CHARACTERIZATION OF NON-TREATED AND IONIC LIQUID-TREATED SAWDUST

by

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DECLARATION

I declare that this thesis entitled "Characterization Of Treated And Non-Treated And Ionic Liquid-Treated 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.

Signature : _____

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Date : 07.01.2017

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This study is based on the research to characterize of non-treated and Ionic liquid-treated sawdust. I am grateful for the number of people that encourage and help me until I finish the study.

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Characterization Of Non-Treated And Ionic Liquid-Treated Sawdust

ABSTRACT

Biomass pre-treatment can be done with ionic liquid (IL) and this study is certainly use one type of ionic liquid namely 1-butyl-3-methylimidazolium chloride ([BMIM]CL). In this study the sawdust was treated with ([BMIM]CL) as a process of chemical treatment. In this study, sawdust was treated with ([BMIM]CL) at different temperature and different treatment time as the changing parameters. The temperatures were 80℃ 100C 120℃ and the range of treatment time is 24 hours and 48 hours. The Tga analysis was done with the FT-IR and the Xrd analysis. The results showed that the higher temperature used, the higher chances for the decompose of the sawdust occur and the treatment time also not suitable to be longer than 24 hours.

Keyword: Crystallinity; X-ray diffraction (XRD); Fourier transform Infrared (FT-IR); Ionic liquid

Pencirian Serbuk Kayu Yang Tidak Dirawat dan Yang Dirawat Menggunakan Cecair Ionik

ABSTRAK

Biojisim prarawatan yang boleh dilakukan dengan menggunakan cecair ionik (IL) dan kajian ini menggunakan satu jenis cecair ionik iaitu 1-butil-3-methylimidazolium klorida ([BMIM]CL). Dalam kajian ini habuk kayu telah dirawat dengan menggunakan ([BMIM]CL) sebagai proses rawatan kimia untuk mengubah suai kandungan biojisim. Prarawatan habuk kayu dengan cecair ionik hanya boleh dilakukan dalam cairan minyak yang dipanaskan 70℃ dan ke atas kerana suhu lebur cecair ionik adalah 70℃. Dalam kajian ini, habuk kayu dirawat dengan suhu yang berbeza dan masa rawatan yang berbeza sebagai pemboleh ubah dimanipulasi. Suhu yang digunakan adalah 80℃, 100℃ dan 120℃. Julat masa rawatan adalah 24 jam dan 48 jam. Analisis Thermogravimetri telah dilakukan bersama ujian spektroskopi inframerah transformasi Fourier dan berlawanan sinar X. Kesimpulan yang dapat diuraikan adalah jika suhu yang lebih tinggi digunakan, peluang lebih tinggi untuk habuk papan terurai berlaku dan masa rawatan juga tidak sesuai untuk dijadikan lebih lama daripada 24 jam.

Kata kunci: Penghabluran; Sinar X-pembelauan (XRD); Spektroskopi inframerah transformasi Fourier; cairan ionic

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LIST OF ABBREVIATION

NO.		
1	FT-IR	Fourier Transform Infrared Spectroscopy
2	XRD	X-ray Powder Diffraction
3	TGA	Thermogravimetric Analysis
4	CI	Crystallinity index

LIST OF SYMBOLS

NO.		
1	g	Gram
2	℃	Degree celcius
3	µm	Micro meter
4	Cm^{-1}	Reciprocal Centimeter
5	%	Percent
6	Wt%	Weight percentage
7	a.u	Arbitary unit

CHAPTER 1

INTRODUCTION

1.1 Background of study

In recent years, there is study about the ways to enhance the properties of wood composites. This study is based on the sawdust form which are used as the raw materials to make a wood composites. Every type of wood needed to be process into sawdust before making any progression for the wood composite itself. Sawdust is in the form of powdery particles of woods produced by sawing. There is difference in properties and reaction of the ionic liquid based on different wood such as softwood, non-wood and hard wood. But sawdust used in this study are taken from industrial waste which the type of wood was mixed.

Softwood is the wood from a conifer as distinguished from broadleaved trees and hardwood is wood from dicot angiosperm trees that usually broad-leaved temperate and tropical forests. Besides, non-wood is a tree that biological origin other than wood derived from forest, other wooded land or trees outside forest. The sawdust will be process until it is in the forms of fine powdery before it was undergoes chemical treatment. Chemical treatment is important that can change the properties of composite produced. For the chemical pre-treatment, a few choices of chemical uses such as sodium hydroxide, 1-butyl-3-methylimidazolium acetate ([C4MIM][OAc]) and 1-ethyl-3-methylimidazolium diethyl phosphate ([EMIM]DEP).

Ionic liquid can enhance the properties of woods by undergoes a treatment to improve the compatibility between the hydrophilic wood fibre and hydrophobic

polymer matrix (Borysiak & Doczekalska, 2005). There is difference in properties and reaction of the ionic liquid on woods based on treatment time and different temperature use.

This study is about characterization of untreated and treated of agriculture biomass with ionic liquid. Ionic liquid basically is the salt in liquid state and it is largely made of ions and short-lived ion pairs known as “solvent of the future”. An ionic liquid is characterized by a specific conductivity in the $mScm^{-1}$ range as a minimum, together with a molar conductivity probably exceeding 0.1 $Scm^2\ mol^{-1}$ and it contains ions with lesser numbers of ion pairs or parent molecules (Johnson, 2007). All the pre-treatments will be modified the chemical composition of agriculture biomass and led to its weight loss. Complete deacetylation, partial delignification of agriculture biomass will be resulted after the pre-treatment but it will not cause the apparent loss of cellulose.

There is a lot of type ionic liquid but in this study, 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) is uses as a pre-treatment solvent. The cellulose crystallinity, surface morphology, structures and compositions of sawdust were significantly changed after the ionic liquid pre-treatment was carried out under a wide range of temperatures and reaction times (Thi et al., 2015). In this study, the sawdust used are the industrial waste that collected at the sawmill and the type of woods are mixed. The range of temperature used are 80℃ until 120℃ and the reaction times are 24 hours and 48 hours.

1.2 Problem statement

The main components in woods are cellulose, lignin, hemicellulose and extractives (Kilpelainen et al., 2007). The preparation of biopolymer-based materials remains a challenge due to the limited solubility of many biopolymers in conventional solvents. Therefore, a lot of attention has been drawn recently in devising new organic ecologic solvents to prepare biopolymer (especially wood or cellulose)-based composite materials (Croitoru & Patachia, 2014) and Ionic Liquid are nowadays frequently used as organic solvents. These components can be altered its chemical and physical properties by undergo a pre-treatment used this organic solvent.

The changing parameter of the treatment time and wide range of temperature will affect the rate of reaction between the sawdust and the treatment solvents during the pre-treatment.

The purpose of this study is to investigate possibility of the ionic liquid to dissolve sawdust and enhance its properties. Past research had showed that sawdust are treated with the ionic liquid such as sodium hydroxide for the pre-treatment process (Borysiak & Doczekalska, 2005). Therefore, the objective of this study is to study the effectiveness of temperature and treatment time on ionic liquid-treated sawdust.

1.3 Objectives

The objectives of this study are:

1. To investigate the effectiveness of ionic liquid as pre-treatment of solvents.
2. To compare the effectiveness of wide range of temperature on ionic liquid-treated sawdust.
3. To compare the effectiveness of treatment time on ionic liquid-treated sawdust.

1.4 Expected outcome

After sawdust are treated with the ionic liquid, the cellulose of the treated sawdust will become less crystalline (Darji et al., 2015). It was expected that ionic liquid can enhance the mechanical and physical properties of wood. Moreover, it is also expected that ionic liquid is more effective than the sodium hydroxide (NaOH) as a pre-treatment solvent. This is because NaOH are more corrosive than ionic liquid. It might degrade the sawdust itself and disturb the properties of sawdust.

1.5 Scope of Study

The scopes of this study is to determine the characterization of the untreated sawdust and Ionic liquid-treated sawdust using the structural analysis such as Fourier transform infrared (FT-IR), X-ray diffraction (XRD) and Thermogravimetric analysis (TGA). The sawdust that used in this study are industrial waste that collected from sawmill. Moreover, the chemical used for pre-treatment are ionic liquid, namely 1-butyl-3-methylimidazolium chloride ([BMIM]CL) with concentration of 10% wt.

1.6 Significant of Study

The significant of this study is to make sure that the characterization of the contents of sawdust were different between the untreated and ionic liquid-treated. After the prepared sawdust treated with ionic liquid, the contents of cellulose of the sawdust should be changed into cellulose II that have different composition of structure. The quality of sawdust produced must be in high quality that ensure which temperature and treatment time that suitable to use as good and safe wood product. By using the industrial waste that might be throw away, this research can sustain the Malaysia Environment by reducing uses of fresh wood to make product such as wood composites. This research shows that sawdust from industrial waste can be reducing

and reuse to decrease the waste from industry that are constantly increase through the years.

1.7 Limitation of Study

The limitation of this research are possibly due to the lack of technologies and laboratory equipment that are available in the process to identify the changes in the lignocellulosic biomass of sawdust. This study also short in time for the preparation and also lack of knowledge and experienced in terms of making the preparation and to characterize the treated sawdust.

CHAPTER 2

LITERATURE REVIEW

2.1 Sawdust

Sawdust or we can call as wood dust are by-product of cutting, grinding, drilling, sanding or otherwise wood that been pulverized by any other material with a saw or others tools. This sawdust was composed of fine particles of wood itself. Most of the sawdust are used in making of wood composites.

By knowing it is the by-product of wood so it has the same elements with the woods itself. The cellulose and lignin are the major components that stands in the sawdust. This sawdust is the industrial waste that mostly will be burn or disposed. By using the industrial wasted we can reduce the uses of fresh wood in making new product such as wood composites because we recycling the waste of sawdust from sawmill.

Wood has the fibrous structure tissue and were porous. This can be found in the stems or the roots off trees. It is an organic material which consist of natural composite of cellulose fibres embedded in the matrix of lignin which resists compression. Wood are consisted of few layer of woody that envelops from the entire stem. So the sawdust was consisted of all this woody layer. Lignocellulosic biomass are the main components in every wood that contains polymers of cellulose, hemicellulose, and lignin, bound together in a complex structure (Agbor et al., 2011).

In the case of wood, the cell walls polymers (cellulose, hemicelluloses, and lignin) are the components that, if modified, would change the properties of the resource. If the properties of wood are modified, the performance of wood will be

changed. This is the basis of chemical modification of wood to change properties and improve performance (Rowell et al.,).

In the process to extract the lignocellulose, pre-treatment are needed. For the previous study, it was stated that ionic liquid dissolve cellulose in various agricultural biomass, such as corn fibre, wheat straw, switchgrass, olive cake and etc, so it was expected for the ionic liquid to dissolve rice husks (Nam et al., 2011). This sawdust can be treated with ionic liquid to change the content of the biomass.

Another previous study also stated that chemical structure of cellulose was disrupted by formation of O-H bonding between the hydroxyl of cellulose and ion of ionic liquid during the dissolution time with ionic liquid resulted in the broken of cellulose network and less in crystalline structure (Che Kamarludin et al., 2014)

In the past research, there was study about using ionic liquid as a pretreatment on oil palm frond (OPF). The result show OPF tested with FT-IR spectra and a comparison is made between before treated and after treated. There were some different in peaks trend which explained there were some chemical structure changes within the OPF samples. There were some appearances and disappearances of certain peak were observed after the IL pretreatment especially the peak at band near 1700 cm^{-1} and 1550 cm^{-1} (Che Kamarludin et al., 2014).

FTIR analysis is a useful tool for obtaining rapid information about the functional group and chemical changes taking place in cellulose due to various pretreatments. These shows that ionic liquid can be used to substitute sodium hydroxide as a chemical used for pretreatment without degrade the properties of sawdust. As a result, the cellulose network broken and less in crystalline structure.

As the result of past study, it was showed that ionic liquid had successfully extracted and the properties of the Rubberwood are enhanced. According to the past research (Darji et al., 2015), the ionic liquid dissolution pretreatment with microwave irradiation can be used as an alternative method for the pretreatment of rubber tree biomass because the result showed better dissolution due to high hydrogen basicity while anion acetate plays a key role in the dissolution of rubber biomass. It was showed that ionic liquid can be used as a substitution for the chemical pretreatment and due to the green properties of ionic liquid, it become more suitable to use.

2.2 Cellulose

Cellulose is an organic compound and it was an important structural component of the primary cell wall of plants and wood. Cellulose are one of the abundant organic polymer that exist on Earth. Cellulose is a long chain of linked sugar molecules that gives wood its remarkable strength. It is the main component of plant cell walls. $(C_6H_{10}O_5)_n$ is the chemical formula of the cellulose which a polysaccharide that consists of linear chain of several hundred to many thousands of β(1→4) linked D-glucose units. In Figure 2.1 shows the cellulose, a linear polymer of D-glucose units (two are shown) linked by β(1→4)-glycosidic bonds.

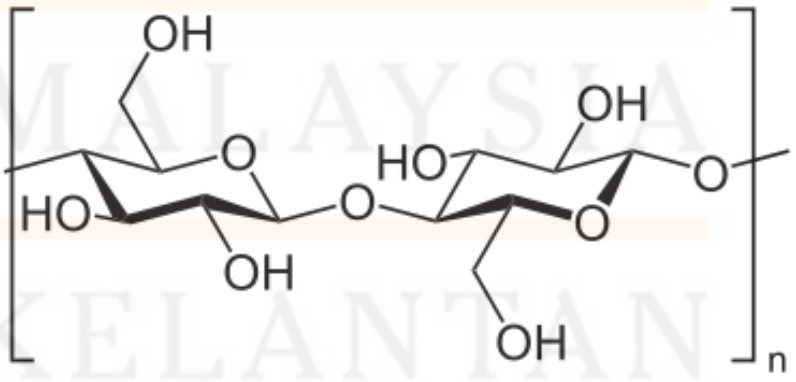

Figure 2.1: The structure of cellulose

Cellulose is a polymer that made of repeating glucose molecule attached end to end. It may be in the form of thousand glucose unit long and it is similar to the complex carbohydrates such as starch and glycogen. Cellulose molecule is long and rod-like and it is straight chain polymer and it cannot be broken down into its glucose subunits by any enzyme produced by animal. The cellulose chain linked by hydrogen bond shown in Figure 2.2.

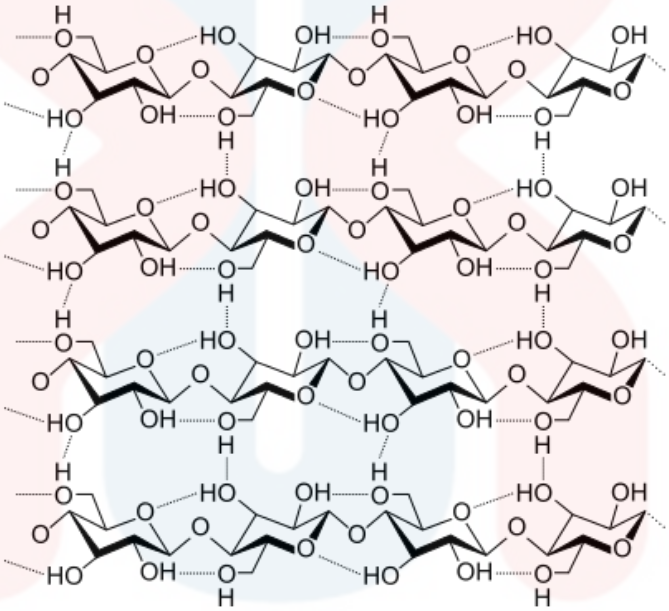

Figure 2.2: The hydrogen link of cellulose

Cellulose are an odourless and had no taste to begin with. The structure of cellulose is hydrophilic with the contact angle of 20-30 degree and it was insoluble in water but it is biodegradable. Cellulose are more crystalline than starch but past research shown that cellulose required a temperature of 320℃ and pressure 25 MPa to for it to become amorphous in water. By undergoes chemical treatment the cellulose I can changed into cellulose II. Cellulose from wood pulp has typical chain length between 300 and 1700 unit.

2.3 Lignin

Lignin was a class of complex organic polymers that formed important structural materials in the support tissues of vascular plants. Lignin particularly was an important component in the formation of cell walls, especially in wood and bark. This is because they lend rigidity and does not easily rots. The structure of lignin are cross-linked phenolic polymers.

As a biopolymer, lignin was an unusual due to it heterogeneity and lack of a defined primary structure. The most commonly noted function is the support through strengthening of wood that is mainly composed of xylem cells and lignified sclerenchyma fibres in vascular plants.

Lignin is an amorphous polymer whose attributes include providing rigidity to the plant cell wall. In the Figure 2.3, it shows the structure of the lignin. Pure lignin is basically an amorphous form consisted of aromatic ether backbone that can be potential substrates for the production of aromatic chemicals (Chakar & Ragauskas, 2004).

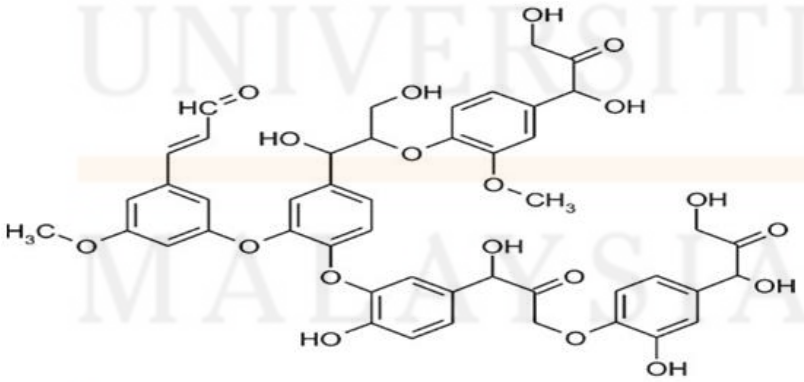

Figure 2.3: The structure of lignin

Lignin can be isolated in large quantity from lignocellulosic materials by a strong dilute acid, alkaline treatment, organosolve isolation or sulphite pulping

process (Pouteaua, et al., 2003; Fernandez-Bolanos, et al., 1999). Ionic liquid have been spreads as the new green solvents that are environmentally and can be used as a solvents to dissolve complex macromolecules and polymeric materials (Adlie & Corresponding, 2010).

However, the physical and chemical features of the cell wall in the plant make a major obstacle towards the efficient conversion due to the presence of lignin (10-25%) a constructed physical barrier to protect cellulose (35-50%) and hemicellulose (20-35%) from degradation (Darji et al., 2015).

2.4 Ionic liquid

Ionic liquid come in a wide variety combination of melt salt. Ionic liquid is the new green solvent that starts to get some place in the focus of researcher due to the potential it has to regenerate and chemically modify the cellulose compare with other process.

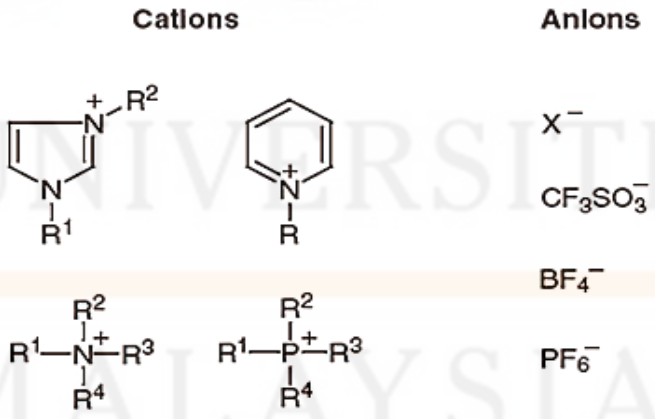

Figure 2.4: The structure cation and anion of the ionic liquid.

Figure 2.4 illustrated that ionic liquid is a salt that consists of cations such as imidazolium, pyridinium, quaternary ammonium and quaternary phosphonium, and

also anions such as halogen, triflate, tetrafluoroborate and hexafluorophosphate, which are existed in the liquid state at relatively low temperatures.

Ionic liquid is the new 'green solvent' that is environmentally and does not harmful towards the users and the woods. Ionic liquid has the same ability as alkali in their own way to treat woods. Furthermore, ionic liquid does not degrade the woods and this might help in enhance the properties of wood much better that alkali. Since ionic liquids are environmentally friendly, reusable and can easily dissolve a large number of biomass, they will serve as the reaction media in effectively removing lignin and hemicellulose as well as in reducing cellulose crystallinity (Darji & Som., 2013)

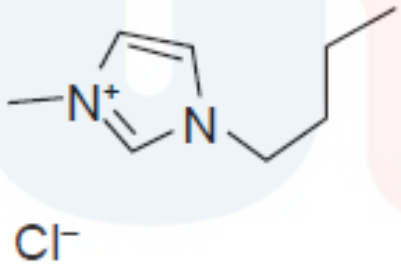

Figure 2.5: The structure of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl)

This ionic liquid have unique properties such as low density simultaneously with high mechanical strength, low cost, renewability, biodegradability, good film-forming performance, chemical stability and enormous of chemical derivation (Reddy et al., 2014). Due to these unique properties it can dissolve many organic and inorganic materials. Figure 2.5 shows the structure of the 1-butyl-3-methylimidazolium chloride which are one of the example of ionic liquid and that is the one we use for this research.

Ionic liquids are nowadays frequently used as environmentally friendly organic solvents for a wide range of biopolymers and synthetic polymers, due to their high chemical stability and low volatility (Croitoru & Patachia, 2014). So it is can be expected ionic liquid can enhance the mechanical properties of sawdust. The chemical modification of cellulose and wood (cellulose functionalization) has been achieved in ionic liquids under homogeneous conditions and relative mild temperature regime (90-120 °C), by comparing with traditional wood modification process (180-200 °C) (Croitoru & Patachia, 2014).

These ionic liquids have received extensive attention not only because of their low reactivity with water but also because of their large electrochemical windows. Usually, these ionic liquids can be well dried with the water contents below 1 ppm under vacuum at temperatures between 100-150 °C

All the ionic liquids were able to dissolve rice husk cellulose to varying extents, with the highest dissolution (36.7%) given by 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) followed by 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) (31.3%) and 1-ethyl-3-methylimidazolium diethyl phosphate ([EMIM]DEP) (16.0%) at the 10th hour of heating.

All the regenerated cellulose was found to be more amorphous as compared to the untreated rice husk. The energy study showed that both [EMIM]OAc and [BMIM]Cl had lower energy requirement compared to [EMIM]DEP. The results of energy requirement complemented the findings of dissolution ability of the ionic liquid. Both [EMIM]OAc and [BMIM]Cl are potential ionic liquids to be used in the pretreatment of rice husk, as they dissolved rice husk equally well (Nam et al., 2011)

CHAPTER 3

MATERIAL AND METHODS

3.1 Material

The 250 g of sawdust weighted to treat with the ionic liquid. The concentration of the sawdust was 10% wt. For each sample was calculated and weighted with 2.5 g sawdust to be immersed in the 22.5 g ionic liquid. The pre-treatment varied with the different chemical composition by varies the treatment time and used wide range of temperature. The temperature used are in the range of 80℃ until 120℃ and the treatment time used are within 24 hours and 48 hours. This sawdust that treated with different parameter is then characterized by FT-IR, XRD and TGA to identify the structure, chemical compositions as well as their physical properties. The non-treated sawdust is characterized as the main comparison to the changes happen towards the ionic liquid-treated sawdust. Each the sample that treated with different temperature and treatment time shown a difference physically due to their colour of the sample and the structure of the sample changed. But after the test were conducted there will be major difference in terms of contents of the sawdust included the chemical composition.

3.2 Methodology

3.1.1 Preparation of sawdust

Sawdust are collected from local sawmill of Kilang Papan Jeli Sdn. Bhd. The sawdust was the industrial wastes and the type of woods are mixed. Sawdust are the dried at 70 ℃ in a vacuum oven. After dried, the raw material will be sieved to remove any lumps. The sawdust was still in the form of big size to be sieved into 250

µm sieve. The sawdust then grinded to obtain powdery particles like shown in Figure 3.1.

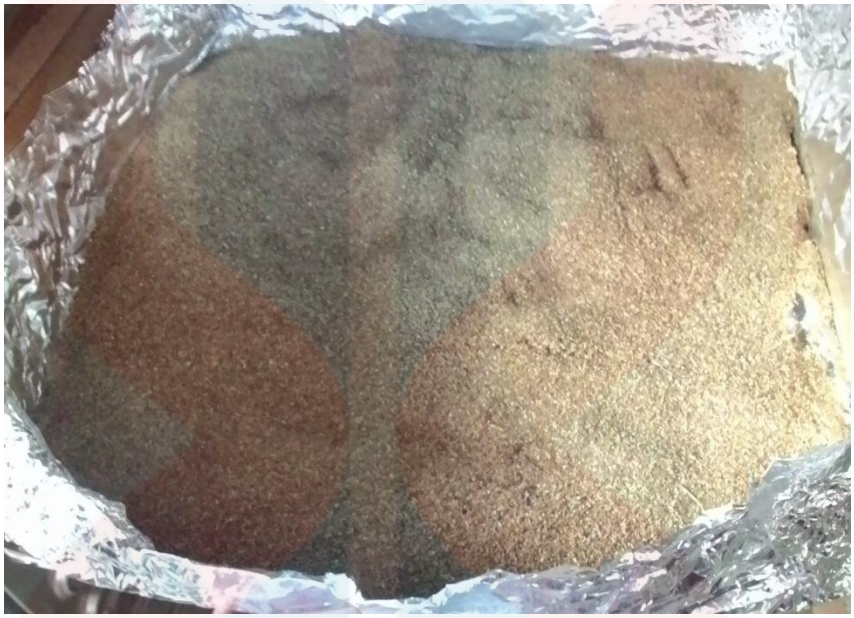

Figure 3.1: The sawdust after heated and grind.

After getting the fine powder form, the sawdust then been dried at 100 ℃ for 24 hours and stored in a sealed container and later sieved used 250 µm sieve. (Shaaban et al., 2015). Figure 3.2 shown the sawdust being sieved used 250 µm sieve.

Figure 3.2: The sawdust being sieved by 250 µm sieve.

3.1.2 Pre-treatment of sawdust with ionic liquid.

The wood sawdust will be added gradually in ([BMIM]Cl) preheated in an oil bath at 80℃, 100℃ and 120℃ in a closed container. The sawdust/([BMIM]Cl) mixture were stirred continuously at varies temperature for 24 hours and 48 hours. Figure 3.3 shown the pre-treatment of sawdust/([BMIM]Cl) conducted The sawdust will be immersed in the distilled water at room temperature to wash it simultaneously and the complete ionic liquid removal from the sawdust will be obtained between 72 and 100 hours and Figure 3.4 shown the treated sawdust being immersed in distilled water in closed container before it is being filtered.

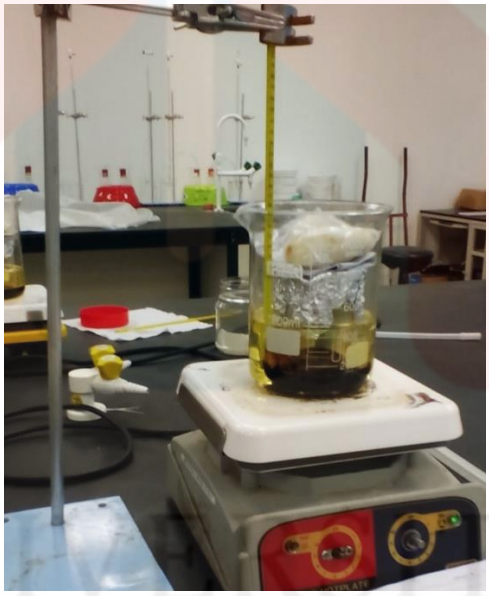

Figure 3.3: The pre-treatment of sawdust/([BMIM]CL).

Figure 3.4: The treated sawdust being immersed in distilled water to wash the Ionic liquid.

3.1.3 Characterization

3.1.3.1 Fourier transform-infrared (FT-IR) spectroscopy.

FT-IR spectra will be used to obtain the result of the regenerated cellulose after treated and before treated. The compositional and structural changes of the regenerated cellulose will be characterizing by using FT-IR. The FT-IR will offer quantitative and qualitative analysis for organic and inorganic materials. The machine will process in the way of identified the chemical bonds in the molecule itself by producing an infrared absorption spectrum. This machine very effective to find the functional groups and characterizing covalent bonding information from the sample. Figure 3.5 and 3.6 shown the machine (FT-IR) that will be used and the closed up of the tips to place the sample.

Figure 3.5: FT-IR machine used in this study and Figure 3.6: the tips of the FT-IR which is very important to characterize the compositional and structural of the sample.

3.1.3.2 Xray Diffraction (XRD) analysis

XRD is a rapid analytical technique that were used in this study for phase identification of a crystalline material and can provide information on the unit cell dimension. XRD can run sample in three form which are solid, liquid and powder. The multiple beams of XRD will creates a three dimensional picture of the electron density from any crystalline structure. The concept of the XRD is based on the X-

rays generated by the cathode tube, filtered to produce a monochromatic radiation which then collimated to concentrate and will be directed towards the sample. The condition of the concept satisfied the Bragg's law that relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in the crystalline sample. This is non-destructive test and it is fast with high accuracy. Scans collected from $2\theta = 5^{\circ}$ to 60° with step size of 0.03 at 4 s per step.

3.1.3.3 Thermogravimetric Analysis (TGA)

TGA is the method used for thermal analysis which the changes of the physical and chemical of the sample will be measured as a function of increasing of the temperature. It will measure the amount of weight change of the material, either as function of increasing temperature or as a function of time. This testing need to run in the helium, nitrogen, air or other gases. The sample are heated with the temperature of 50-600 ℃ at a rate of 10 ℃/min in the presence of nitrogen (20ml/min). Figure 3.7 shows the machine used for TGA testing.

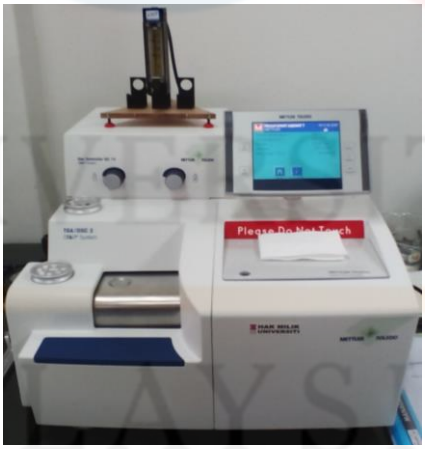

Figure 3.7: The machine used for TGA testing in this study

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Fourier Transform Infrared (FT-IR) Test Results.

4.1.1 Different Temperature

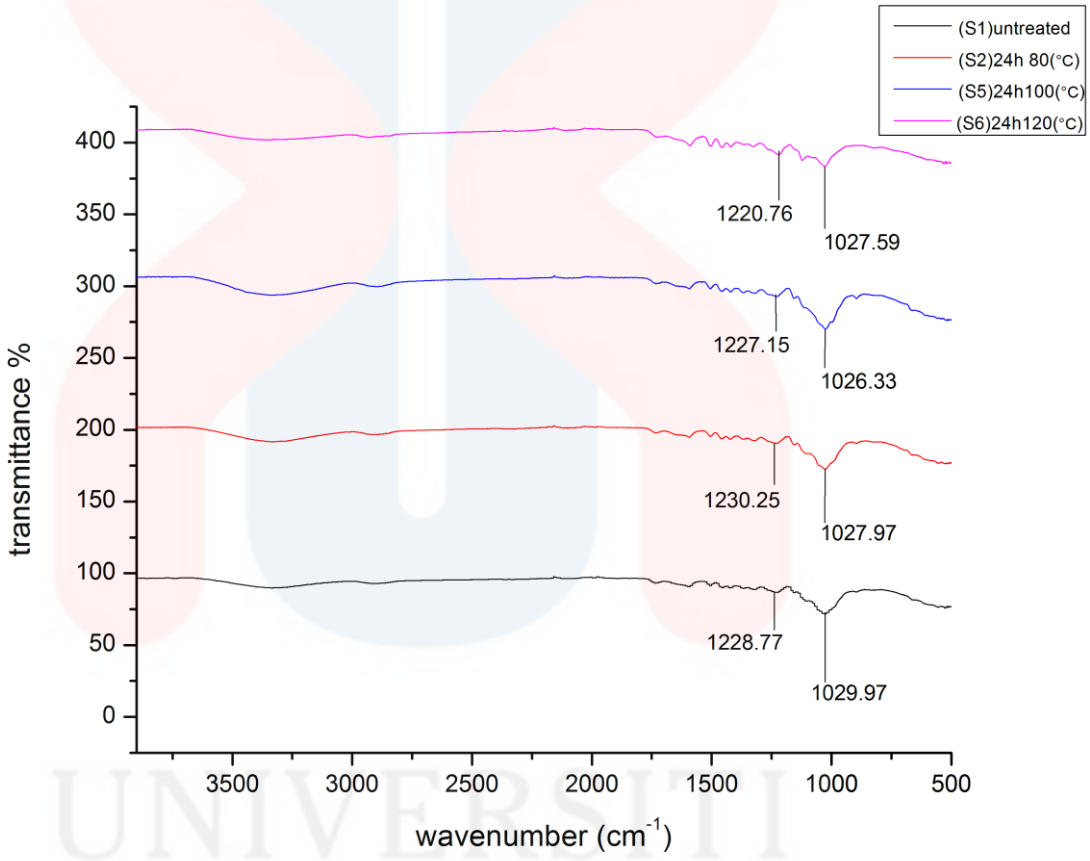

Figure 4.1: Untreated sawdust vs sawdust treated with Ionic Liquid at 24 hours with different temperature which is 80°C, 100°C and 120°C respectively.

The FT-IR spectra in the Figure 4.1 shows the unmodified sawdust and the chemically treated sawdust at a constant time (24 hours) but at different temperature which is 80°C, 100°C and 120°C respectively. This modified sawdust was treated with ionic liquid at 10 wt%. (There is clear different within each one of the graph. There is different with the treated and untreated sawdust can be detected in the

infrared spectra in terms of different absorbance value and shapes of the bands and also their location. showed clearly the typical absorbance bands expected for the hemicellulose polymer, and the peak in the region of 500 – 4000 cm^{-1} which are respectively used to study the fine structural characteristic of cellulose (Hurtubise et al., 1960). Spectra of all the regenerated cellulose show the strongest absorption band at range 1030 cm^{-1}. This band correspond to the C-O stretching vibration in cellulose/hemicellulose and aryl-OH group in lignin. There is slightly decreases at this absorption band in between the untreated and treated sawdust. The untreated shows high absorption band, 1029.97 cm^{-1} but for the 80℃, 100℃ and 120℃ it shows a slight decrease which is 1027.63 cm^{-1}, 1026.33 cm^{-1}, 1027.59 cm^{-1}. At 120 ℃, the peak is the lowest shows slowest dissolution of the sawdust. This shows that the regenerated cellulose exhibited reduced absorbance, which have resulted from the degradation of cellulose/hemicellulose during heating (Ang et al., 2012)

At 1290 cm^{-1}, the asymmetric bending of CH_3 and methoxy ($-OCH_3$) groups present in lignin. Untreated sawdust and sawdust treats at 24 hours, 100℃ shows only slight difference while sawdust treats at 80℃, 24 hours show increases and sawdust treats at 24 hours, 120℃ shows big decreases. This indicates that there is reduction of hydroxyl group content in the sawdust after the reaction has been taken places. The higher the temperature used to treat the sawdust, the slowest the dissolution of sawdust so in the meantime, this proved that high temperature more than 100℃ are not suitable condition to treats sawdust in ([BMIM]Cl). Moreover, the degradation of cellulose also reduced C-H stretching at 3000 cm^{-1} of these regenerated cellulose.

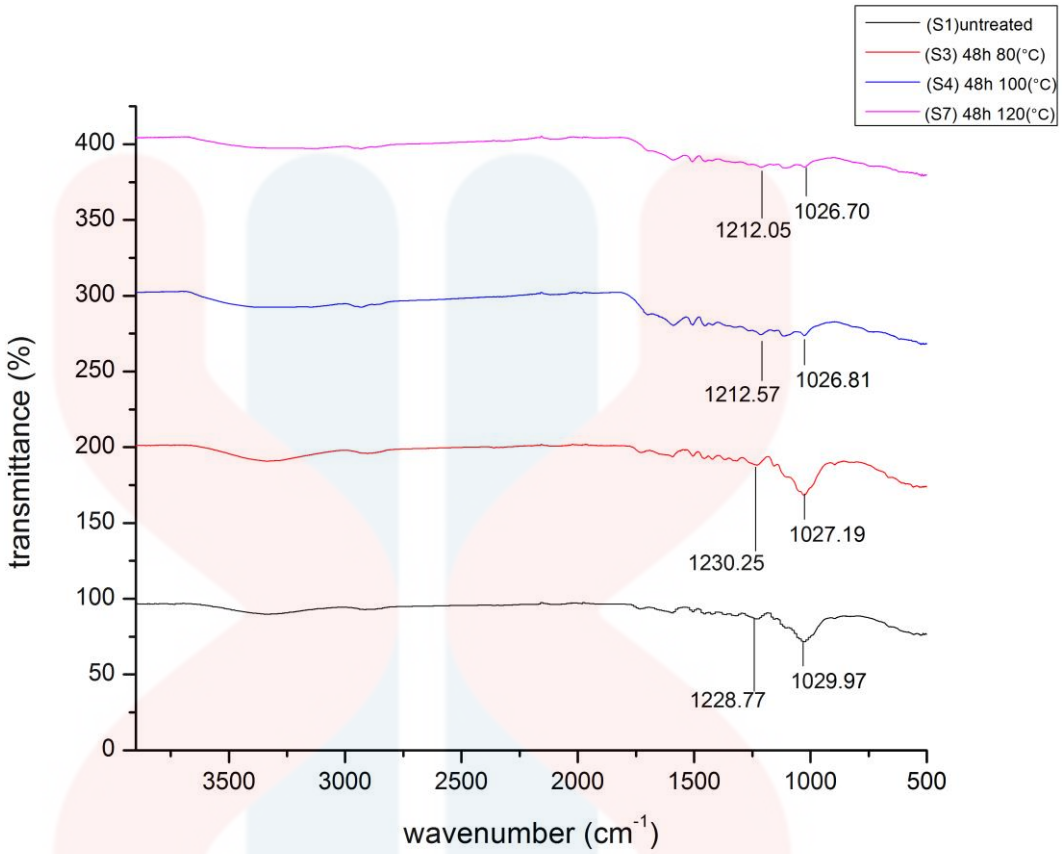

Figure 4.2: Untreated sawdust vs sawdust treated with ionic liquid at 48 hours at different temperature which is 80°C, 100°C, and 120°C respectively.

The FT-IR spectra in Figure 4.2 shows unmodified sawdust and the modified sawdust that being treated for 48 hours but using different stated of temperature which is 80°C, 100°C and 120°C. The treated sawdust was treated with the same ratio of 10% by weight. The result of the FT-IR spectra shows the slight difference than the first result in the figure 4.1 due to the longer treatment time are applied for the result showed in figure 4.2.

Sawdust treats at 48 hours which heated with the temperature 80°C, does not showed much changes with the untreated because the dissolution of the cellulose was efficient at this temperature eventhough the treatment time are longer. Sawdust treats at 100°C and 120°C was high temperature used during the treatment showed a slight

defect of decrease in the spectra bands. Spectra of all the regenerated cellulose show the strongest absorption band at about 1035 cm^{-1}. This band correspond to the C-O stretching vibration in cellulose/hemicellulose and aryl-OH group in lignin.

Sawdust treats at 100℃ and 120℃ showed the cellulose are degraded and the peak of band are decrease slightly than the untreated sample. This prove that high temperature does not suitable to treated with longer period. The spectra bands at 1300 cm^{-1} for the sawdust treats at 100℃ and 120℃ are quite similar but decrease when we verified with sawdust treats at 80℃ and untreated sawdust. This indicates that there is reduction of hydroxyl group content in the sawdust after the reaction has been taken places.

Temperature and treatment time was giving effect to the result obtain. The spectra band showed there was reduced absorbance at higher temperature and longer treatment time. The efficient treatment time are 24 hours and the efficient temperature used are supposedly not more than 100℃. Degradation of cellulose also reduced C-H stretching in cellulose material at 3000 cm^{-1}. At 3000 – 4000 cm^{-1}, the O-H bond are stretching and free, all the results showed the same patterns of peak at the spectra band (Oh et al., 2005).

4.1.2 Different treatment time

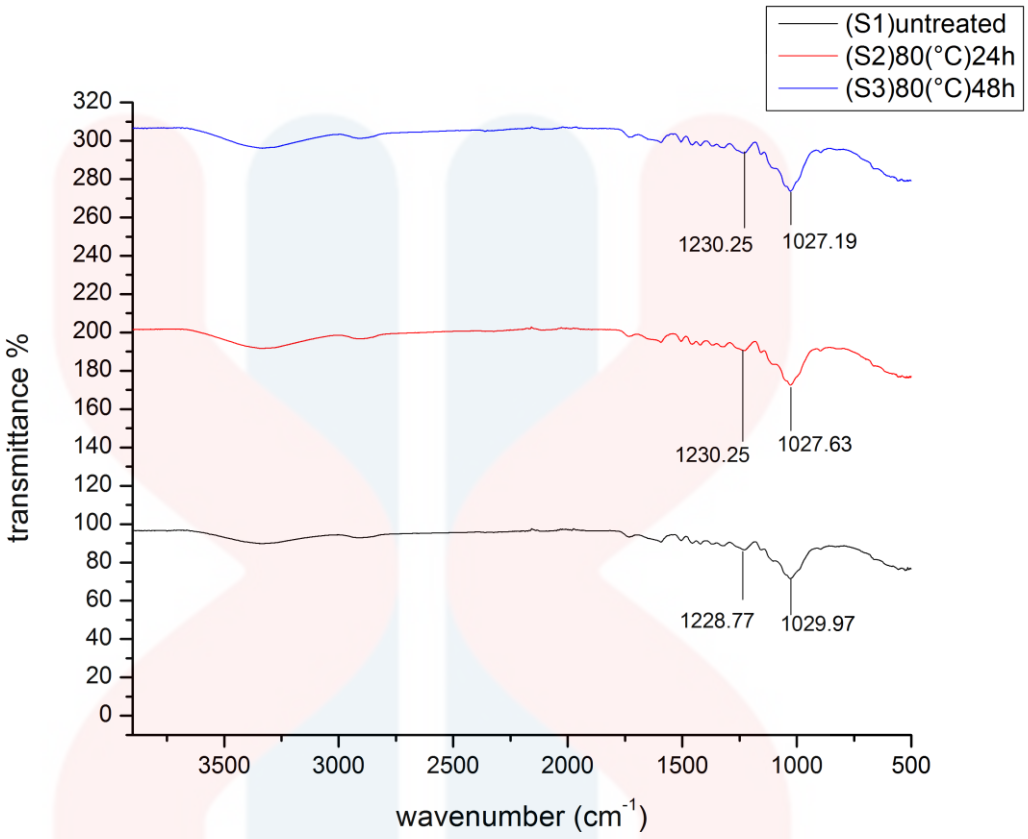

Figure 4.3: Untreated sawdust vs sawdust treated with Ionic Liquid at 80°C with different treatment time which is 24 hours and 48 hours.

Figure 4.3 show the FT-IR spectra bands of the untreated sawdust and the treated sawdust with ([BMIM]Cl) at constant temperature (80°C) but different treatment time. The spectra band does not show much different, at 1030 cm^{-1} where the regenerated cellulose is at the strongest peaks, the spectra band for 24 hours and 48 hours only shows small decrease to 1027.63 cm^{-1} and 1027.19 cm^{-1} from 1029.97 cm^{-1} shown by untreated sawdust. This bands correspond to the C-H stretching vibration in both cellulose/hemicellulose and lignin of the sawdust.

The treated sawdust showed that the cellulose was degraded and the bond of the carbon and hydrogen are being breaks at this spectra bands, which is at range of 1035 cm^{-1}. For the second spectra bands, both of the results show a slight increase

which is from 1228.77 cm^{-1} into 1230.25 cm^{-1} simultaneously. This happen at the range of spectra band at 1300 cm^{-1}, this indicates that higher amorphousity of the regenerated cellulose are present at this peak. At this peak, the regenerated cellulose was amorphous than untreated sawdust. This due to the dissolution and subsequent regeneration of the hemicellulose fraction might contribute the result to get to the higher degree of amorphousity of the regenerated cellulose.

At 80°C, the treatment time does not give big differences and this temperature are suitable for the treatment of the sawdust to stretch vibrates the C-O and C-H groups present in lignin. The degradation of cellulose/hemicellulose might happen during the heating and results in the slight decreases at the strongest absorption band (1030cm^{-1}).

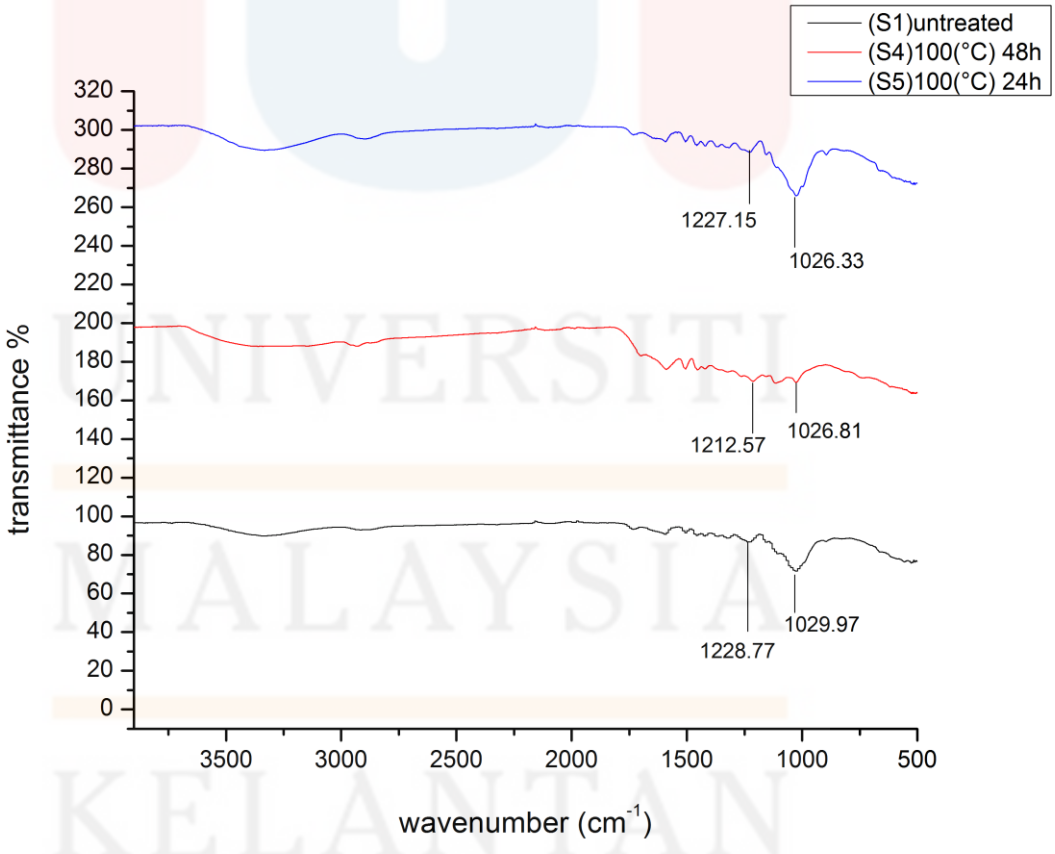

Figure 4.4: Untreated sawdust vs sawdust treated with Ionic Liquid at 100°C with different treatment time which is 24 hours and 48 hours.

For figure 4.4, the temperature of the treated sawdust is 100℃ with two different treatment time which is 24 hours and 48 hours. In this results shown, the spectra band for sawdust treats for 48hours are decrease rather than sawdust treats for 24hours does not show big difference with the untreated sawdust. At 1030 cm^{-1} where the regenerated cellulose is at the strongest peaks, the spectra bands for 24 hours and 48 hours sample shows a small decrease from 1029.97 cm^{-1} to 1026.33 cm^{-1} and 1026.81 cm^{-1} simultaneously.

For 48 hours the peak of the spectra band shows decreases because of the high temperature used for longer time. The bond of the C-O and C-H band are stretch vibrates and breaks the bonding which results in the dissolution of cellulose/hemicellulose (Nelson et al., 1964). When the bond are breaks the cellulose are dissolve and the peaks will decrease and the pattern of the spectra band will not be the same with the untreated sawdust and the spectra band shows for sawdust treats for 24 hours. This shows that treatment time also played a role in the dissolution of cellulose. The longer the treatment time, the higher cellulose that will be dissolve. Longer treatment time cannot be apprehending on the high temperature.

The spectra bands at 1300 cm^{-1} of the untreated sawdust and sawdust treated for 24 hours show small difference which is 1228.77 cm^{-1} to 1227.15 cm^{-1} simultaneously but for sawdust treated for 48 hours the spectra bands is 1212.57 cm^{-1}. This indicates that, the degradation might happen during the heating due to the higher temperature with longer treatment time.

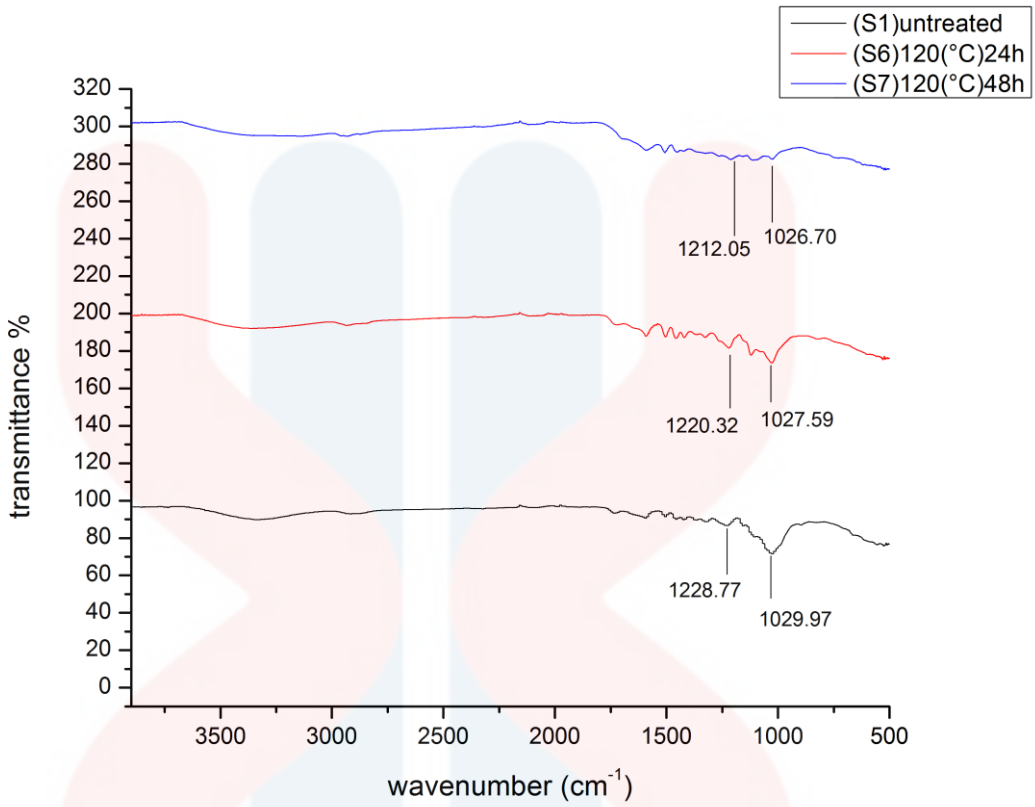

Figure 4.5: Untreated sawdust vs sawdust treated with Ionic Liquid at 120°C with different treatment time which is 24 hours and 48 hours.

Investigation results on the figure 4.5, indicates that there are big decreases between the untreated sawdust and the treated sawdust at 120°C for 24 hours and 48 hours. Spectra of all the regenerated cellulose show the strongest absorption band at about 1030 cm^{-1}. This band correspond to the C-O stretching vibration in cellulose/hemicellulose and aryl-OH group in lignin. There is slightly decreases at this absorption band in between the untreated and high temperature treated sawdust.

At 24 hours, the pattern still shows there is still high peaks and strong absorption but at 48 hours, the pattern of the spectra band shows slight decreases. This might due to the high temperature and longer exposed time for the treatment. The C-O stretching vibration in cellulose/hemicellulose and asymmetric bending of CH_3 and methoxy ($-OCH_3$) groups present in lignin are corresponds at 1027.59 cm^{-1}

and 1026.70 cm^{-1} (Labbe et al., 2005). At the second spectra band, there is only small decrease 24 hours treated sample which is from 1228.77 cm^{-1} into 1220.32 cm^{-1}. But for 48 hours treated sample, the is big decrease which is 1212.05 cm^{-1}. When the bond are breaks the cellulose are dissolve and the peaks will decrease and the pattern of the spectra band will not be the same.

Higher temperature for treatment are not suitable because the cellulose was dissolved due to the reaction between the ionic liquid that are heated in high temperature and longer treatment time. The longer the treatment time and the higher temperature used, the higher cellulose dissolving. This due to the breaks of the carbon and hydrogen bond in the cellulose compounds and also C-H in lignin compounds.

4.2 X-ray Diffraction (XRD) Results.

XRD analysis are done to determine the crystallinity of the treated and untreated sawdust. The proportion of the amorphous and crystalline of the cellulose and the disordered components can be found when the sample undergoes XRD analysis. This proportion of amorphous and crystalline was expressed in the form of crystallinity index.

The diffraction pattern for all the untreated and treated sawdust showed only two peaks that indicates amorphous and crystalline peak. The high peak was considered as crystalline peak and the lowest peak are considered as amorphous peak. The diffraction pattern shows two peaks at $2\theta = 15^{\circ}$and 22°. The I_{002} represents the peak at $2\theta=22^{\circ}$, while the I_{am} represents the height of the minimum between the $2\theta = 15^{\circ}$and 22° which is at 17°.

Table 4.1 shows the crystallinity index (CI) calculated from the Equation below:

$$CI\ (\%) = \frac{I002 - Iam}{I002} \times 100$$

Sample	Crystallinity Index (CI)(%)	Amorphous (%)
Sample 1 (untreated)	45.59%	54.41%
Sample 2 (24 hours, 80°C)	41.65%	58.35%
Sample 3 (48 hours, 80°C)	40.50%	59.25%
Sample 4 (48 hours, 100°C)	16.13%	83.87%
Sample 5 (24 hours, 100°C)	39.64%	60.36%
Sample 6 (24 hours, 120°C)	17.87%	82.13%
Sample 7 (48 hours, 120°C)	18.47%	81.53%

Table 4.1: The crystallinity index of the untreated and treated sawdust with the amorphous percentage.

The crystallinity index was obtained from the equation above while the amorphous percentage was obtained by minus the crystallinity index with 100%. So the minus of 100% with the crystallinity index resulted in the percentage of amorphous like equation shown below:

100 - (CI) = amorphous

4.2.1 Different temperature

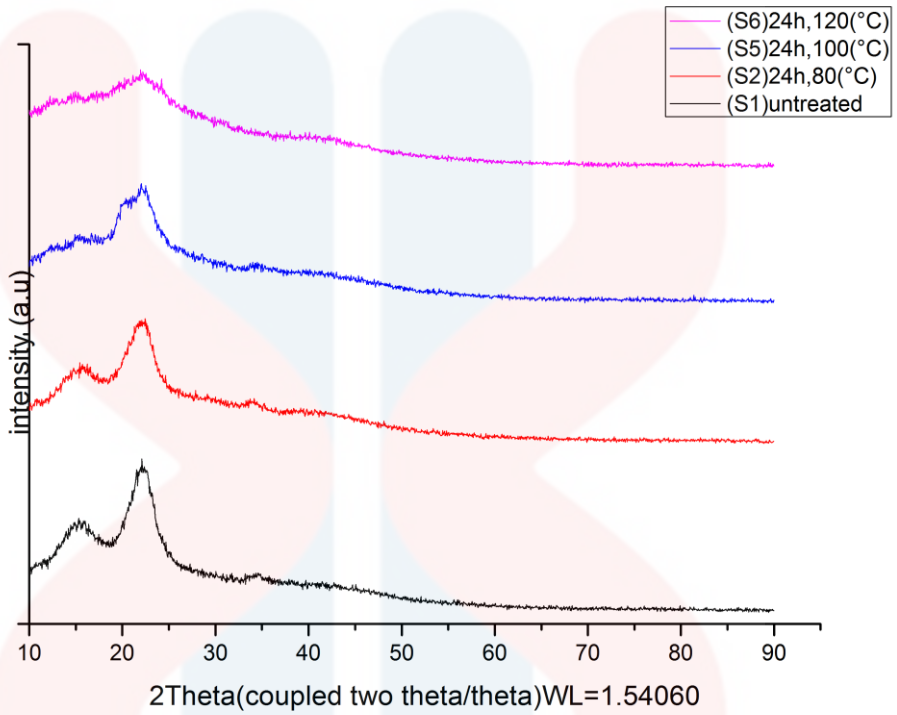

Figure 4.6: The diffract pattern untreated sawdust vs sawdust treated with Ionic Liquid at constant treatment time (24hours) with different temperature which is 80°C, 100°C, 120°C.

The X-ray diffract pattern above explains about the crystallinity and amorphous of proportions. The diffraction pattern for untreated sawdust shows two peaks that indicates at 2θ=15˚ is amorphous and at 2θ=22˚ is crystalline (Kuo et al., 2009). The untreated sawdust shows a high peak and this means it have highest crystallinity to compare with the treated sawdust. All this treated sawdust in the figure 4.6 are treat at constant treatment time which is 24 hours but with different temperature. The higher the temperature used to treat the sawdust, the lower the crystallinity of the sawdust.

The untreated sawdust shows 45.59% of crystallinity index, the treated with 80°C, shows 40.08% of crystallinity index. Where the others treated with 100°C and 120°C shows 39.64% and 17.87% respectively. There is decreases in the crystallinity

when the temperature used for the treatment is high. For sawdust treats at 120℃, the peaks show very low crystallinity and there is almost no appearance of two peaks to differentiate between crystalline and amorphous. This is because, the cellulose changed to regenerated cellulose and the growing of crystallites might be incomplete and disrupted due to the high treatment temperature. The cellulose might degrade and the sample lost properties of compositions of sawdust.

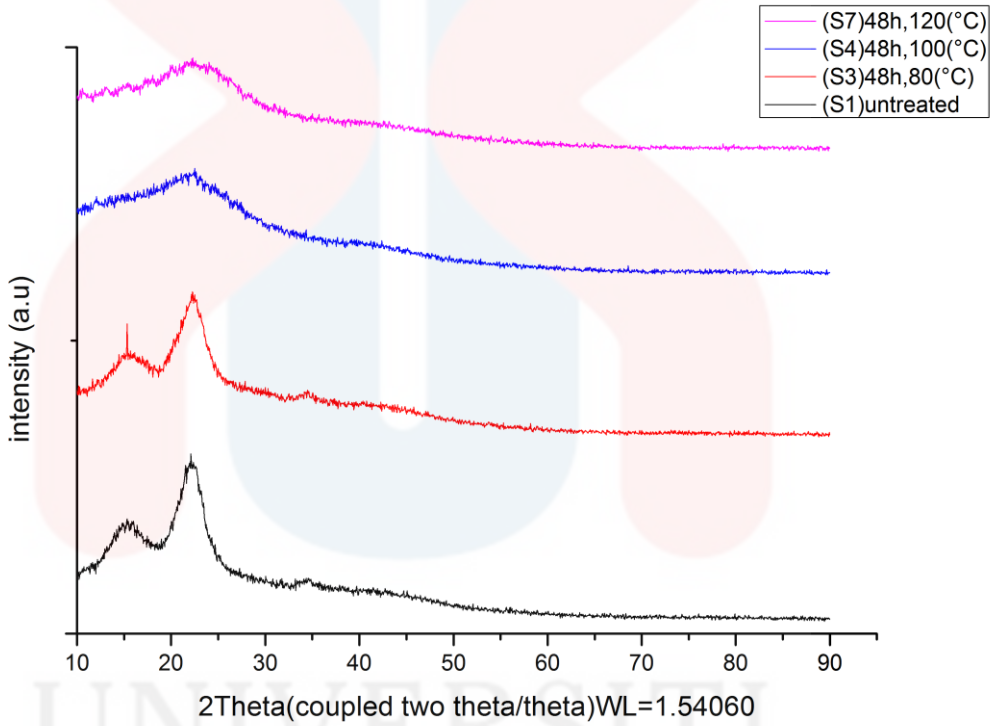

Figure 4.7: The diffract pattern untreated sawdust vs sawdust treated with Ionic Liquid at constant treatment time (48hours) with different temperature which is 80℃, 100℃, 120℃.

Figure 4.7 indicates the untreated sawdust with the treated sawdust at different treatment temperature and longer treatment time which is 48 hours. The diffract pattern of the untreated 2θ=15˚ is amorphous and at 2θ=22˚ is crystalline. There is only treated sawdust at temperature 80℃ shows that there were still two peaks of the diffract pattern that show the character for amorphous and crystalline

while the other two treatment temperature, 100℃ and 120℃ shows slightly only one peaks that is wide and not gabled.

The percentage of the crystallinity index for sawdust treats at 80℃ is 42.74%, 100℃ is 16.13% and 120℃ is 18.47%. High treatment temperature might degrade the composition of the sawdust itself and finally resulted the diffract pattern shown on the figure 4.7. Eventhough at 24 hours' treatment time, the sample treated at 100℃ does not show sign of degradation occur but at 48 hour treatment time which is longer than 24 hour resulted in the degradation of the composition of the cellulose and the sawdust itself. The longer treatment time and high temperature are not suitable for the pretreatment of the sawdust with the ([BMIM]Cl).

Sawdust treats at 100 ℃ shows lower crystallinity index than sawdust treats at 120℃ for 48 hours eventhough the temperature used for this treated sawdust are higher than sawdust treats at 100℃ for 48 hours. This condition occur might be there is some mistake happen during the experimental procedure. There is error occur where the hot plate used lost control and heated the sample until temperature higher than 120℃ for a few minutes. This happens a few time because the hot plate used are difficult to stabilize its temperature. The degradation of the sawdust occurs during this heated treatment and the properties composition lost for this sawdust itself.

4.2.2 Different treatment time

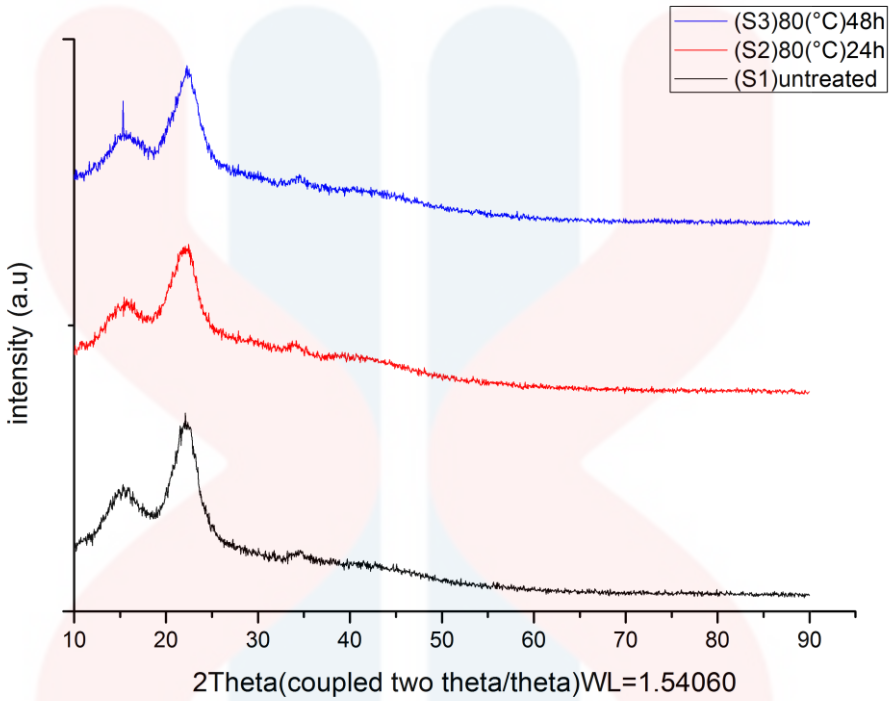

Figure 4.8: The diffract pattern untreated sawdust vs sawdust treated with Ionic Liquid at 80℃ temperature but different treatment time (24 hours and 48 hours).

The diffract pattern of the figure 4.8 shows there are decreases between untreated sawdust and the treated sawdust at 2θ=15˚ and 2θ=22˚, from 45.59% to 40.08% (24 hours) and 42.74% (48 hours) respectively. There is slight decrease for sample that treated at 48 hours but for sample treated at 24 hours have lower crystallinity compare to the 48 hours' sample.

There is not much different of the crystallinity index of this temperature used either short or longer treatment time because 80℃ is the optimum temperature for the heating process of the pretreatment used ([BMIM]Cl).

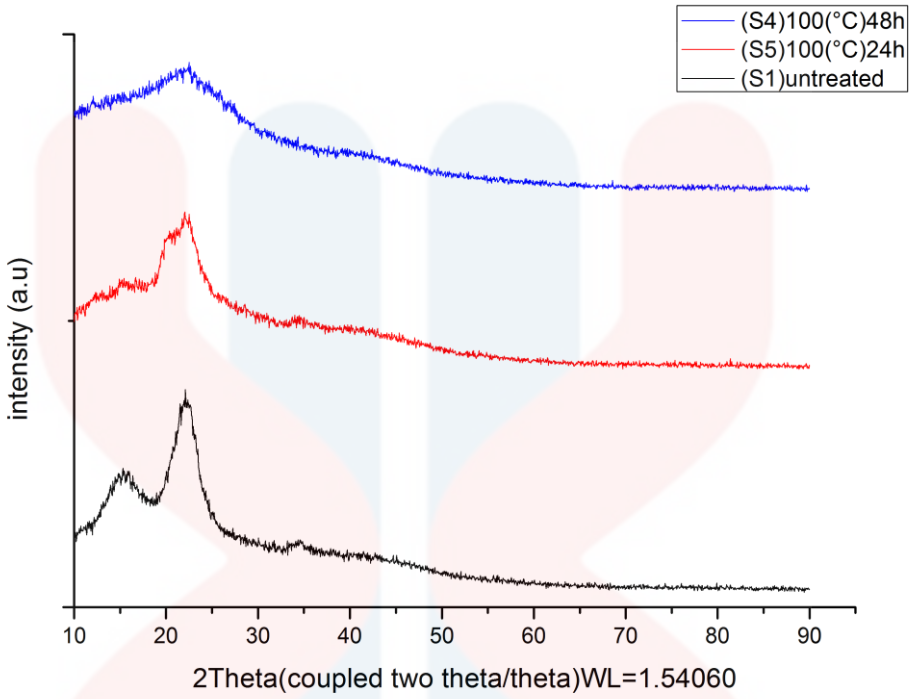

Figure 4.9: The diffract pattern untreated sawdust vs sawdust treated with Ionic Liquid at 100℃ temperature but different treatment time (24 hours and 48 hours).

The figure 4.9 above illustrate the diffract pattern for both samples untreated and treated sample at 100℃ at different treatment time which is 24 hours and 48 hours. As the figure shown above, the diffract pattern for 100℃ really show a different pattern between the untreated and treated sample. For the sawdust that treats for 24 hours show only slight decrease of the crystallinity percentage from 45.59% into 39.64% but for sawdust treats for 48 hours, there is huge decrease which is turn into 16.13%.

Sawdust that treats for 48 hours treated at longer time than sawdust treats for 24 hours and this resulted in the degradation of the cellulose in the composition of sawdust itself because it is treated at high temperature with longer treatment time. The higher temperature and longer treatment time used does not resulted in good

dissolution of cellulose but the sawdust will degrade and lose properties compositions of the sawdust itself.

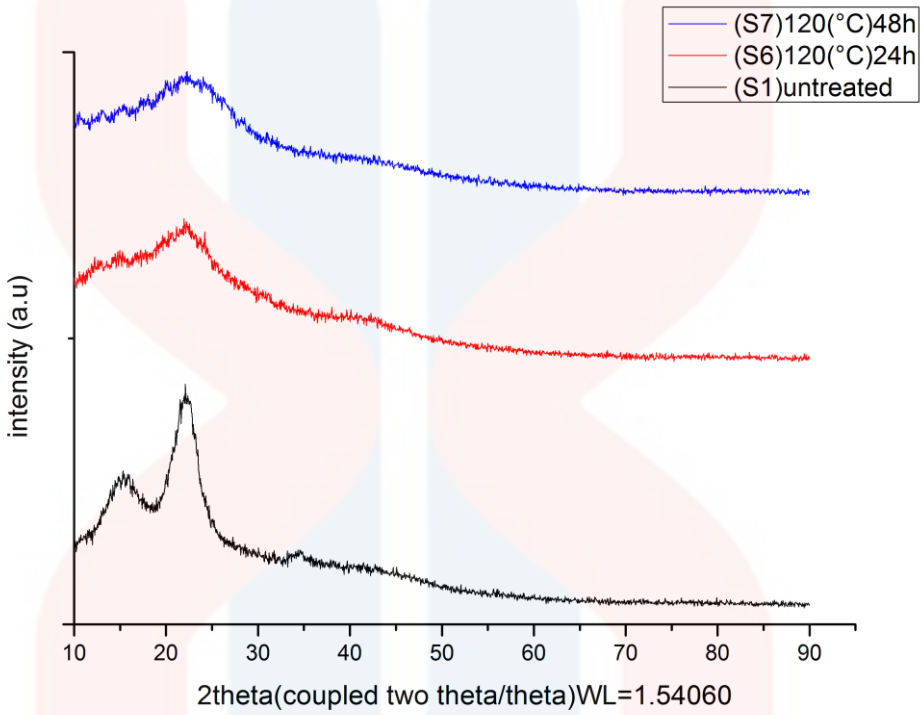

Figure 4.10: The diffract pattern untreated sawdust vs sawdust treated with Ionic Liquid at 100℃ temperature but different treatment time (24 hours and 48 hours).

Figure 4.10 showed diffraction results for sample that treated with 120℃ at 24 hours and 48 hours compared with the untreated sawdust. At 2θ=15˚ and 2θ=22˚, the untreated sample shows 45.59% of crystallinity index while for sawdust treats for 24 hours and 48 hours is 17.87% and 18.47% respectively. There is huge decreases for this treated sample due to the percentage of crystallinity index that we calculated from the equation.

The two peaks from the diffract pattern indicates that there are amorphous and crystalline phases exist in the sawdust sample but for the sample that treated at high temperature and longer treatment time shows that there is changes of diffract

pattern. The peak for amorphous and crystalline are losing it shape because the composition of the sawdust had degraded and change the rate of dissolution of the treated sawdust (Ang et al., 2012).

4.3 Thermogravimetric Analysis (TGA) Results.

Thermogravimetry (TG) was employed in process to understand the interactions between the Ionic Liquid ([BMIM]Cl) and the lignocellulosic biomass. This thermal testing was decomposed of profile from seven samples with IL pretreatment at different temperature and treatment including one untreated samples that studied by TG. The sample are treated with different treatment time which is 24 hours and 48 hours, their treatment temperature used in this study are 80℃, 100℃ and 120℃.

TG will provide the information on the thermal decomposition profiles of respective components (Marcilla et al., 2013), which can be used to follow the physiochemical changes that occur during pretreatment processes (Caballero et al., 1997; Chen et al., 2010). The TG was performed with the samples of 5-10 mg placed in the alumina crucibles were heated from 50℃ - 600℃ at a rate of 10℃/min in the presence of nitrogen (20ml/min).

TG will measure the instantaneous biomass weight at specific temperature as biomass temperature is increased accordingly. Form the curves for untreated and treated sawdust, the cellulose, hemicellulose and lignin was obtained their assessment of this mechanisms that contribute to IL pretreatment of biomass. The TGA curves can be divided into three primary zones where at stages one, the hemicellulose zone (245-290℃), cellulose zone (290-350℃) and lignin zone (350-550℃) (Singh et al., 2013).

4.3.1 Different temperature

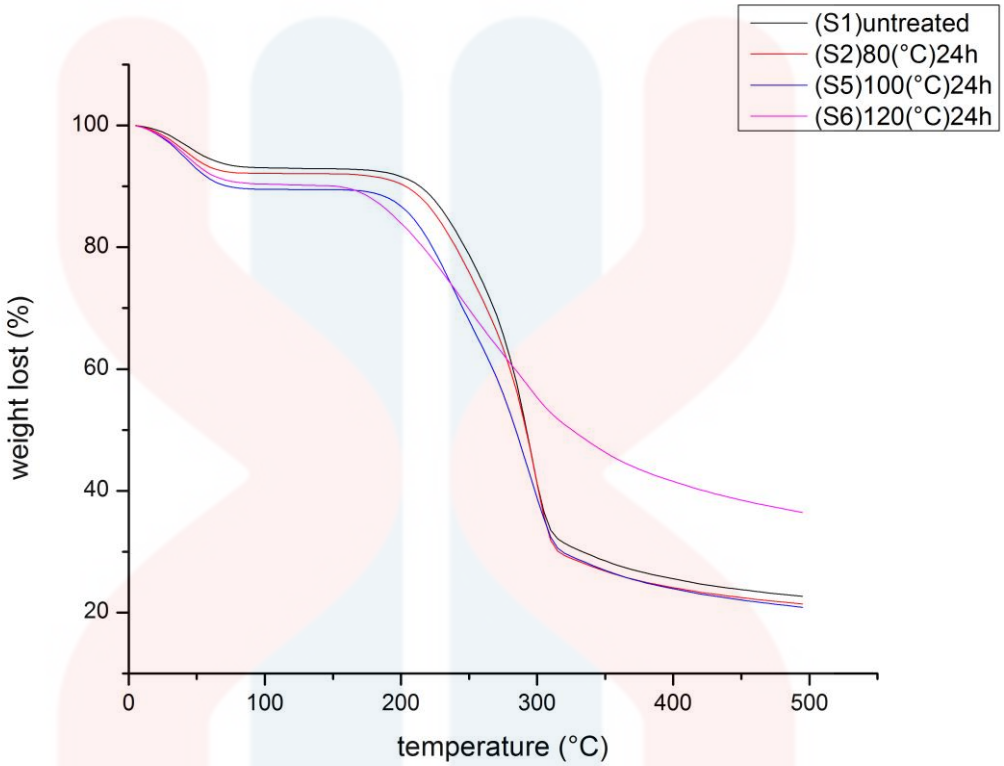

Figure 4.11: TGA results of the untreated sawdust vs treated sawdust with the constant treatment time (24hours) but heated with different temperature (80℃, 100℃ and 120℃)

Figure 4.11 shows the TGA curves for the untreated sawdust and treated sawdust that used constant treatment time which is 24 hours but with different temperature which is 80℃, 100℃ and 120℃. The cellulose had converted into amorphous form and may also be fully hydrolysed even in small units, into monomeric and dimeric glucose units (Li et al., 2010). The different kind of cellulose and sugar will need different weight lost.

This peaks shows two peaks that indicates there is amorphous and crystalline materials are presence in this sawdust. It is easier to break down an amorphous material rather than breaks down a crystalline material so the first weight lost is due

to the amorphous component of the material decompose at low temperature. Moreover, at the high temperature, the crystalline material was decomposed.

From figure above, the sawdust that treated with higher temperature during pretreatment show higher weight lost compared to the untreated samples. This might due to the effect of IL on the dissolution of lignocellulosic biomass, the cellulose are breaks down easily effect of the bond of the components in the treated sawdust breaks. The sawdust will lose more weight due to the decompose of the cellulose, hemicellulose and lignin (Dadi et al., 2007).

For treated sawdust at 120°C, the TGA curve shows differently from the other two, this is because of the high temperature during the pretreatment that had indicates low dissolution of cellulose. The amorphous peak are breaks down just the same with the other two but for the crystalline peak, it breaks at early temperature which is at 160°C in compare to those breaks at temperature 200°C and above. So the high temperature used during pretreatment will affect the weight lost for TG curve. This implies that the sample lost properties of composition of the sawdust during the pretreatment process because of the exposed towards high temperature.

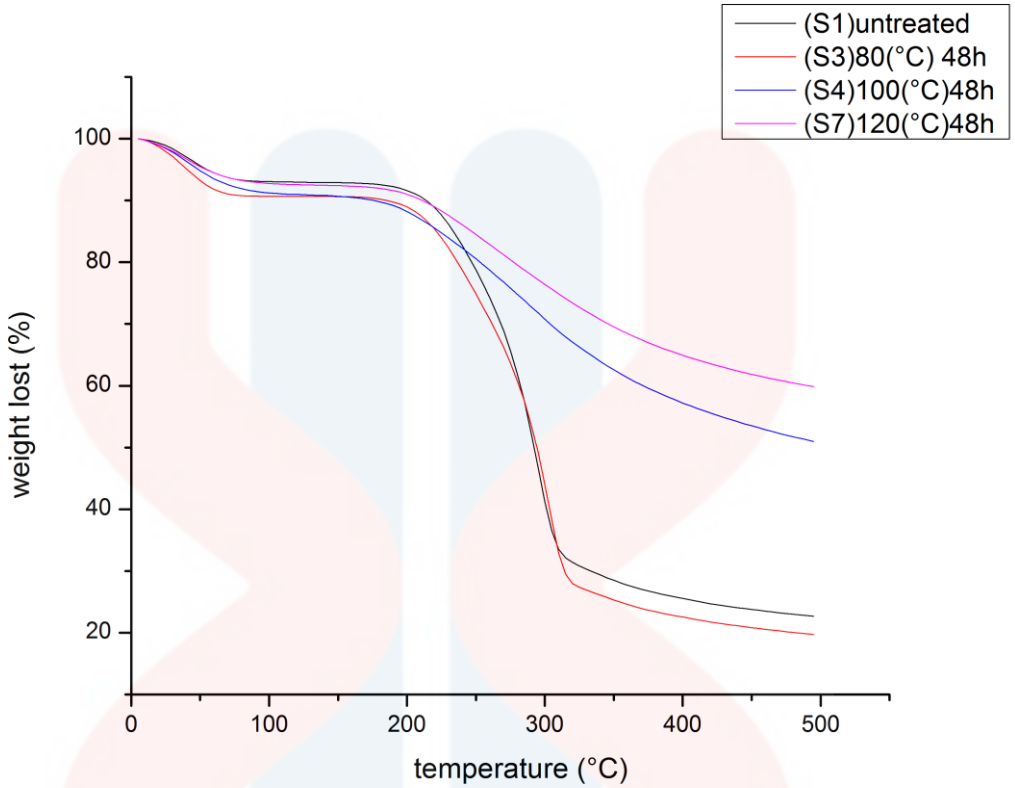

Figure 4.12: TGA results of the untreated sawdust vs treated sawdust with the constant treatment time (48hours) but heated with different temperature (80°C, 100°C and 120°C)

Figure 4.12, show the TGA results for 48 hours' treatment time for 3 range temperature which is 80°C, 100°C and 120°C. As we can see, the weight loss of the sample that used low temperature during pretreatment show a smooth curve and does not differ much with the untreated sample curves. But at high temperature used during pretreatment had affected the weight lost for the crystallinity peak and the longer treatment time also effect the shape of the curve itself.

The crystallinity of the sample used high temperature and longer treatment time are low than the sample that used low temperature and short treatment time. This is because the crystalline structure inside the sawdust are broke down earlier during the pretreatment. The high temperature decomposes the cellulose component

including lignin. The sawdust degrade and the composition of the sawdust lost during the treatment and the properties of hemicellulose, cellulose and lignin are demolished due to the high temperature and longer treatment time.

4.3.3 Different treatment time

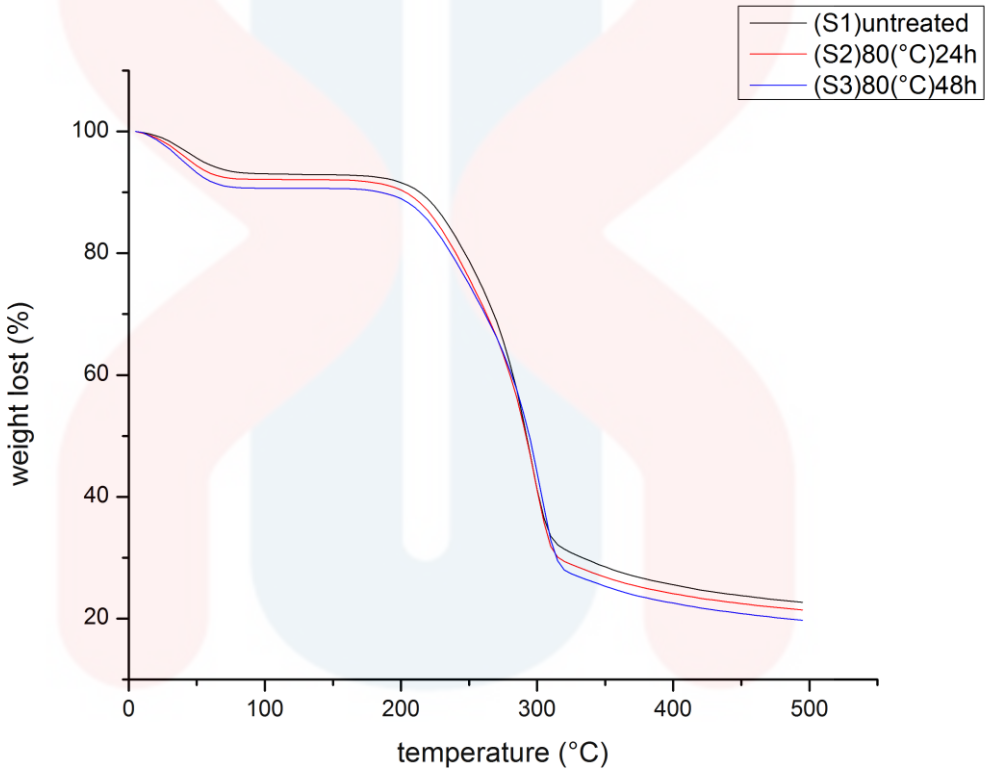

Figure 4.13: TGA results of the untreated sawdust vs treated sawdust heated with the constant temperature (80°C) but with different treatment time (24 hours and 48 hours)

The figure 4.13 above shows the TGA results of untreated sawdust and treated sawdust heated at 80°C but different treatment time which is 24 hours and 48 hours. The sample treated at 48 hours show more weight lost than sample treated at 24 hours but both of this treated sample lost weight when compare with the untreated sawdust.

The weight loss of the treated sawdust was because of the dissolution of cellulose. The composition of the sawdust also dissolves during the pretreatment and the optimum temperature used for pretreatment is 80℃ for 24 hours' treatment time.

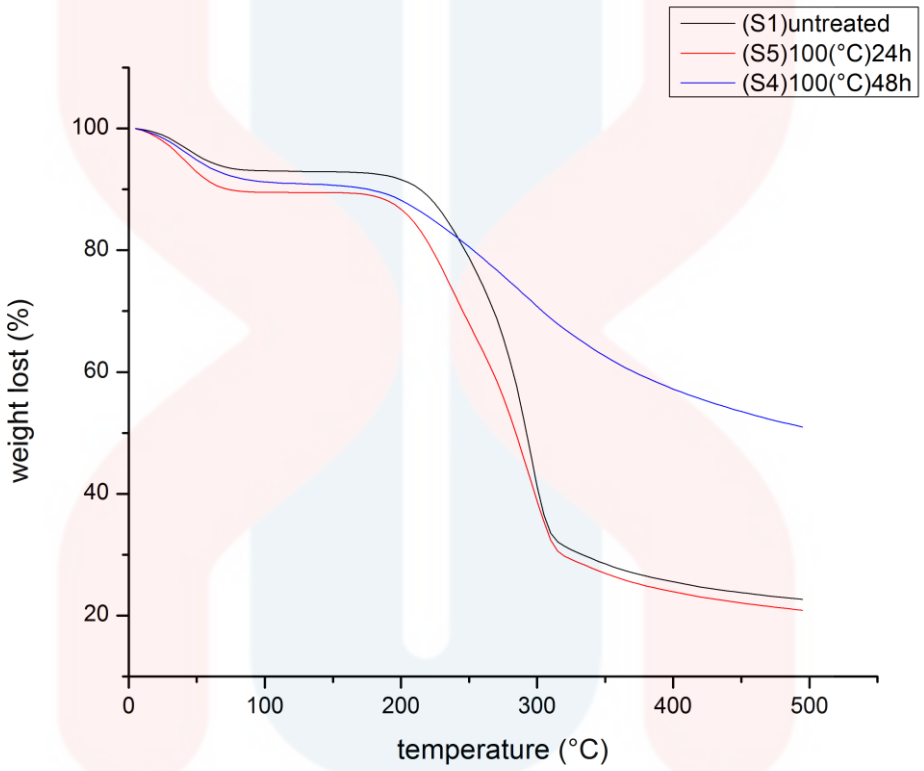

Figure 4.14: TGA results of the untreated sawdust vs treated sawdust heated with the constant temperature (100℃) but with different treatment time (24 hours and 48 hours)

Figure 4.14 showed the TGA results of the treated sawdust at 100℃ at 24 hours and 48 hours. When compare with the untreated sample, the weight lost for the sample at 100℃ for 24 hours is decrease slightly. At temperature below than 100℃, the sample 5 had lost weight below 90% compared to the treated sample that just lost about 95% of weight. For sample 4 the pattern of the graph indicates that the sample might decompose the composition of the sawdust itself during pretreatment. This is the only reason why the pattern of the graph is distorted and weight lost stop until 50% only. The sawdust had lost it characteristic during the high temperature and

longer treatment time. The optimum temperature used for pretreatment of sawdust with ([BMIM]Cl) is 80℃ until 100℃ and the treatment time that suitable is 24 hours. The longer the treatment time have decomposed the sawdust composition.

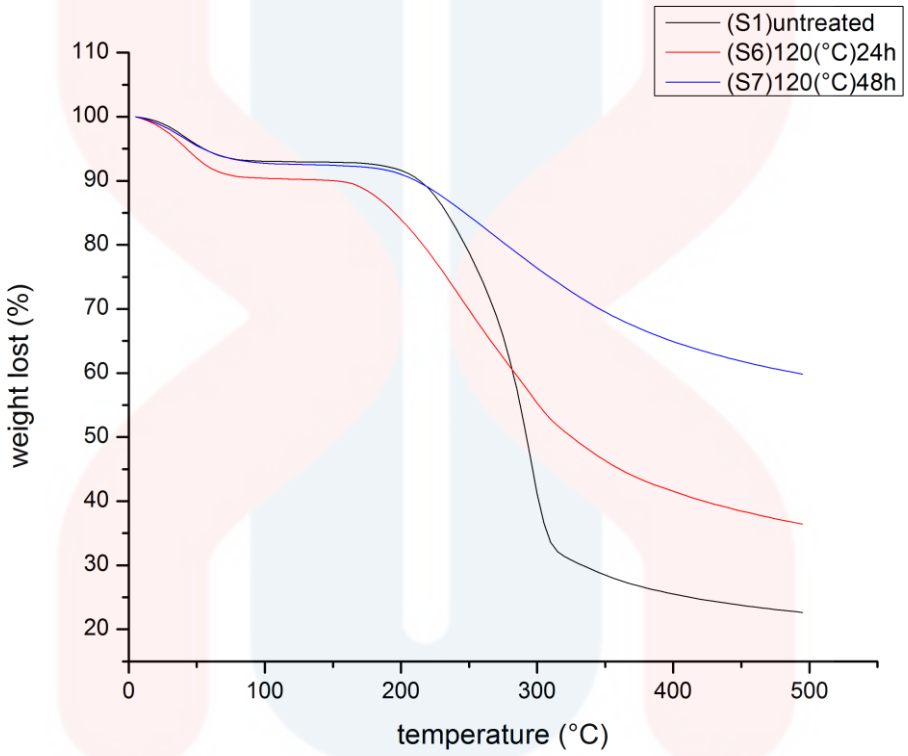

Figure 4.15: TGA results of the untreated sawdust vs treated sawdust heated with the constant temperature (120℃) but with different treatment time (24 hours and 48 hours)

Figure 4.15 showed the pattern of the TGA curve of the untreated sawdust compared with the treated sawdust at high temperature which is at 120℃. The pattern of the curve for both of the treated was distorted and weight lost for sample treated at 24 hours stop at 35% and for the sample treated at 48 hours stop at 60%. The longer treatment time resulted in the decompose of the sawdust. When the sawdust treated with ([BMIM]Cl) at high temperature, the Ionic liquid will degrade the composition of the sawdust and the sawdust lose it properties and when tested, the characteristic of the sawdust is distorted

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

In this study, the sawdust was treated with ionic liquid namely 1-butyl-3-methylimidazolium chloride ([BMIM]CL) at 24 hours and 48 hours heated with temperature 80℃, 100℃ and 120℃. Result obtain after the treatment proved that the structure and composition of the sawdust has altered. Although the physical appearance does not differ much, but the quality and the characteristic of the sawdust changed when treated with Ionic liquid during the experiment.

From FT-IR results, the treated sawdust shows a massive changed in the spectra band of the treated sawdust when compared to the untreated sawdust. The spectra band showed there was reduced absorbance at higher temperature and longer treatment time. There is reduction of hydroxyl group content and the C=O carbonyls in the sawdust after the reaction has been taken places. When the high temperature (120℃) are used for the heated process, the spectra band showed unstable peak and this indicates that there was lost of sawdust composition.

For XRD analysis, the results obtained showed peak for the ([BMIM]Cl) treated sawdust also changed when compared to the untreated sawdust. The diffract pattern show there is decreases in the crystallinity index of the treated sawdust compared to the untreated sawdust. Sample that showed most decline of the crystallinity is the sample that treated at high temperature in longer treatment time.

TGA showed the decreases of weight lost when compared the treated sawdust and untreated sawdust. The higher temperature (120℃) used during treatment

showed the characteristic of the sawdust was lost due to the degradation of the composition but the optimum temperature used (80℃) the dissolution of sawdust occurred and the composition of the sawdust was altered perfectly.

The efficient treatment time was 24 hours and the efficient temperature used are supposedly not more than 100℃. In the range of 80℃ until 100℃ was the optimum temperature for the treatment process. Longer treatment time also does not ensure good results. The longer the treatment time, the high degradation of composition of the sawdust occurred and the sawdust will lost it composition properties so the characteristic of the sawdust also gone. 24 hours was the optimum time to treat the sawdust.

5.2 RECOMMENDATION

Characterization of the untreated and Ionic liquid-treated sawdust should be done in the range temperature 85-95℃ because through this study proven that optimum range of temperature and treatment time is 80-100℃ and 24 hours respectively. The higher temperature used, the higher degradation of the sawdust composition occurred. Longer treatment time also does not bring any positive resulted and the moderate and optimum treatment time is 24 hours.

There was equipment problem during the experiment that affected result of the pretreatment process. The temperature of the hot plate used are not stable so the resulted for the sawdust treats at 100℃ at 24 hours showed a little sign of degradation occurred. There were a few times the treatment temperature rises above 120℃ for this sample and the degradation occurred. Stabilization of hot plate are very important.

REFERENCES:

Adlie, A., & Corresponding, S. (2010). Isolation and Characterization of Lignin from Rubber Wood in Ionic Liquid Medium. *Modern Applied Science*, *4*(11), 19–27.

Agbor, V. B., Cicek, N., Sparling, R., Berlin, A., & Levin, D. B. (2011). Biomass pretreatment: Fundamentals toward application. *Biotechnology Advances*, *29*(6), 675–685.

Ang, T. N., Ngoh, G. C., Chua, A. S. M., & Lee, M. G. (2012). Elucidation of the effect of ionic liquid pretreatment on rice husk via structural analyses. *Biotechnology for Biofuels*, *5*(1), 67.

Borysiak, S., & Doczekalska, B. (2005). X-ray Diffraction Study of Pine Wood Treated with NaOH, *13*(5), 87–89.

Croitoru, C., & Patachia, S. (2014). Biocomposites obtained from wood saw dust using ionic liquids. *Acta Chemica Iasi*, *22*(2), 113–134.

Darji, D., Alias, Y., Mohd Som, F., & Abd Razak, N. H. (2015). Microwave heating and hydrolysis of rubber wood biomass in ionic liquids. *Journal of Chemical Technology and Biotechnology*, *90*(11), 2050–2056.

Darji, D., & Som, F. M. (n.d.). 1-butyl-3-methyl Imidazolium Acetate Ionic Liquid, *16*(3), 169–178.

Johnson, K. E. (2007). What' s an Ionic Liquid ? *The Electrochemical Society Interface*, 38–41.

Kilpel??inen, I., Xie, H., King, A., Granstrom, M., Heikkinen, S., & Argyropoulos, D. S. (2007). Dissolution of wood in ionic liquids. *Journal of Agricultural and Food Chemistry*, *55*(22), 9142–9148.

Nam, T., Yoon, L. W., Lee, K. M., Ngoh, G.-C., Chua, A. S. M., & Lee, M. G. (2011). Efficiency of Ionic Liquid in the Dissolution of Rice Husk. *BioResources*, *6*(4), 4790–4800.

Pengisaran, K. P., Ionik, C., & Kelapa, P. (2014). EFFECT OF MECHANICAL GRINDING AND IONIC LIQUID PRE- TREATMENT ON OIL PALM FROND, *18*(3), 737–742.

Reddy, K. O., Zhang, J., Zhang, J., & Rajulu, A. V. (2014). Preparation and properties of self-reinforced cellulose composite films from Agave microfibrils using an ionic liquid. *Carbohydrate Polymers*, *114*(DECEMBER 2014), 537–545.

Shaaban, A., Se, S. M., Ibrahim, I. M., & Ahsan, Q. (2015). Preparation of rubber wood sawdust-based activated carbon and its use as a filler of polyurethane matrix composites for microwave absorption. *Xinxing Tan Cailiao/New Carbon Materials*, *30*(2), 167–175.

Singh, S., Varanasi, P., Singh, P., Adams, P. D., Auer, M., & Simmons, B. A. (2013). Understanding the impact of ionic liquid pretreatment on cellulose and lignin via thermochemical analysis. *Biomass and Bioenergy*, *54*, 276–283.

Thi, L., Trinh, P., Ju, Y., Lee, J., & Lee, H. (2015). ScienceDirect Characterization of ionic liquid pretreatment and the bioconversion of pretreated mixed softwood biomass. *Biomass and Bioenergy*, *81*, 1–8.

Chakar, F. S., & Ragauskas, A. J. (2004). Review of current and future softwood kraft lignin process chemistry. *Industrial Crops and Products, 20*, 131-141.

Pouteaua, C., Dole, P., Cathala, B., Averous, L., & Boquillon, N. (2003). Antioxidant properties of lignin in polypropylene. *Polymer Degradation and Stability, 81*, 9-18.

Rowell, R. M. 2004. Chemical modification. Enclyclopedia of forest sciences: volume three. Oxford: Elsevier Academic Press, 2004: Pages 1269-1274.

Marcilla, A., Garcia, A.N., Pastor, M,V., Leon, M., Sanchez. A.J., Gomez, D.M., 2013. Thermal decomposition off the different particles size fractions of almonds shells and olive stones. Thermal behaviour changes due to the milling processes. Thermochim. Acta 564, 24-33.

Caballero, J.A., Marcilla, A., Conesa, J.A., 1997. Thermogravimetric analysis of olive stones with sulphuric acid treatment. J. Anal. Appl. Pyrol. 44, 75-88.

Chen, W.H., Tu, Y.J., Sheen, H.K., 2010. Impact of dilute acid pretreatment on the structure of bagasse for bioethanol production. Int. J. Energ. Res. 34, 265-274.

Hurtubise FG, Krassig H: Classification of fine structural characteristics in cellulose by infrared spectroscopy. Anal Chem 1960, 32:177-181.

Labbe N, Rials TG, Kelley SS, Cheng ZM, Kim JY, Li Y: FT-IR imaging and pyrolysis-molecular beam mass spectrometry: new tools to investigate wood tissues. Wood Sci Tech 2005, 39:61-77.

Nelson ML, O'Connor RT: Relation of certain infrared bands to cellulose crystallinity and crystal lattice type. Part II. A new infrared ratio for estimation of crystallinity in cellulose I and II. J Appl Polymer Sci 1964, 8:1325-1341.

Oh SY, Yoo DI, Shin Y, Seo G: FT-IR analysis of cellulose treated with sodium hydroxide and carbon dioxide. Carbohydr Res 2005, 340:417-428.
Kuo C-H, Lee C-K. Enhancement of enzymatic saccharication of cellulose by cellulose dissolution pretreatments. Carbohydr Polymer 2009, 77:41-46.

Li C, Knierim B, Manisseri C, Arora R, Scheller HV, Auer M, et al. Comparison of dilute acid and ionic liquid pretreatment of switchgrass: biomass recalcitrance, delignification and enzymatic saccharification, Bioresour Technol 2010; 101:4900-6.

Dadi AP, Schall CA, Varanasi S. Mitigation of cellulose recalcitrance to enzymatic hydrolysis by ionic liquid pretreatment. Appl Biochem Biotech 2007; 137-140:407-21.

APPENDIXES

Example calculation taken from data of sawdust treated at 24 hours, 100 ºC (sample 5)

	A	B	C
140	16.987	881	
141	17.038	926	
142	17.088	977	
143	17.139	946	
144	17.19	892	
145	17.24	899	
146	17.291	854	
147	17.341	931	
148	17.392	961	
149	17.443	902	
150	17.493	871	
151	17.544	890	
152	17.594	871	
153	17.645	943	
154	17.696	920	
155	17.746	937	
156	17.797	870	
157	17.848	854	
158	17.898	890	
159	17.949	870	
160	17.999	948	
161	18.05	912	

	A	B	C
239	21.998	1571	
240	22.049	1592	
241	22.099	1524	
242	22.15	1526	
243	22.201	1524	
244	22.251	1501	
245	22.302	1477	
246	22.352	1491	
247	22.403	1505	
248	22.454	1447	
249	22.504	1569	
250	22.555	1516	
251	22.606	1485	
252	22.656	1501	
253	22.707	1394	
254	22.757	1394	
255	22.808	1454	
256	22.859	1317	
257	22.909	1340	
258	22.96	1361	
259	23.01	1330	
260	23.061	1299	

Data of XRD result obtained. The diffraction pattern shows two peaks at 2θ = 15˚and 22˚. The I_{002} represents the peak at 2θ=22˚, while the I_{am} represents the height of the minimum between the 2θ = 15˚and 22˚ which is at 17˚.

$$CI\ (\%) = \frac{I002 - Iam}{I002} \times 100$$

$$CI\ (\%) = \frac{1592 - 977}{1592} \times 100$$

CI (%) = 39.64%

Amorphous (%) = 100 – 39.64

= 60.36%