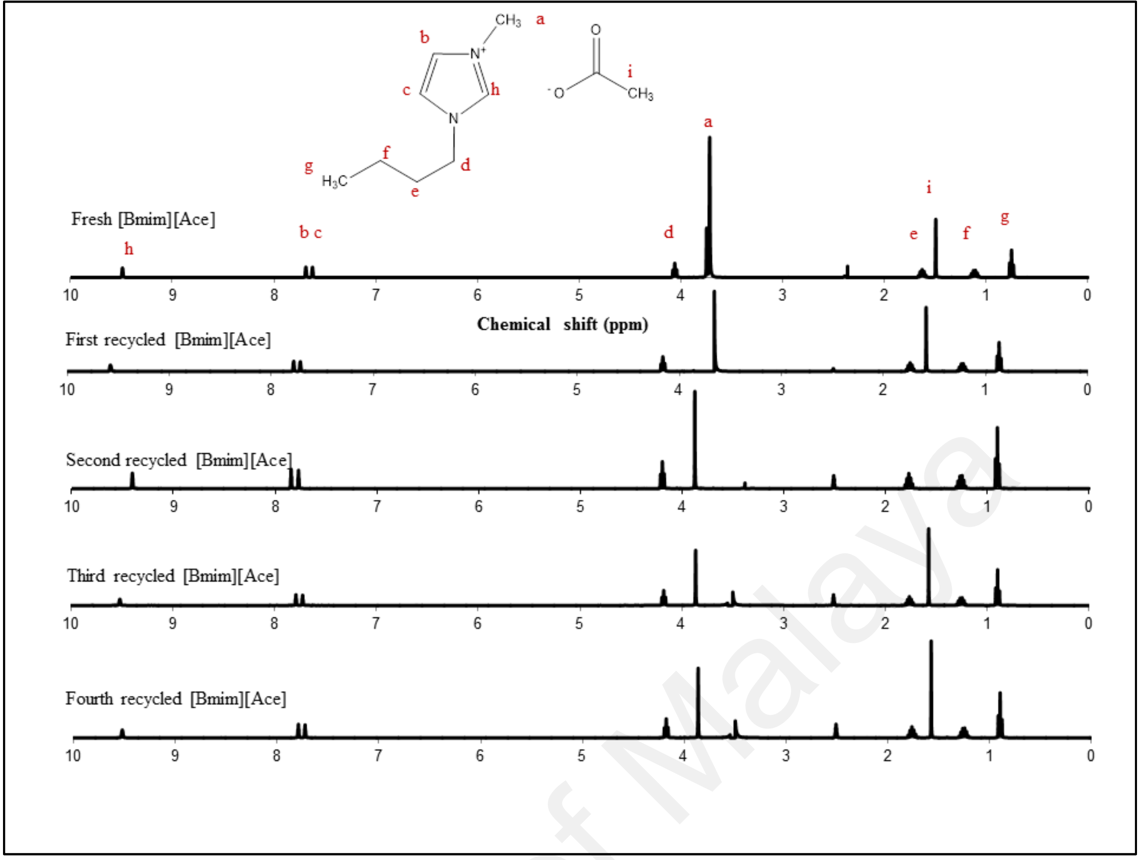
Appendix E 3- TGA curve of third cycle of AILs.



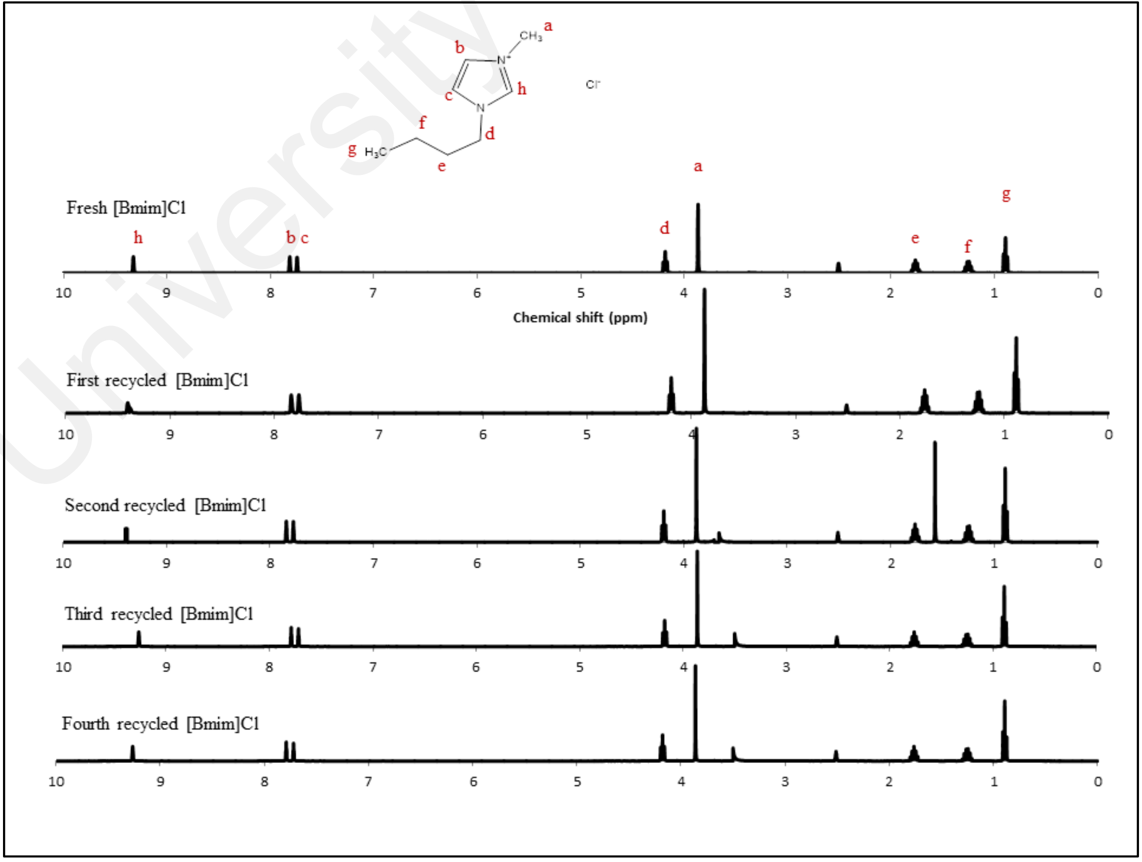
Appendix E 4- TGA curve of fourth cycle of AILs



APPENDIX F 1- ^{1}H NMR of fresh and recycled [Bmim][Ace] up to four times



APPENDIX F 2- ^{1}H NMR of fresh and recycled [Bmim]Cl up to four times



APPENDIX F 3- ^{1}H NMR of fresh and recycled [Emim]Cl up to four times