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# **THE EFFECT OF IONIC LIQUID PRETREATMENT ON SAWDUST**

by

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## DECLARATION

I declare that this thesis entitled “The Effect of Ionic Liquid Pretreatment on Sawdust” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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## The Effect of Ionic Liquid Pretreatment on Sawdust

### ABSTRACT

Sawdust is a waste by product from timber industry. Sawdust mainly consists of cellulose that can be utilized as carbon source for microorganism the hydrogen production under anaerobic fermentation. Pretreatment of sawdust can be either physical or chemical pretreatment. In this research, chemical treatment is choosing as pretreatment method of sawdust. To overcome some problem of other type chemical pretreatment which are not environmental friendly and also involve harmful particle. Ionic liquid or known as green solvent is use as alternative way for pretreatment. To overcome the higher consumption of ionic liquid for pretreatment, co-solvent dimethylsulfoxide (DMSO) was employed together with ionic liquid. The objectives of this study are to study the effect of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) pretreatment on sawdust at different sawdust concentration and to study the effect of co-solvent dimethylsulfoxide (DMSO) on the ([BMIM]Cl) treated sawdust. In this research sawdust undergo sieve, grind and dry process. In dissolution of sawdust different concentration of sawdust dispersed in different concentration of DMSO and ([BMIM]Cl). Three type of concentration use 5 wt%, 10 wt% and 15 wt% in pretreatment process at constant temperature and time which are 80°C and 24 hours. Sawdust structure characterize with XRD, FT-IR and TGA. The result classify into two, effect concentration of sawdust and effect of concentration of DMSO. Both uses XRD, FTIR and TGA for characterize the changing of sawdust structure for untreated and pretreated sawdust. Based on the observation, showed that the higher concentration of sawdust not gives high effect in the pretreatment respectively. It also showed that the uses of DMSO not give effect to the structure of sawdust. DMSO save to use as co-solvent on ([BMIM]Cl) treated sawdust.

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## Kesan Prarawatan Cecair Ionik Terhadap Serbuk Kayu

### ABSTRAK

Serbuk kayu adalah bahan yang terbuang dari industri pembalakan. Serbuk kayu kebanyakannya mempunyai selulosa yang boleh digunakan sebagai sumber karbon untuk mikroorganisma menghasilkan hidrogen pada penapaian anerobik. Prarawatan awal serbuk kayu boleh dilakukan dengan prarawatan fizikal atau prarawatan kimia. Dalam kajian ini, prarawatan kimia dipilih sebagai langkah prarawatan terhadap serbuk kayu. Ia adalah untuk mengatasi beberapa masalah yang dihadapi oleh prarawatan kimia yang lain dimana tidak mesra alam dan mengandungi zarah yang berbahaya. Cecair ionik atau dikenali sebagai rawatan kimia bersifat hijau digunakan sebagai cara alternatif untuk prarawatan. Untuk mengatasi penggunaan cecair ionik yang banyak, co-pelarut dimetilsulfoxide (DMSO) digunakan bersama cecair ionik. Tujuan kajian ini dilakukan adalah untuk mengkaji kesan 1-butil-3-metilimidazolium klorida ([BMIM]Cl terhadap prarawatan serbuk kayu pada kepekatan yang berbeza dan untuk mengkaji kesan co-pelarut dimetilsulfoxide (DMSO) pada prarawatan ([BMIM]Cl. Dalam kajian ini, serbuk kayu melalui proses penapisan, pengisaran dan pengeringan. Dalam proses pelarutan, serbuk kayu dari kepekatan yang berbeza direndam bersama DMSO dari kepekatan berbeza dan ([BMIM]Cl. Tiga jenis kepekatan yang digunakan ialah 5 wt%, 10 wt% dan 15 wt% dalam proses prarawatan pada suhu dan masa yang sama iaitu 80°C dan 24 jam. Struktur serbuk kayu dicirikan menggunakan XRD, FT-IR dan TGA. Keputusan dicirikan kepada dua, kesan kepekatan serbuk kayu dan kesan kepekatan DMSO. Keduanya menggunakan XRD, FT-IR dan TGA untuk mencirikan perubahan struktur serbuk kayu untuk serbuk kayu tanpa rawatan dan prarawatan serbuk kayu. Berdasarkan pemerhatian, kepekatan serbuk kayu yang tinggi tidak memberi kesan yang tinggi pada prarawatan. Ia juga menunjukkan penggunaan DMSO tidak memberi kesan pada struktur serbuk kayu. DMSO selamat digunakan sebagai co-pelarut pada ([BMIM]Cl serbuk kayu yang dirawat.

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## LIST OF ABBREVIATIONS

BMIMCl	1-butyl-3-methylimidazolium chloride (BMIMCl)
IL	Ionic Liquid
[EMIM] <sup>+</sup> [ACE] <sup>-</sup>	1-ethyl-3-methylimidazolium acetate
DMSO	Dimethylsulfoxide
[C <sub>2</sub> mim] [DEP]	1-ethyl-3 methylimidazolium diethyl phosphate
TGA	Thermogravimetric analysis
FT-IR	Fourier transform-infrared Spectroscopy
XRD	X-ray diffraction
DP	Degree of polymerization
DMSO/TBAF	Dimethylsulfoxide/tetrabutylammonium
DMSO/NMI	Dimethylsulfoxide/ N-methylimidazole
DMSO/ LiCl	Dimethylsulfoxide /lithium chloride
VOC	Volatile organic compounds
IR	Infrared
HITRAN	High -resolution transmission molecular absorption
WPG	Weight percentage gain
CrI	Crystallinity index

## LIST OF SYMBOLS

$w/w$	Mass fraction
$M_0$	Before dry weight sawdust
$M_1$	After dry weight sawdust
$I_{002}$	The intensity for crystalline portion of biomass
$I_{am}$	The peak for amorphous portion of biomass
$\Theta$	Theta

# CHAPTER 1

## INTRODUCTION

### 1.1 Background of study

Wood waste that used as a biofuel feedstock has get momentum over the past decade. This is because of the significant developments in techniques and applications. Hardwoods is consider as lignocellulosic biomass, with a significant proportion of cellulose between 45 and 55 w/w%, 24-40 w/w% of hemicellulose and 18-25 w/w% of lignin by comparing with softwoods (Trevorah & Othman, 2015). Sawdust is a waste by product from timber industry that is either used as a packing material.

Sawdust is just not only abundant, but it provide some advantages to be used an efficient adsorbent that is effective to many types of pollutants such as dyes, salts and heavy metals (Batzias & Sidiras, 2004). Sawdust mainly consists of cellulose that can be utilized as carbon source for microorganism the hydrogen production under anaerobic fermentation. The conversion of lignocellulose biomass into some other valuable forms of energy become important among global research focus (Menon & Rao, 2012). It is because the efficient and cost effective conversion of the polysaccharides present in the cell walls of lignocellulose biomass into fermentable sugars.

These sugars can be modified and converted into variety of biofuels which are range from ethanol to fatty acid esters. The conversion process involves pretreatment, saccharification and fermentation. Pretreatment of biomass is necessary because to alter its chemical and physical properties and to ease the enzymatic digestibility of the recovered polysaccharides (S.Singh et al., 2013). Among various pretreatment methods

developed for enzymatic digestibility, the ionic liquid (IL) pretreatments gained attentions due to the ability of ILs to dissolved cellulose under relatively mild conditions (Menon & Rao, 2012).

IL pretreatment provide some advantages such as increase the surface area, decrease cellulose crystallinity and lignin content that help to improved hydrolysis efficiency (M. S. Singh et al., 2012). Various ionic liquids is prefer to use such as 1-butyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium acetate, and 1-ethyl-3-methylimidazolium diethyl phosphate have been before enzymatic saccharification for reducing sugar yields. In this study, 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) is used as ionic liquid for pretreatment (Ang et al., 2012).

More recent study also shown that lower IL concentration which is (10-50 w/v %) in water also can be the effective ways in pre treating biomass, reduce the amount of washing required to enzymatic saccharification. In addition, using IL-water mixtures as pretreatment agents give some advantages such as it helps to reduce viscosity, eliminate gel formation during pretreatment and reduce the energy input, reduce cost associated with IL, facilitating scale up and also downstream processing.

In this study, the pretreatment medium (co-solvent) use is dimethylsulfoxide (DMSO). DMSO is used as co-solvent in pretreatment of sawdust as because it is help to reduce the viscosity of ionic liquid. It also can help to reduce the cost of pretreatment process because DMSO liquid cost not too costly compare to ionic liquid that more costly. In this study also, the aim is to study what concentration of DMSO effect the properties of sawdust. Thermogravimetric analyses (TGA), Fourier transform-infrared (FT-IR) Spectroscopy, X-ray diffraction are used as characterization method in this study.

## 1.2 Problem Statement

Conversion process of lignocellulose biomass into other valuable forms of biodegradable material becomes a global research. Pretreatment of sawdust can be either physical or chemical pretreatment. Chemical treatment is choosing as pretreatment method of sawdust. Many chemical such as (NaOH,  $\text{NH}_4\text{OH}$ ,  $\text{FeCl}_3$ ) have been used to help break down the complex lignin in order to improve the adsorption performances of many lignocellulosic residues. However those chemical are not environmental friendly and it is also involve harmful particle. To overcome this problem, ionic liquid or known as green solvent is introduced as the alternative way for pre treatment. It is because green solvent have some properties such as low vapor pressure, good thermal stability, non explosivity and recyclability, have been proposed as suitable solvents for the components of wood. In this study, pretreatment medium (co-solvent) dimethylsulfoxide (DMSO) is use as agent to reduce the viscosity. The effect of the DMSO and IL to the sawdust have to study by analyze with some characterization methods. The methods are Thermogravimetric analysis (TGA), Fourier transform-infrared (FT-IR) Spectroscopy, X-ray diffraction.

## 1.3 Objectives

The objectives of this study are:

1. To study the effect of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) pretreatment on sawdust at different sawdust concentration.
2. To study the effect of co-solvent dimethylsulfoxide (DMSO) on the ([BMIM]Cl) treated sawdust.

#### 1.4 Expected Outcome

In this research, sawdust will be treated with 1-butyl-3-methylimidazolium chloride ([BMIM]Cl). It is expected that the sawdust fiber will be modified after pretreatment. Ionic liquid ([BMIM]Cl) and DMSO as co-solvent will be used to treat the sawdust fiber. Different concentration of sawdust and concentration of DMSO as changing parameter use in the pretreatment of sawdust.

The purpose of the pretreatment is to modify cellulose fiber surface in order to reduce the hydrophilic nature of sawdust. It was expected that ionic liquid can enhance mechanical and physical properties of wood. Besides, in this research it is also expected that by choosing ionic liquid as chemical pretreatment of sawdust is more effective than other chemical treatment such as acid and alkali pretreatment. It was expected also, the uses of co-solvent DMSO in this research can affect the chemical structure of sawdust and help to decrease the viscosity of ionic liquid to ease the pretreatment process.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Sawdust as renewable source.

The example of renewable energy sources is lignocellulosic biomass, which environmentally friendly because they emit less pollution without contributing net carbon dioxide to the atmosphere. Lignocelluloses can be classified to wood residues that include sawdust and paper mill discards, grasses, waste paper, agricultural residues such as straws, stoves, peelings, cobs, stalks, nutshells, non-food seeds, bagasse's, domestic waste, food industry residues, municipal solid waste. The current sustainable source of organic carbon nowadays is plant biomass. Biomass is defined as organic matter that available on a renewable basis. Biofuels is derived from plant biomass and only sustainable class of liquid fuels. Biofuels also include bio-alcohols (ethanol, butanol), biodiesel, bio-oils and syngas derivatives. The production of bioethanol from lignocellulosic biomass involves three steps. There is size reduction and pretreatment which make the lignocellulosic material amenable to enzymatic/microbial/chemical analysis. Besides, hydrolysis of cellulose and hemicellulose to fermentable reducing sugars and lastly is fermentation of the sugar to ethanol or other fermentation products (Vancov et al .,2012).

#### 2.2 Pretreatment of sawdust

The aim of pretreatment is to make cellulose accessible to hydrolysis for conversion into sugar and subsequently into ethanol. Enzymes usually use as catalyzer



for hydrolysis of cellulose or lignocellulose to monosaccharides. Basically, most pretreatment can change the physical and chemical structure of the lignocellulose biomass and improve hydrolysis for conversion to constituent sugars. An effective lignocellulose pretreatment and fractionation method should have some of the following features which are produce high monomeric sugar yields, generate highly digestible cellulose for rapid hydrolysis with lower enzyme use, minimize production and release of sugar and lignin degradation products, low energy consumption, low capital and operational costs (Vancov et al., 2012). Pretreatment includes both physical and chemical pretreatment. Physical pretreatment refers to the reduction of physical size of biomass feedstock to increase enzyme accessible surface areas. Chemical pretreatment refers to the process of using chemicals to remove or modify key chemical components that interfere with biomass cellulose saccharification that mainly is hemicellulose and lignin. Feedstock pretreatment that gained attention from most researcher is chemical pretreatment (Gao et al., 2013).

### **2.2.1 Physical Pretreatment**

Physical pretreatment is one of pretreatment method chosen by researcher because it used to increase the accessible surface area and pore size of lignocelluloses and also to decrease the crystallinity and degree of polymerization of the cellulose present in lignocellulose. There are some different types of physical processes such as milling (ball milling, two-roll milling, hammer milling, colloid milling and vibro energy milling), chipping, grinding and/or irradiation (gamma rays and electron beam). It can be used to improve the enzymatic digestibility of lignocellulosic waste materials. Size reduction is one of the most effective methods to increase the enzymatic accessibility to

lignocelluloses. Size reduction used in most research studies of hydrolysis but only little information about the characteristics of the substrate and energy consumed during the process. But, many of the physical methods for size reduction (milling and grinding) are not economically feasible because require high-energy. Studies also shown that milling can cause increase biogas, bioethanol, and bio hydrogen yields. The other physical treatments that prefer involve the use of gamma rays that cleave the then give a larger surface and lower crystallinity. This method is very expensive, and need huge environmental and safety concerns (Agbor et al., 2011).

### **2.2.2 Chemical Pretreatment**

Chemical pretreatment has become one of the promising methods to improve biodegradability of cellulose by removing lignin and/or hemicellulose. It also to decrease the degree of polymerization (DP) and crystallinity of the cellulosic component in lignocelluloses. Some investigated are done by previous study, the using of chemical pretreatment in the used for delignification of cellulosic material in the pulp and paper industry and also to enhanced biomass digestibility in an industrial pretreatment process. It also reported that some chemicals have significant effect on the native structure of lignocellulosic biomass, do not produce toxic residues for the downstream processes and reaction that carried out at room temperature and pressure. Chemical pretreatments can be oxidizing agents, alkali, acids, ionic liquid and salts can be used to degrade lignin, hemicelluloses and cellulose from lignocellulosic wastes. Organic acids such as oxalic acid, acetylsalicylic acid and salicylic acid can also be used as catalyst whereas organic or aqueous organic solvent mix with inorganic acids (HCl or H<sub>2</sub>SO<sub>4</sub>) is used to break the internal lignin and hemicellulose bonds. Concentrated acids are not preferred because

they are corrosive and must be recovered (Behera et al., 2014). Dilute acid pretreatment in hydrolysis of hemicellulose to its monomeric units, rendering the cellulose more available. For acid pretreatment it requires the use of an alkali that function to neutralize the hydrolyses. Alkaline pretreatment disrupts the lignin structure and breaks the linkage between and the other carbohydrate fractions in lignocellulosic biomass (Agbor et al., 2011).

### **2.3 Ionic Liquid**

Among various pretreatment methods developed to mitigate biomass recalcitrance for enzymatic hydrolysis, the ionic liquid pretreatment attract researcher interest as because it act as "green solvent" and its potential to regenerate and chemically modify the cellulose compare with other process. Ionic liquid are molten salts with glass transition or melting temperatures below 100°C (Wang et al., 2012).

Ionic liquid have advantages such as excellent dissolubility, high ionic conductivity, low vapors pressure, low toxicity, chemical stability, thermal stability, near zero volatility and recyclability (Reddy et al., 2014). Due to their non-volatile and non flammable properties, they are considered as ideal replacements for conventional environmentally harmful molecular solvents (Vancov et al., 2012).

Ionic liquid offer potentially clean method for chemical reaction it is because they able dissolve complex macromolecules and polymeric materials with high efficiency (Wang et al., 2012). Ionic liquid also able to dissolve lignocellulosic biomass essentially depends on the type of anion and cation (Auxenfans et al., 2014). This indicates that ionic liquid dissolution is selective on the type of substrate, and the

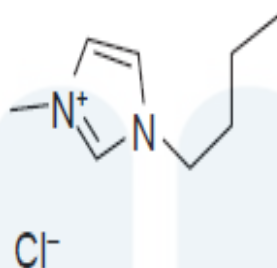
selectivity of ionic liquids could be attributed to their ionic functional groups (Javier et al., 2015).

The use of ionic liquid in the field of lignocellulosic biomass chemistry is expanding fast. Ionic liquid use for pretreatment including dissolution and fractionation of lignocellulosic biomass to produce enzyme digestible carbohydrates. A Common feature of ionic liquid process is that biomass must dissolved first in ionic liquid prior to the extraction and recovery processes (Moghaddam et al., 2014).

It also reported that woods with different hardness can be dissolved in various imidazolium-based ionic liquid under mild condition. Previous study also showed that ionic liquid could be used as reaction media for homogenous functionalization of lignocelluloses

As green solvent the specific functional ionic liquid can be designed such as ([BMIM]Cl) to dissolve cellulose, lignin and even wood. It is also can be a potential method that effectively converse lignocellulosic biomass into chemicals ([BMIM]Cl) has a melting point of 41 and decomposition temperature of 254°C (Vancov et al., 2012).

Fig. 2.1 shows the structure of ([BMIM]Cl). A single crystal of ([BMIM]Cl) a prototype ionic liquid that successfully been prepared and an X-ray crystallographic analysis has been performed. It reveals the presence of hydrogen bonding network involving the chloride anion and the ring n-butyl groups of (BMIM) cation and structure of the imidazolium rings (Croitoru et al., 2014).



**Fig. 2.1** The structure of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl)

## 2.4 Dimethyl sulfoxide (DMSO)

Biomass has complex structure and makes it nearly impossible to dissolve in common molecular solvents. Recent discoveries also proved that there are some suitable system that may allow the dissolution of lignocellulosic materials, such as dimethyl sulfoxide/tetrabutylammonium (DMSO/TBAF), dimethylsulfoxide/N-methylimidazole (DMSO/NMI), dimethylsulfide/lithium chloride (DMSO/LiCl). However we must noted that the three organic solvent systems based on DMSO are limited to analysis of the chemical structure of the wood component especially for lignin. These solvents also are volatile organic compounds (VOC) (Sun et al., 2013).

## 2.5 Materials Characterization

In this session, there are a few techniques that were used to identify the material characteristics of samples such as TGA, FT-IR and XRD.

### 2.5.1 Thermogravimetric analysis (TGA) measurement

Thermogravimetry analysis (TGA) provide information on the thermal decomposition profiles of respective component (Marcilla et al., 2013). This machine

also can provide detailed information on change of mass of a sample as a function of temperature or time under a controlled atmosphere (S.Singh et al., 2013). It is a useful technique for studying thermal behavior of solid samples during pyrolysis and determining kinetics of the thermal events.

The thermogravimetric (TG) curve plot based on mass lost against increasing temperature or time. The benefits of the TGA technique are its simplicity in utilization and good repeatability (Vhathvarothai et al.,2014). Besides, TGA can also provide specific information on each individual component within lignocellulosic based on their temperature response and rate of volatilization or decomposition.

TGA is a very sensitive technique and able to use to find minor difference in biomass composition. In the presence of inert gases, this loss of mass is attributed to the loss of volatile matter and decomposition as a function of temperature (S. Singh et al., 2013). Several studies have applied TGA technique to investigate thermal decomposition profiles and kinetics during pyrolysis of various types of samples. The samples are including biomass fuels, coals and their blends.

From previous study, (Vuthaluru, 2003), observed that thermal behaviors during copyrolysis biomass fuels including wood waste, wheat straw and coal using TGA. During the copyrolysis, three thermal events were identified. The first two events were linked to the biomass pyrolysis whereas for the third event was dominated by the coal pyrolysis which arose at higher temperatures. No interaction occurs between the biomass and coal was detected during pyrolysis.

(Kyoo et al., 2010) studied of copyrolysis characteristics of sawdust and subbituminous coal blend through TGA. The study identified that the different devolatilisation rate between sawdust and subbituminous coal mainly because of their



structural properties. It were observed from previous studies on thermal behavior during copyrolysis. Moreover only few studies were conducted on copyrolysis of biomass and coal blends using biomass as the major component (Vhathvarothai et al., 2014).

### **2.5.2 Fourier transform- infrared (FT-IR) measurement**

Fourier transforms infrared (FT-IR) spectroscopy being a modern non-destructive analytical method. It was more often used for the structure elucidation and quantification of a large variety of organic, inorganic and biological samples. FT-IR has also been used in conjunction with fast pyrolysis reactors such as a heated grid reactor or a commercially available CDS Pyro probe for quantitative analysis.

For typical biomass samples, the quantitative data are obtained on nearly 20 volatile species. There are some advantages of IR spectroscopy are 1) the analyzed samples are not subjected to any chemical treatment thus avoiding secondary reactions; 2) all the compounds present in the sample are measured simultaneously, thereby simplifying and speeding up the analysis. FT-IR spectroscopy frequently applied in environmental analyses including soil organic matter (Grube et al., 2006).

A common method use for analysis of FT-IR spectra is by selecting individual peaks that can be easily assigned or by taking peak ratios. The concentration of thermal decomposition products are determined by comparing the FT-IR data with the calibration spectra measure at the same conditions. From previous study, a different approach suggested by den Blanked which is based on evaluation of the concentration from the measured spectra using molecular spectroscopic databases, like the HITRAN database.

This approach is suggested for FT-IR spectroscopy with an intermediate resolution. An alternative approach is to use multivariate analysis techniques. In this technique the most significant spectral features are highlighted based on their correlation with the analysis being undertaken, and not simply by selecting the largest or most easily assigned vibrations. Biomass components have a multitude of overlapping IR absorption bands; this makes quantification of single bands tedious and often unreliable.

Frequently, the reability of analysis can be improved by application of statistical multivariate methods, including principal component analysis and partial least squares (Bahng et al., 2009).

### **2.5.3 X Ray Diffraction (XRD) measurement**

The crystallinity of cellulose has been recognized by using X-ray diffraction (XRD). It gained attraction from researcher to be as one of the major supramolecular structure properties which determines the hydrolysis rate. XRD is a versatile. XRD consist of some properties such as rapid, non- destructive method that reveals detailed information about the chemical composition and structure of crystalline materials and is applicable to probe structures from approximately 1nm to hundreds of nanometers.

The wavelength of X-rays used in XRD is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in solid materials (Bahng et al., 2009). Basically current studies using XRD to focus on comparing the changes of diffraction peaks, cellulose crystallinity or size of crystallite between untreated and after- treated samples. Then, it indicates the influence of structure modification on pretreatment effect or the subsequent anaerobic digestion.



In the process of pretreatment, dynamic variation of crystalline and amorphous region is important for exploration about co-pretreatment mechanism that is have less explored by previous study. The objective of this study by using XRD to investigate the morphology and spatial structure, crystallinity and microcrystalline size at different periods during chemical pretreatment.



## CHAPTER 3

### MATERIALS AND METHOD

#### 3.1 Materials and preparation

Sawdust were taken from sawmill and filtered using 250  $\mu\text{m}$  sieve sizes and were ground to a smaller size. Then, the samples were sieved again using the same sieve size. Next, the sawdust was dried at 105°C for 24 hours. The dried and sieved material was stored in zipping bag at room temperature for subsequent analysis.

#### 3.2 Dissolution of sawdust

Sawdust 5 wt% was dispersed in 5 wt% dimethylsulfoxide (DMSO) and was mixed with ([BMIM]Cl) 90 wt% in a vial equipped with magnetic stirrer. Then, the sample mixture was stirred at 80°C in oil bath for 24 hours. After a determined time, the samples solution were poured with distilled water, while the solid residues were filtered out and washed with distilled water to eliminate ([BMIM]Cl), DMSO and by-products, and then dried in an oven with air circulation 60°C for 48 hours. The experiment was repeated based on Table 3.1.

Table 3.1 Concentration of sawdust, DMSO and ionic liquid in wt% for all nine samples

SAWDUST wt%	DMSO wt%	IONIC LIQUID wt%
5	5	90
5	10	85
5	15	80
10	5	85
10	10	80
10	15	75
15	5	80
15	10	75
15	15	70

The extent of reaction was calculated as weight percent gain (WPG) to determine differences in oven dry weight of the sample before modification and after modification. The weight percentage gain (WPG) of modified sawdust was calculated according to the Equation 3.1.

$$\text{WPG} = 100 \frac{M_1 - M_0}{M_0} \quad \text{Equation 3.1}$$

$M_0$  and  $M_1$  are the oven dry weights of sawdust before and after pretreatment, respectively.

### 3.3 Material Characterization

After pretreatment of sawdust, sawdust was characterized to identify and determine the characterization of the final product by using TGA, FT-IR and XRD.

#### 3.3.1 Thermogravimetric analysis (TGA) measurement

TGA is the method used for thermal analysis. TGA measure the amount of weight lost of each sample. The brand name of the machine use is TGA/ DSC 2, STAR<sup>o</sup> System and the model name is Mettler Toledo. For each sample, analysis was carried out and approximately 18.8 mg of sample was used. The testing need to run in the helium, nitrogen, air or other gases. The temperature of the sample heated was 50°C - 600°C at a rate 10 K/min in the presence of nitrogen 20 ml/min. The results of this experiment were than compared untreated and pretreated samples to measure the changes of the physical and chemical of the sample as function of increasing concentration of sawdust or concentration of DMSO.

### 3.3.2 Fourier transform- infrared (FT-IR) spectroscopy measurement

The chemical structure of untreated and pretreated sawdust was characterized using Fourier transform- infrared (FT-IR) spectroscopy. This machine very effective to find the functional group and characterize covalent bonding of the molecule for the sample. The brand name of the machine use is Thermo Scientific and the model is Nicolet iZ10 FT-IR Spectrometer. Approximately 50-100 mg of the ground sample was required to fill the sample well of the diamond- composite ATR sample cell. The sample cell was equipped with a spring-loaded anvil to reproducibly press the solid sample uniformly and tightly against the diamond surface. Mid-IR spectra were obtained by averaging 512 scans from 4000 to 400 $\text{cm}^{-1}$ , at 2- $\text{cm}^{-1}$  resolution. The spectra were represented as relative transmittance percentage (%) of wave number ( $\text{cm}^{-1}$ ).

### 3.3.3 X Ray Diffraction (XRD) measurement

XRD can run sample in three form such as solid, liquid and powder. XRD were used to characterize the crystallinity of lignocellulosic materials for pretreated and untreated of sawdust. After that, the XRD pattern of each samples were recorded with a Bruker D2 Phase Powder Diffractometer. By using XRD testing, scans collected from  $2\theta = 5^\circ$  to  $60^\circ$  with step size of 0.03 at 4 s per step.

Crystallinity index (CrI) was determined based on the XRD data and calculated using the Equation 3.2.

$$\text{CrI} = \frac{(I_{002} - I_{\text{am}})}{I_{002}} \times 100 \quad \text{Equation 3.2}$$

In which,  $I_{002}$  is the intensity for crystalline portion of biomass at about  $2\theta = 22^\circ$  and  $I_{\text{am}}$  is the peak for the amorphous portion such as cellulose, hemicelluloses and

lignin at about  $2\theta = 17^\circ$ . The second highest peak after  $2\theta = 22^\circ$  was  $2\theta = 17^\circ$ , and was assumed to correspond to amorphous region.

The amorphous was determined based on XRD data and calculated using the Equation 3.3.

$$\text{Amorphous} = 100 - \text{CrI}$$

Equation 3.3

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Effect of reaction parameters

Pretreatment of lignocellulosic material represents one of the most effective ways to enhance the properties of lignocellulosic material. In the present study, the parameters of the homogeneous reaction between sawdust, DMSO and ionic liquid including the mass ratio of sawdust to ionic liquid, reaction time, reaction temperature, as well as its possible mechanism were investigated. The results are given in Table 4.1.

The WPG was used to evaluate the extent of modification on the homogeneous reaction of sawdust with DMSO and ionic liquid. The effects of reaction temperature, reaction time, concentration sawdust and DMSO were examined.

Table 4.1 Esterification condition examined for the derivatization of sawdust

SAWDUST wt %	DMSO wt %	IONIC LIQUID wt %	WPG %
5	5	90	-21.2
5	10	85	-13.2
5	15	80	-20.0
10	5	85	-6.8
10	10	80	-5.2
10	15	75	-2.0
15	5	80	-12.5
15	10	75	-5.3
15	15	70	-3.7

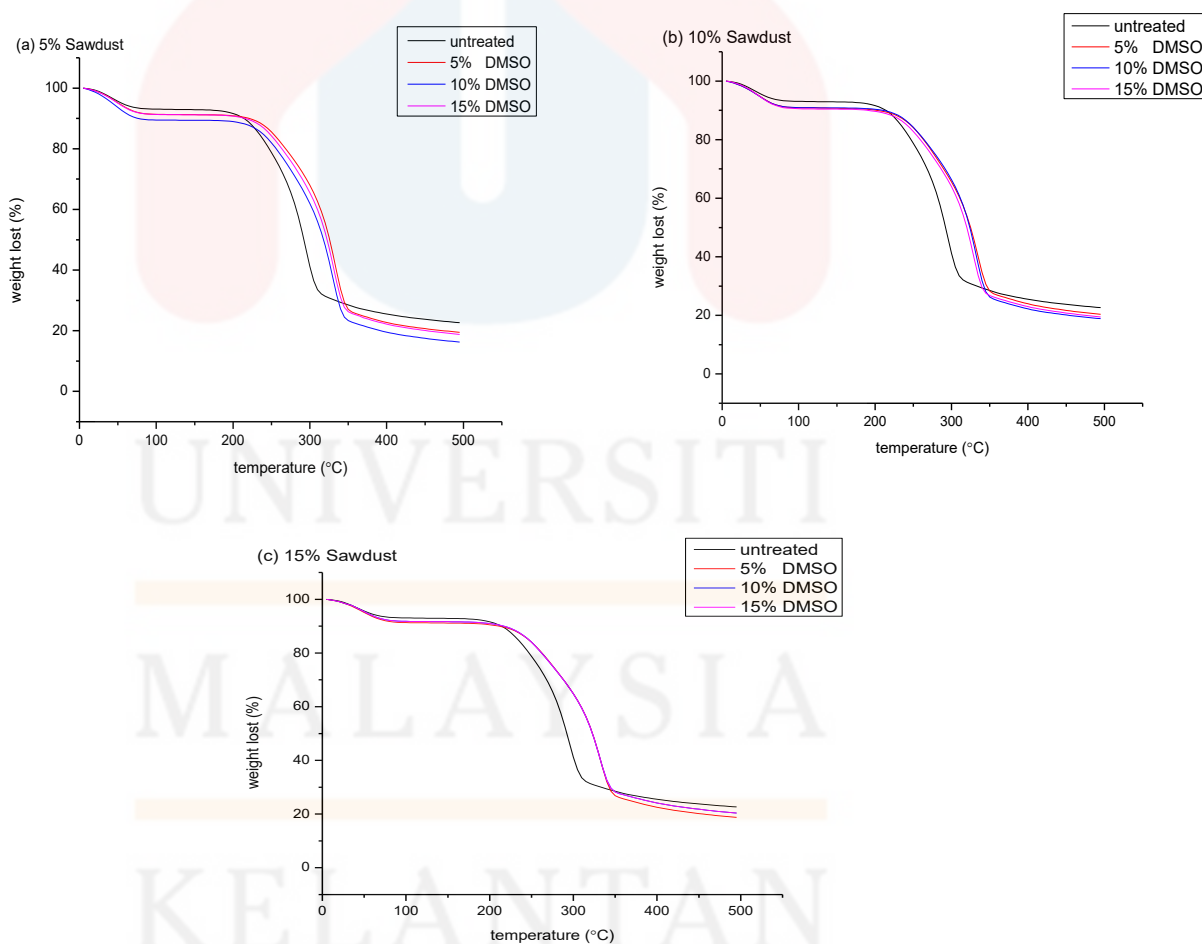
Table 4.1 shows the esterification condition examined for the derivatization of sawdust. Generally, an increase of ionic liquid concentration ([BMIM]Cl) determine an increase in WPG 3.7 to -21.2. A maximum WPG of -21.2 was obtained when sawdust samples was reacted with 90 wt% ([BMIM]Cl).

## 4.2 Effect of concentration of sawdust

In this session, a few techniques were used to identify the effect of concentration of sawdust. It used to identify the thermal properties, FT-IR spectra and X Ray Diffraction.

### 4.2.1 Thermal properties

Fig. 4.1 shown the thermogravimetric (TG) curve of (a) 5 wt% sawdust with 5, 10, 15 wt% DMSO (b) 10 wt% sawdust with 5, 10, 15 wt% DMSO (c) 15 wt% sawdust with 5, 10, 15 wt% DMSO



**Fig. 4.1** Thermogravimetric (TG) curves of the pretreatment of sawdust with DMSO at different concentration of sawdust (a) 5 wt% sawdust with 5, 10, 15 wt% DMSO (b) 10 wt% sawdust with 5, 10, 15 wt% DMSO and (c) 15 wt% sawdust with 5, 10, 15 wt% DMSO and compare with untreated sawdust.

In each TG curve based on the figure shown, there are 4 samples in each figure which are untreated sample and pretreated sample with different concentration of sawdust. TG curve (a), (b) and (c) is in similar trend. Some overlapping for certain point is occurred for certain samples but only for small changes around 5 % to 15 % due to some minor error while preparing the samples.

As a whole, the TG curves can be divided into three different regions, according of what materials are tested. For temperature below 100°C (the first stage) the slight decay of the sample weight is due to the release of unbound water with the drying procedure. When the temperature between 100°C and 350°C (the second stage) a significant drop in weight is observed. Once the temperature is higher than 400°C (the third stage) for the case of the three samples, the weight lost is not as significant as the previous period (Wei et al., 2012). Mainly as a consequence of thermal decomposition of lignin (heavy component).

Among the three components, hemicellulose show the lowest thermal stability, cellulose is relatively thermal stable due to its highly crystal structure and lignin degrades over a wide temperature range. The thermal decomposition of the lignocellulosic materials can be classified into three stages. The first one is between 245°C and 290°C for the hemicellulose zone, the second one is between 290°C and 350°C corresponding to cellulose zone, and third one for lignin zone 350°C - 550°C (S. Singh et al., 2013).

Based on TG curve, all untreated sample start decomposes at 172°C and it maximum rates of weight lost at 315°C. Weight loss at 50 % of untreated sawdust was achieved when temperature reach 294°C. The residue of untreated sawdust was 22.32 %. For (Fig. 4.1a), which is 5 wt% sawdust with 5 wt% DMSO it start decompose at 201°C,



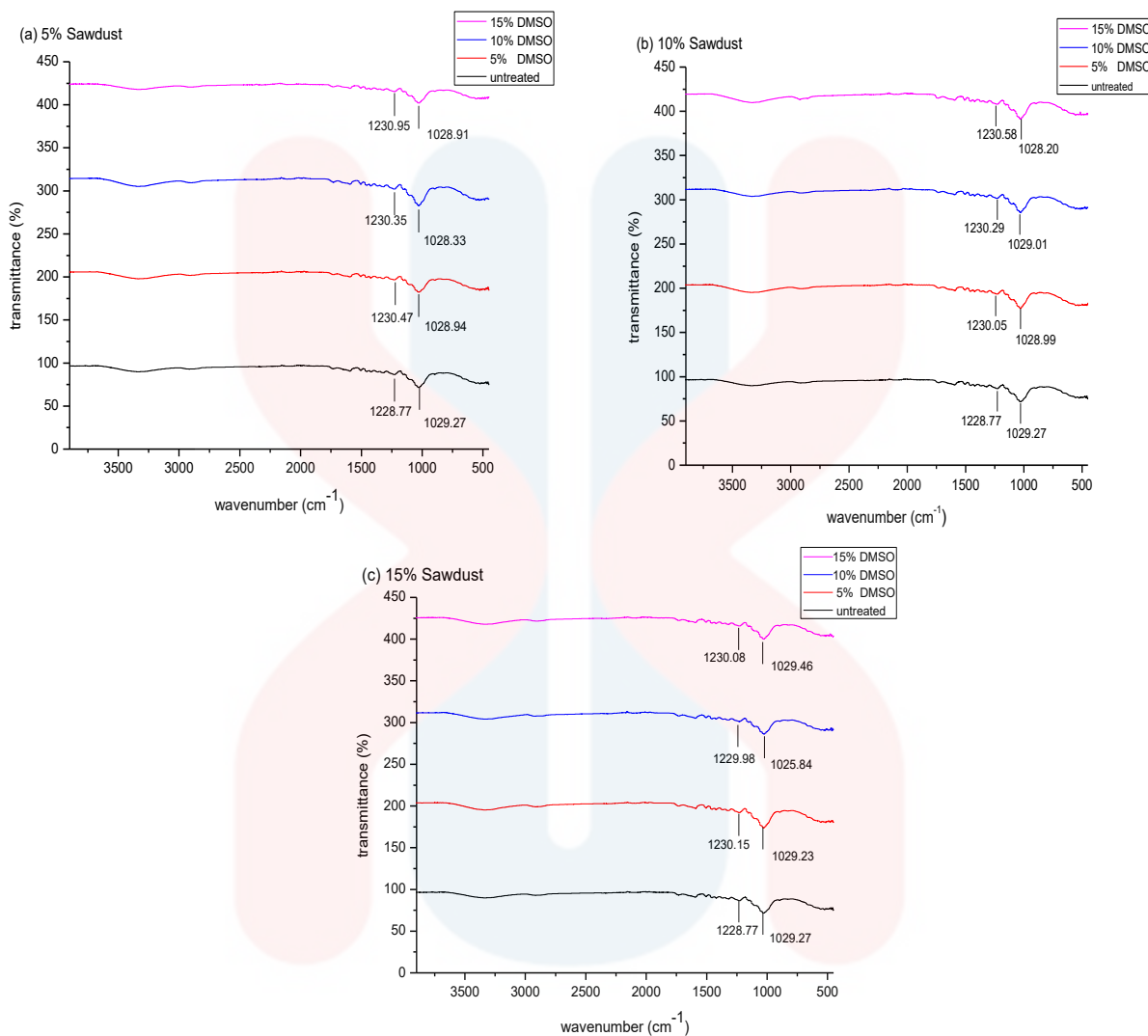
maximum weight lost achieved at temperature 349°C and the residue is 19.71 %. For 5 wt% sawdust with 10 wt% DMSO, decomposed start at temperature 201°C, maximum weight lost at temperature 345°C and the residue is 15.88 %. For 5 wt% sawdust with 15 wt% DMSO it decompose at temperature 201°C, maximum weight lost at temperature 349°C and the residue is 18.52 %.

For (Fig. 4.1b), which is 10 wt% sawdust with 5 wt% DMSO start decompose at 197°C, maximum weight lost at temperature 352°C and the residue is 20.64 %. For 10 wt% sawdust with 10 wt% DMSO it start decompose at 197°C, maximum weight lost at temperature 345°C and the residue is 19.77 %. For 10 wt% sawdust with 15 wt% DMSO, it start decompose at 197°C, maximum weight lost at temperature 345°C and the residue is 19.46 %.

For (Fig. 4.1c), 15 wt% sawdust with 5 wt% DMSO, it start decompose at 201 °C, maximum weight loss at temperature 348°C and the residue is 18.58%. For 15 wt% sawdust with 15 wt% DMSO, it start decompose at 201°C, maximum weight lost at temperature 350°C and the residue is 20.33 %. Based on TG curve for the effect of concentration of sawdust, 5 wt% sawdust with 5 wt%, 10 wt% and 15 wt% DMSO show high weight loss compare to 10 wt% sawdust and 15 wt% sawdust.

#### 4.2.2 FT-IR spectra

FT-IR is use to determine the functional groups involved in bio sorption of ionic liquid onto sawdust. Fig. 4.2(a) 5 wt% sawdust with 5, 10, 15 wt% DMSO (b) 10 wt% sawdust with 5, 10, 15 wt% DMSO and (c) 15 wt% sawdust with 5, 10, 15 wt% DMSO. The figure is explained for the effect of using different concentration of sawdust 5 wt%, 10 wt% and 15 wt% as constant parameter.



**Fig. 4.2** FT- IR spectra of the pretreatment of sawdust and DMSO at different concentration of sawdust (a) 5 wt% sawdust with 5, 10, 15 wt% DMSO (b) 10 wt% sawdust with 5, 10, 15 wt% DMSO and (c) 15 wt% sawdust with 5, 10, 15 wt% DMSO and compare with untreated sawdust

The FT-IR spectra confirmed changes in functional groups and surface properties of the bio sorbent, illustrated by the shift of some functional groups (Wahab et al., 2010). In each FT-IR spectra based on the figure shown, there are 4 sample in each figure which are untreated sample, (a) 5 wt% DMSO, (b) 10 wt% DMSO, (c) 15 wt% DMSO. FT-IR spectra are in similar trend for (a), (b) and (c). For untreated sawdust the absorption bands at wavenumber near  $3329 \text{ cm}^{-1}$  and  $2908 \text{ cm}^{-1}$  are due to stretching vibration of O-H alcohol and C-H methyl and methylene groups respectively.

The specific maximum at  $1033\text{ cm}^{-1}$ , this band is corresponding to the C-O stretching vibration in cellulose/hemicellulose and aryl-OH group in lignin. An intensive absorption band at wavenumber near  $880\text{ cm}^{-1}$  is assigned to the  $C_1$  group frequency or ring frequency, it suggesting the presence of dominant linkage between xylopranose units in the main xylan chains (Sun et al., 2012).

The absorption band at wavenumber near  $1598\text{ cm}^{-1}$  is attributed to uronic acid carboxylate, and a signal at wavenumber near  $1416\text{ cm}^{-1}$  is from the symmetric stretching vibration in the glucuronic acid groups as side chains. The band at wavenumber  $1464\text{ cm}^{-1}$  is assigned to  $\text{CH}_2$  symmetric bending, while the bands at  $1359\text{ cm}^{-1}$  and  $1311\text{ cm}^{-1}$  arise from C-H stretching and O-H or C-O is bending vibration. Furthermore the appearance of a small signal at  $1502\text{ cm}^{-1}$  for C=C stretching of the aromatic ring in all the hemicellulose fractions revealed that small amounts of associated lignin were present in the hemicellulose.

Based the figures of FT-IR spectra, after sawdust was treated there is no obvious change and similar features were also observed between FT-IR spectra obtained for unmodified and chemically modified sawdust. The high peaks and absorption is mostly occurring at 5 wt% DMSO. Based on the results, there are slightly increase or decrease occur at wavenumber reading of the chemically modified sawdust when compare with unmodified sawdust wavenumber. This may be occurring because of the interaction between the functional group after the some modification happen.

For example after pretreatment the absorption band of all sample occur at wavenumber near  $3338\text{ cm}^{-1}$  and  $2908\text{ cm}^{-1}$  are due to stretching vibration of OH and CH, respectively. The specific maximum at  $1024\text{ cm}^{-1}$  this band is corresponds to the C-O stretching vibration in cellulose/hemicellulose and aryl-OH group in lignin. An

intensive band at  $899\text{ cm}^{-1}$  is assigned to the  $C_1$  group frequency or ring frequency, it suggesting the presence of dominant linkage between xylopranose units in the main xylan chains.

The band at  $1598\text{ cm}^{-1}$  is attributed to uronic acid carboxylate, and a signal at  $1416\text{ cm}^{-1}$  is from the symmetric stretching vibration in the glucuronic acid groups as side chains. The band at  $1454\text{ cm}^{-1}$  is assigned to  $\text{CH}_2$  symmetric bending, while the bands at  $1368\text{ cm}^{-1}$  and  $1320\text{ cm}^{-1}$  arise from C-H is stretching and O-H or C-O bending vibration. Furthermore the appearance of a small signal at  $1502\text{ cm}^{-1}$  for C=C stretching of the aromatic ring in all the hemicellulose fractions revealed that small amounts of associated lignin were present in the hemicellulose.

Based on the FT-IR band spectra, two strongest absorption peaks is observed the changing in wavenumber. First peak is at wavenumber near to  $1033\text{ cm}^{-1}$  which is at this band position corresponds to the C-O stretching vibration in cellulose/hemicellulose and aryl-O-H group in lignin. Second peak is at wavenumber near to  $1234\text{ cm}^{-1}$  which is O-H stretching which is hydroxyl group occurs. For (Fig. 4.2a), 5 wt% sawdust with 5 wt% DMSO, the first strong peak is at  $1028.94\text{ cm}^{-1}$  and the second strong peak is  $1230.47\text{ cm}^{-1}$ . For 5 wt% sawdust with 10 wt% DMSO, the first strong peak at  $1028.33\text{ cm}^{-1}$  and the second peak at  $1230.35\text{ cm}^{-1}$ . For 5 wt% sawdust with 15 wt% DMSO are at  $1028.91\text{ cm}^{-1}$  and  $1230.95\text{ cm}^{-1}$ .

For (Fig. 4.2b), 10 wt% sawdust with 5 wt% DMSO are at  $1028.99\text{ cm}^{-1}$  and  $1230.05\text{ cm}^{-1}$ . For 10 wt% sawdust with 10 wt% DMSO are at  $1029.01\text{ cm}^{-1}$  and  $1230.29\text{ cm}^{-1}$ . For 10 wt% sawdust with 15 wt% DMSO are at  $1028.20\text{ cm}^{-1}$  and  $1230.58\text{ cm}^{-1}$ . For (Fig. 4.2c), 15 wt% sawdust with 5 wt% DMSO, are at  $1029.23\text{ cm}^{-1}$  and  $1230.15$

$\text{cm}^{-1}$ . For 15 wt% sawdust with 10 wt% DMSO are at  $1025.84 \text{ cm}^{-1}$  and  $1229.98 \text{ cm}^{-1}$ .

For 15 wt% sawdust with 15 wt% DMSO are at  $1029.46 \text{ cm}^{-1}$  and  $1230.08 \text{ cm}^{-1}$ .

### 4.2.3 X-ray diffraction

X-ray diffraction is. The crystallinity and amorphous for each sample were calculated because if refer to the graph of XRD at Fig. 4.3 the pattern of the graph is in similar trend and cannot observe clearly the changes happen at the peak  $2\theta = 22^\circ$  was  $2\theta = 17^\circ$ . In which,  $I_{002}$  is the intensity for crystalline portion of biomass at about  $2\theta = 22^\circ$  and  $I_{am}$  is the peak for the amorphous portion. The Table 4.2 shown the crystallinity and amorphous of the samples by using X-ray diffraction machine.

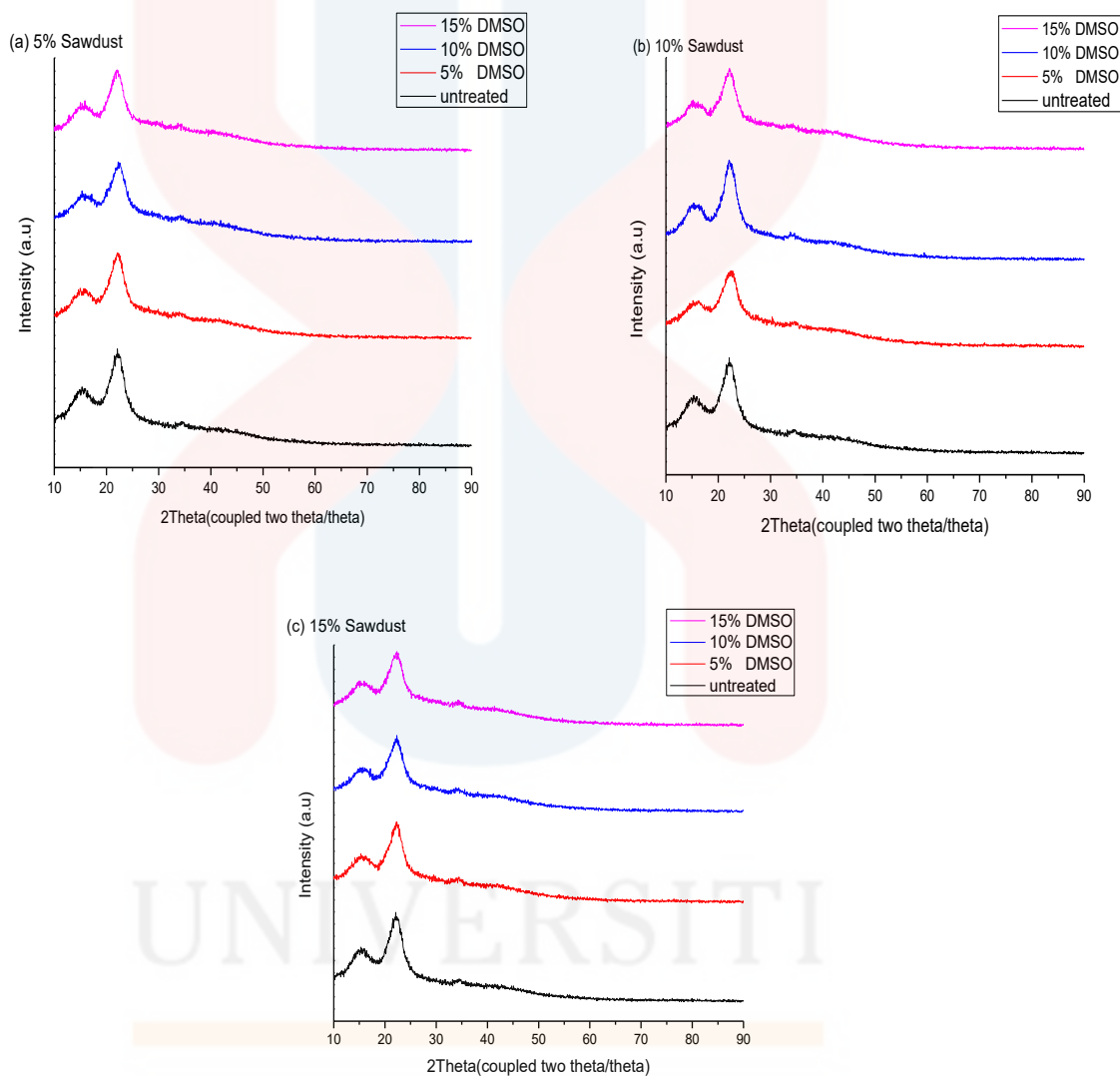
Table 4.2 the crystallinity and amorphous of the samples by using X-ray diffraction machine

SAWDUST wt %	DMSO wt %	IONIC LIQUID wt %	$I_{002}$	$I_{am}$	CRYSTALLINI TY	AMORPHOU S
100	0	0	1994	1085	45.59	54.41
5	5	90	1783	984	44.81	55.19
5	10	85	1685	1075	36.20	63.80
5	15	80	1696	956	43.63	56.37
10	5	85	1620	964	40.49	59.51
10	10	80	1770	1122	36.61	63.39
10	15	75	1723	1004	41.73	58.27
15	5	80	1823	1054	42.18	57.82
15	10	75	1734	1051	39.39	60.61
15	15	70	1689	990	41.39	58.61

The result of crystallinity and amorphous of the sample is transferred into XRD graph pattern. The XRD pattern is plotted based on intensity and 2 theta,  $2\theta$ . Fig. 4.3 shown XRD patterns of the pretreatment of sawdust. From the structural point of view, X-ray diffraction (XRD) patterns it shows a main broad peak at  $2\theta = 22^\circ$  and  $2\theta = 17^\circ$ .

These patterns are characteristics of cellulose I which is composite mixture of two distinct crystalline forms, cellulose  $I_\alpha$  (triclinic) and cellulose  $I_\beta$  (monoclinic) with

proportions depending on the origin of the native samples (Auxenfans et al., 2014). The Fig. 4.3 (a) 5 wt% sawdust with 5, 10, 15 wt% DMSO (b) 10 wt% sawdust with 5, 10, 15 wt% DMSO and (c) 15 wt% sawdust with 5, 10, 15 wt% DMSO.



**Fig. 4.3** XRD patterns of pretreatment of sawdust and DMSO at different concentration of sawdust (a) 5 wt% sawdust with 5, 10, 15 wt% DMSO (b) 10 wt% sawdust with 5, 10, 15 wt% DMSO and (c) 15 wt% sawdust with 5, 10, 15 wt% DMSO and compare with untreated sawdust

In each XRD patterns based on the figure shown, there are 4 sample in each figure which are untreated sample, (a) 5 wt% DMSO, (b) 10 wt% DMSO, (c) 15 wt% DMSO. XRD pattern is in similar trend for (a), (b) and (c).



For (Fig. 4.3a) the crystallinity of 5 wt% sawdust, 5 wt% DMSO is higher than 5 wt% sawdust, 10 wt% DMSO, 5 wt% sawdust, 15 wt% DMSO which are 44.81 %, 36.20 % and 43.63 % while the amorphous are 55.19 %, 63.80 %, 56.37 %. (Fig. 4.3b), the crystallinity of 10 wt% sawdust, 5 wt% DMSO is higher than 10 wt% sawdust, 10 wt% DMSO, 10 wt% sawdust, 15 wt% DMSO which are 40.49 %, 36.41 % and 41.73 % while the amorphous are 59.51 %, 63.39 %, 58.27 %.

For (Fig. 4.3c), the crystallinity of 15 wt% sawdust, 5 wt% DMSO is higher than 15 wt% sawdust, 10 wt% DMSO, 15 wt% sawdust, 15 wt% DMSO which are 42.18 %, 39.39 % and 41.39 % while the amorphous are 57.82 %, 60.60 %, 58.61 %. These changes of the diffraction peaks indicated the significant cleavage of hydrogen bonds in cellulose, leading to the significant decrystallization of lignocellulose after dissolution, chemical modification and regeneration in ionic liquid.

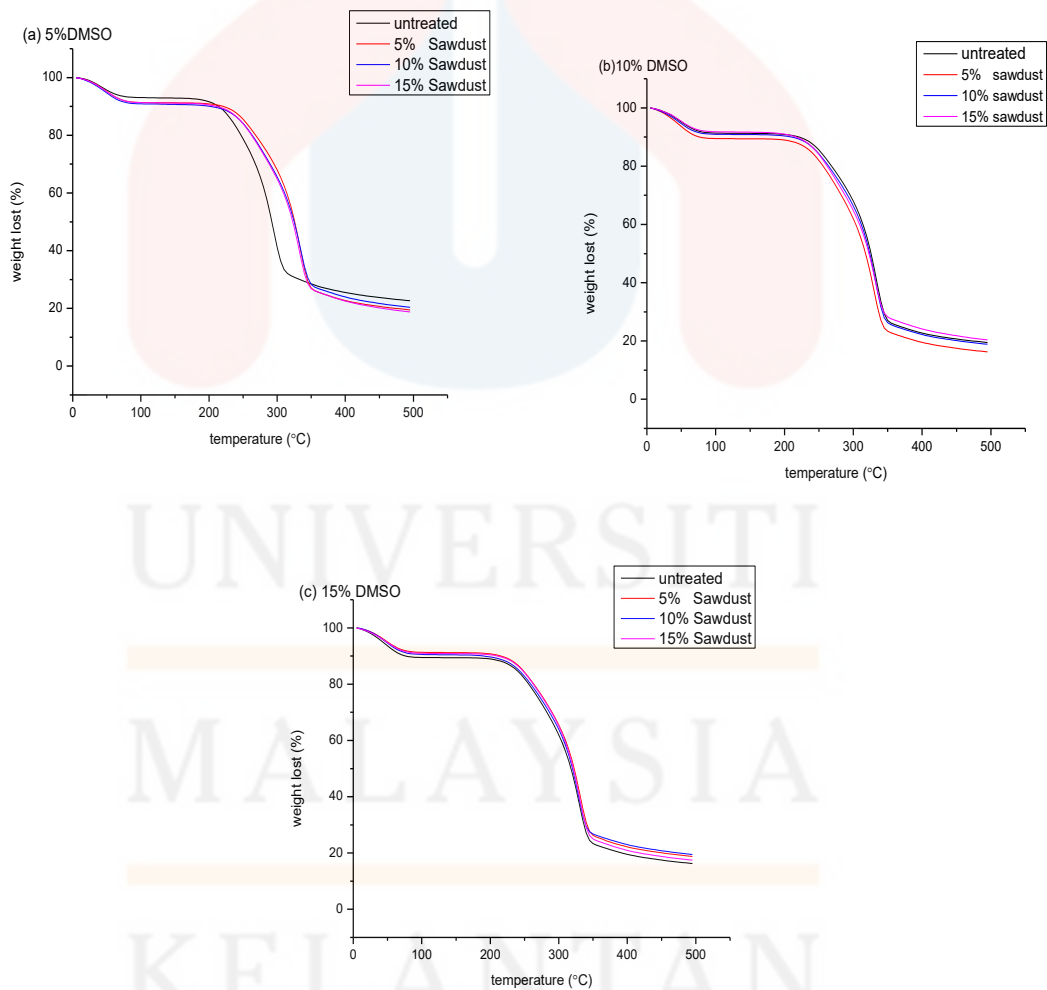
Based on the result for the effect of concentration of sawdust, it shows that crystallinity of 5 wt% sawdust with 5, 10 and 15 wt% DMSO is lower than crystallinity of sawdust at concentration 10 wt% with 5, 10 and 15 wt% DMSO and 15wt% sawdust with 5, 10 and 15 wt% DMSO. The lower the crystallinity of the sawdust, the higher the amorphosity of the sawdust. Reduce crystallinity may help the efficiency enzymatic conversion, desirable to disrupt the structure of cellulose. The pretreatment of sawdust is to reduce the crystallinity of sawdust. Reduce in crystallinity is proved by characterized with XRD.

### 4.3 Effect of concentration of DMSO

The effect of concentration of DMSO was identifying based on the thermal properties, FT-IR spectra and X-Ray Diffraction result.

#### 4.3.1 Thermal properties

Fig. 4.4 shown the thermogravimetric (TG) curve of (a) 5 wt% DMSO with 5, 10, 15 wt% sawdust (b) 10 wt% DMSO with 5, 10, 15 wt% sawdust and (c) 15 wt% DMSO with 5, 10, 15 wt% sawdust. The figure explained for the effect of using different concentration of DMSO 5 wt%, 10 wt% and 15 wt% as constant parameter.



**Fig. 4.4** Thermogravimetric (TG) curves of the pretreatment of sawdust with DMSO at different concentration of DMSO (a) 5 wt% DMSO with 5, 10, 15 wt% sawdust (b) 10 wt% DMSO with 5, 10, 15 wt% sawdust and (c) 15 wt% DMSO with 5, 10, 15 wt% sawdust and compare with untreated sawdust



TG curve for (a), (b) and (c) are in similar trend. There are have a small different in the reading of weight lost and temperature of weight lost for all nine sample and it occur because some minor while preparing the sample. Based on the figure shown, there are 4 samples in each figure. There are untreated sample and three pretreated sample which are 5 wt% sawdust, 10 wt% sawdust and 15 wt% sawdust.

For all untreated sample, the sample start decompose at 172°C and it maximum rates of weight lost at 315°C. Weight lost at 50 % of untreated sawdust was achieved when temperature reach 294°C. The residue of untreated sawdust was 22.32 %. For (Fig. 4.4a), 5 wt% DMSO with 5 wt% sawdust, the weight lost achieve 50 % at temperature 324°C and total weight lost is 80.23%. For 5 wt% DMSO with 10 wt% sawdust, the weight lost achieve 50 % at temperature 324°C and the total weight lost is 79.36%. For 5 wt% DMSO with 15 wt% sawdust, the weight loss achieves 50 % at temperature 324°C and the total weight lost is 81.42 %. In 5 wt% sawdust, the three sample achieved 50 % weight lost at same temperature which is 324°C.

For (Fig. 4.4b), 10 wt% DMSO with 5 wt% sawdust, the weight lost achieve 50 % at temperature 317°C and the total weight lost is 84.34 %. For 10 wt% DMSO with 10 wt% sawdust, the weight lost achieved 50 % at temperature 325°C and the total weight lost is 81.73 %. For 10 wt% DMSO with 15 wt% sawdust, the weight lost achieve 50 % at temperature 325°C and the total weight lost is 79.08 %.

For (Fig. 4.4c), 15 wt% DMSO with 5 wt% sawdust, the weight lost achieved 50 % at temperature 320°C and the total weight lost is 80.82 %. For 15 wt% DMSO with 10 wt% sawdust, the weight lost achieve 50 % at temperature 320°C and total weight lost is 80.23 %. For 15 wt% DMSO with 15 wt% sawdust, the weight lost achieved 50 % at temperature 320°C and the total weight lost is 82.60 %.

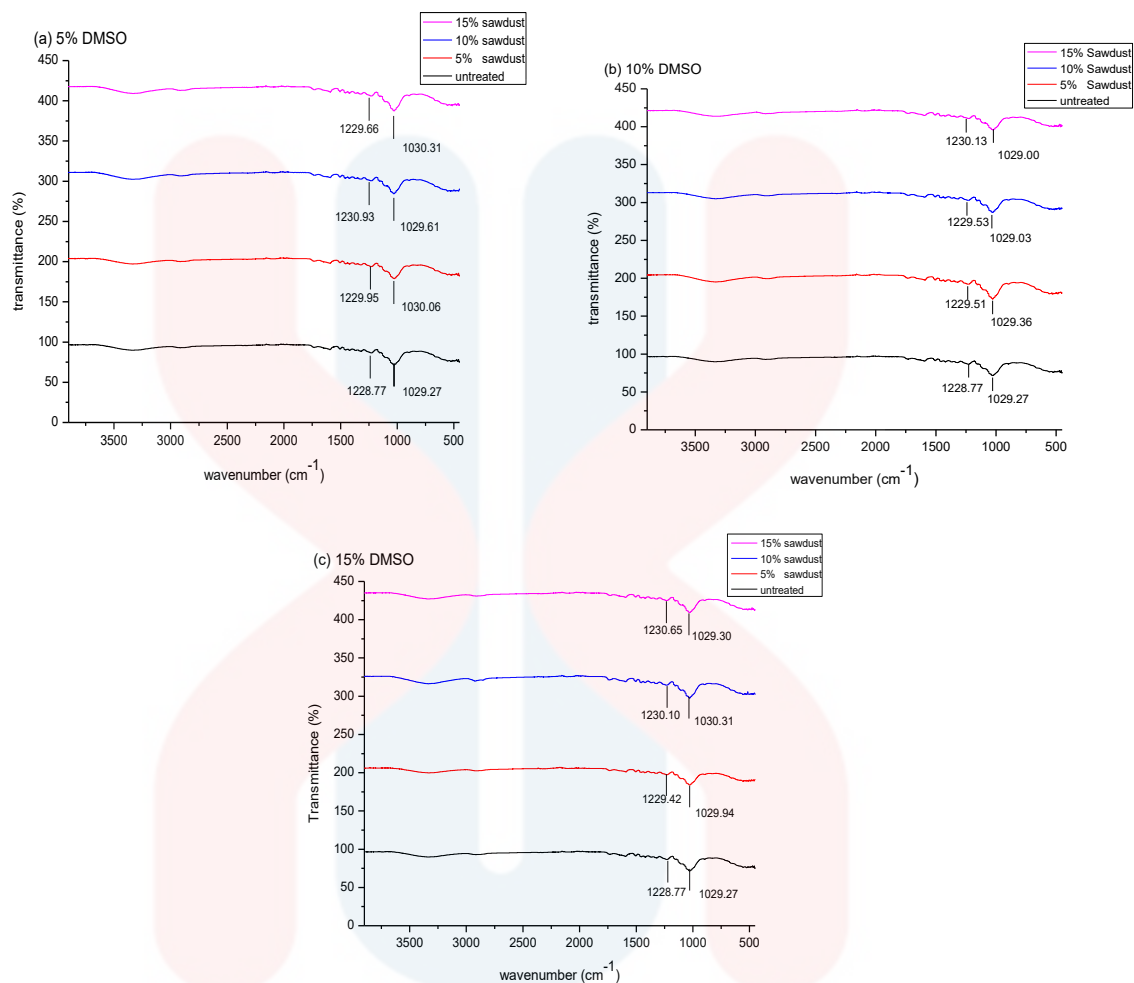
Based on the TG curve result for effect of different concentration of DMSO, it shows that TG curve for 10 wt% DMSO with 5 wt%, 10 wt% and 15 wt% sawdust has high weight lost compare to 5 wt% DMSO and 15 wt% DMSO. The weight loss of 10 wt% DMSO with 5 wt%, 10 wt% and 15 wt% sawdust are 84.34 %, 81.73 % and 79.08 %. The amount of total weight lost is get after subtract the amount of residue left for each sample.

When it comes to higher sawdust loading, the solution was highly viscous and very hard to stir. DMSO can help to reduce the viscosity of the solution. The higher the concentration of DMSO use not gives effect to the structure of the sawdust. The higher use of DMSO, the easier to sawdust dissolve in solvent. It can overcome the problem of difficulty in stirring high sawdust loading in pretreatment of sawdust.

Based on the result of TG curve also show that DMSO not give effect to thermal properties of sawdust. So, DMSO suitable to use in high concentration in pretreatment of sawdust. DMSO also helps to short the relaxation time and decrease monomer friction efficient in cellulose solutions.

#### **4.3.2 FT-IR spectra**

Sawdust is principally made up of lignin and cellulose a negligible portion of lipids and waxes, bearing functional group such as alcohol, ketone and carboxylic groups. The infrared spectrum of sawdust displayed a number of absorption peaks, indicating the complex nature of the examined biomass (Wahab et al., 2010). Fig. 4.5 shown FT-IR spectra of (a) 5 wt% sawdust with 5, 10, 15 wt% DMSO (b) 10 wt% sawdust with 5, 10, 15 wt% DMSO and (c) 15 wt% sawdust with 5, 10, 15 wt% DMSO



**Fig. 4.5** FT- IR spectra of the pretreatment of sawdust and DMSO at different concentration of DMSO (a) 5 wt% DMSO with 5, 10, 15 wt% sawdust (b) 10 wt% DMSO with 5, 10, 15 wt% sawdust and (c) 15 wt% DMSO with 5, 10, 15 wt% sawdust and compare with untreated sawdust

In FT-IR spectra, for each band position from  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  have different functional group. Strong broad OH stretching occurs at ( $3300\text{-}4000\text{ cm}^{-1}$ ). C-H stretching in methyl and methylene groups occurs at band position ( $2800\text{-}3000\text{ cm}^{-1}$ ). The absorption situated at ( $1510$  and  $1600\text{ cm}^{-1}$ ) aromatic skeletal vibration is caused by lignin.

Absorption at band position located at  $1730\text{ cm}^{-1}$  is caused by holocellulose, this indicates the C=O stretch in non-conjugated ketones, carbonyls and in ester group. Absorption at band position located near to  $1618\text{ cm}^{-1}$  is C=C alkene. Absorption at band

position located near to  $1425\text{ cm}^{-1}$  is  $\text{CH}_2$  cellulose, lignin. Absorption at band position located near to  $1346$  is C-H cellulose hemicellulose. Absorption at band position located near to  $1234\text{ cm}^{-1}$  is O-H stretching.

FT- IR spectra of a, b and c are in similar trend for the entire figure above. But there are different in absorption band for untreated sawdust and pretreated sawdust. Clear difference can be detected in the infrared spectra, both in the different absorbance values and shape of the bands and in their location. After sawdust is chemically modified the wavenumber value being shifted to a lower wavenumber because of the vibration and stretching in functional group.

In Fig. 4.5 two absorption bands were discuss because this two absorption band is more obvious and strong peak. For the first strong peak which is absorption at band located near to  $1033\text{ cm}^{-1}$  which this band correspond to the C-O stretching vibration in cellulose/hemicellulose and aryl-OH group in lignin. And the second strong peak at band located near to  $1234\text{ cm}^{-1}$  which is O-H stretching occurs. FT- IR spectra as shown in figure 4.5 consist of untreated and pretreated sawdust.

For untreated sawdust, the first strong peak at wavenumber  $1029.27\text{ cm}^{-1}$  and second peak at wavenumber  $1228.77\text{ cm}^{-1}$ . For (Fig. 4.5a) 5 wt% DMSO with 5 wt% sawdust have absorption at wavenumber  $1030.06\text{ cm}^{-1}$  and  $1229.95\text{ cm}^{-1}$ . For 5 wt% DMSO with 10 wt% sawdust have absorption at wavenumber  $1029.61\text{ cm}^{-1}$  and  $1230.93\text{ cm}^{-1}$ .

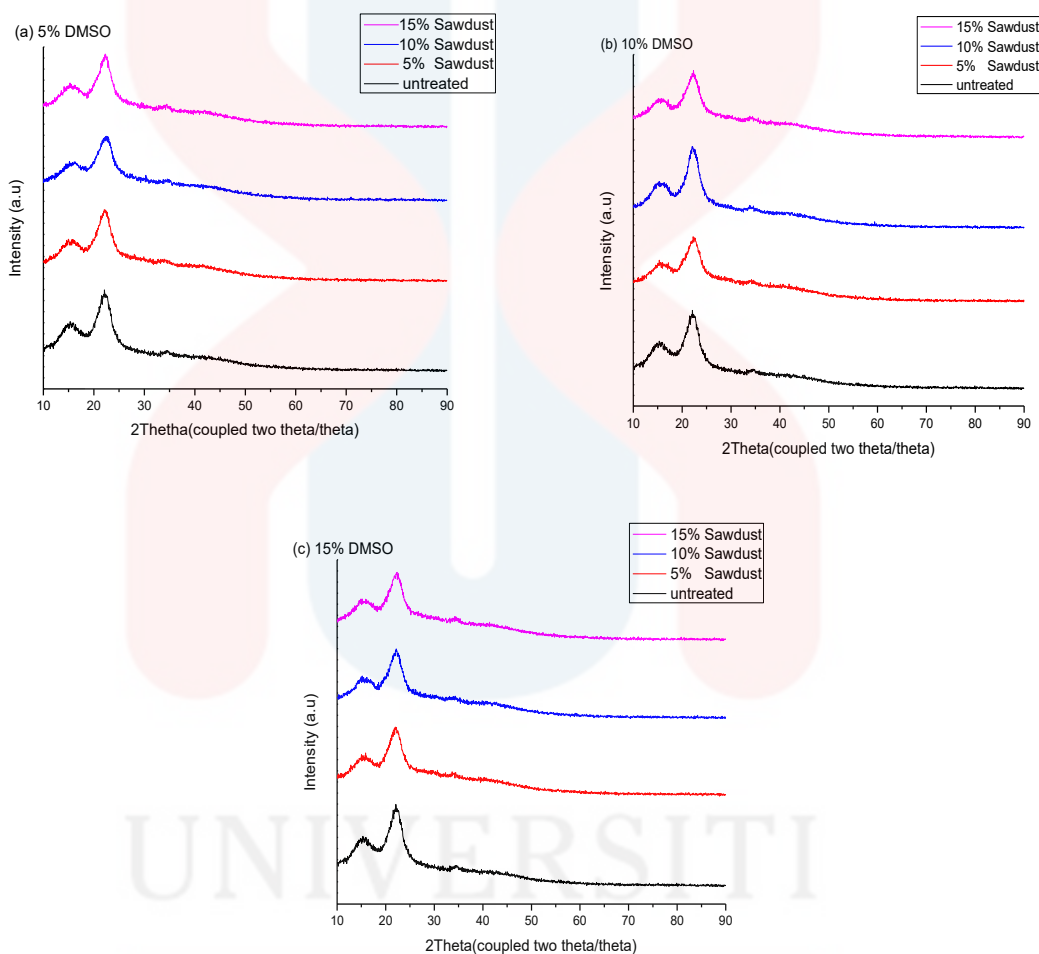
For 5 wt% DMSO with 15 wt% sawdust have absorption at wavenumber  $1030.31\text{ cm}^{-1}$  and  $1229.66\text{ cm}^{-1}$ . There is difference between spectra for unmodified and chemically modified sawdust. The shifted of the absorption band to lower or higher wavenumber probably caused by the interaction between the functional group.

For (Fig. 4.5b), 10 wt% DMSO with 5 wt% sawdust have absorption at wavenumber  $1029.36\text{ cm}^{-1}$  and  $1229.51\text{ cm}^{-1}$ . For 10 wt% DMSO with 10 wt% sawdust have absorption at wavenumber  $1029.03\text{ cm}^{-1}$  and  $1229.53\text{ cm}^{-1}$ . For 10 wt% DMSO with 15 wt% sawdust have absorption at wavenumber  $1029.00\text{ cm}^{-1}$  and  $1230.13\text{ cm}^{-1}$ .

For (Fig. 4.5c), 15 wt% DMSO with 5 wt% sawdust have absorption at wavenumber  $1029.74\text{ cm}^{-1}$  and  $1229.42\text{ cm}^{-1}$ . For 15 wt% DMSO with 10 wt% sawdust have absorption at wavenumber  $1030.31\text{ cm}^{-1}$  and  $1229.82\text{ cm}^{-1}$ . For 15 wt% DMSO with 15 wt% sawdust have absorption at wavenumber  $1029.30\text{ cm}^{-1}$  and  $1230.65\text{ cm}^{-1}$ .

### 4.3.3 X-ray diffraction

The Fig. 4.6 shown the XRD patterns of (a) 5 wt% DMSO with 5, 10, 15 wt% sawdust (b) 10 wt% DMSO with 5, 10, 15 wt% sawdust (c) 15 wt% DMSO with 5, 10, 15 wt% sawdust.



**Fig. 4.6** XRD patterns of pretreatment of sawdust and DMSO at different concentration of sawdust (a) 5 wt% DMSO with 5, 10, 15 wt% sawdust (b) 10 wt% DMSO with 5, 10, 15 wt% sawdust and (c) 15 wt% DMSO with 5, 10, 15 wt% sawdust and compare with untreated sawdust

Based on three figures above (Fig. 4.6a, b and c) the peak of untreated sawdust is sharp and intense compare to treated sawdust with 5 wt%, 10 wt%, 15 wt% DMSO. It is because the untreated sawdust has high crystallinity and low amorphous which are 45.59 % and 54.51%. For (Fig. 4.6a), the crystallinity of 5 wt% DMSO, 5 wt % sawdust is

higher than 5 wt% DMSO, 10 wt% sawdust, 5 wt% DMSO, 15 wt% sawdust which are 44.81 %, 40.49 % and 42.18 % while the amorphous are 55.19 %, 59.51 %, 57.82 %.

For (Fig. 4.6b), the crystallinity of 10 wt% DMSO, 15 wt% sawdust is higher than 10 wt% DMSO, 5 wt% sawdust, 10 wt% DMSO, 10 wt% sawdust which are 39.90 %, 36.20 % and 36.61 % while the amorphous are 60.61 %, 63.80 %, 63.39 %. For (Fig. 4.6c), the crystallinity of 15 wt% DMSO, 5 wt% sawdust is higher than 15 wt% DMSO, 10 wt% sawdust and 15 wt% DMSO, 15 wt % sawdust which are 43.63 %, 41.73 % and 41.39 % while the amorphous are 56.37 %, 58.27 %, 58.61 %.

According to previous study (Martins et al., 2014), the crystalline structure of cellulose was transformed completely from cellulose I to cellulose II after treatment of the isolated cellulose with ionic liquid or chemical modification. The transformation differences of the crystalline structure after dissolution and the modification of lignocellulose and isolated cellulose in ionic liquid may be due to the absent of lignin and hemicelluloses in the isolated cellulose (Iipeläinen et al., 2007). In pretreatment of sawdust the modification of lignocelluloses happens and XRD proved the crystallinity of sawdust.



## CHAPTER 5

### CONCLUSION AND RECOMMENDATION

#### 5.1 Conclusion

The study is about the effect of sawdust content on chemical pretreatment. Based on the objectives of the research are to study the effect of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) pretreatment on sawdust at different sawdust concentration and to study the effect of co-solvent dimethylsulfoxide (DMSO) on the ([BMIM]Cl treated sawdust. For the first objectives, the effect of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) pretreatment on sawdust at different sawdust concentration. Based on the result get, shows that low concentration of sawdust which is 5 wt% sawdust give the best result such as have high weight lost and less crystallinity of cellulose. The second objectives, to study the effect of co-solvent dimethylsulfoxide (DMSO) on the ([BMIM]Cl) treated sawdust. IL pretreatment provide some advantages such as increase the surface area, decrease cellulose crystallinity and lignin content that help to improved hydrolysis efficiency. The effect of sawdust and DMSO concentration onto the structure of sample was characterized using three materials characterizations. There are Thermogravimetric analyses (TGA), Fourier transform-infrared (FT-IR) Spectroscopy, X-ray diffraction characterization. Based on the result get by carried out material characterization, the uses of different concentration DMSO 5 wt%, 10 wt% and 15 wt% not give high effect to pretreatment of sawdust. It is because DMSO has unique capability to penetrate living tissues without causing significant damage is probably relatively related to its relatively polar nature, its capacity to accept hydrogen bonds and



its relatively small and compact structure. This proves the second objective of the research. In this research, it shows that when DMSO concentration increases the uses of amount ionic liquid can be reduced. It also as alternative to reduce the cost and help to reduce the viscosity of ionic liquid. It can be conclude, that in this research the most suitable concentration of sawdust and concentration of DMSO used are 5 wt% sawdust and high concentration of DMSO 10 wt% and 15 wt%.

## 5.2 Recommendation

Researcher can be used another co-solvent to compare the effect of the co-solvent in the pretreatment of sawdust, so that the best and effective co-solvent can be find out. The most effective type of co-solvent can give most effective effect in reducing viscosity of ionic liquid. Researcher also can used another material characterization to know more properties of sawdust pretreatment. One example is Scanning Electron Microscopy (SEM) characterization to better understand the effect of homogeneous concentration sawdust and DMSO on the morphology structure of sawdust in ([BMIM]Cl)/DMSO system. SEM analysis is considered to be non-destructive; x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same material repeatedly.

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## APPENDIX A

Example calculation taken from data of sawdust treated at concentration 5 wt% sawdust with 5 wt% DMSO (Sample 1)

A	B	A	B
16.987	976	21.998	1733
17.038	970	22.049	1782
<b>17.088</b>	<b>984</b>	<b>22.099</b>	<b>1783</b>
17.139	965	22.15	1744
17.19	976	22.201	1752
17.24	952	22.251	1706
17.291	962	22.302	1775
17.341	874	22.352	1719
17.392	940	22.403	1726
17.443	906	22.454	1753
17.493	920	22.504	1631
17.544	892	22.555	1655
17.594	871	22.606	1729
17.645	925	22.656	1710
17.696	936	22.707	1640
17.746	892	22.757	1589
17.797	891	22.808	1624
17.848	875	22.859	1612
17.898	843	22.909	1486
17.949	886	22.96	1587
17.999	810		
18.05	876		

Data of XRD result obtained. The diffraction patterns show two highest peak at  $2\theta = 22^\circ$  was  $2\theta = 17^\circ$ . In which,  $I_{002}$  is the intensity for crystalline portion of biomass at about  $2\theta = 22^\circ$  and  $I_{am}$  is the peak for the amorphous portion.

$$Crl = \frac{(I_{002} - I_{am})}{I_{002}} \times 100$$

$$Crl = \frac{1783 - 984}{1783} \times 100$$

$$Crl = 44.81\%$$

$$\text{Amorphous (\%)} = 100 - 44.81$$

$$= 55.19\%$$