Development of Nanocrystalline Cellulose (NCC) from

Microcrystalline Cellulose (MCC) via Dissolution using

Ionic Liquid: 1-butyl-3-methylimidazolium hydrogen sulfate (BMIM HSO$_4$)

by

Vignesh Kumar a/l Munusamy

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

_____
(AP Dr. Zakaria bin Man)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

June 2010

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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VIGNESH KUMAR A/L MUNUSAMY

ABSTRACT

Nanocrystalline Cellulose (NCC) was prepared by dissolution of Microcrystalline Cellulose (MCC) using Ionic Liquid: 1-butyl-3-methylimidazolium hydrogen sulfate (BMIM HSO$_4$) at dissolution temperatures of 70 °C, 80 °C, and 90 °C, and dissolution time of 30 minutes and 1 hour respectively. Morphological properties of NCC and MCC were examined using Field Electron Scanning Electron Microscope (FESEM). Chemical characterization of NCC was performed for the analysis of crystallinity (X_c) using X-ray Diffraction (XRD) and to analyze the bonds that are present in NCC and MCC using Fourier Transform Infrared Spectroscopy (FTIR). FTIR was also used to analyze the chemical bonds in unused BMIM HSO$_4$ and regenerated BMIM HSO$_4$. Reduction of MCC particle size by BMIM HSO$_4$ dissolution was clearly observed from FESEM images. The crystallinity of NCC obtained through dissolution of MCC in BMIM HSO$_4$ showed a significant increase due to the degradation of amorphous region in cellulose. Both MCC and NCC have the same chemical bonds. Chemical bonds in regenerated BMIM HSO$_4$ were unchanged, indicating that BMIM HSO$_4$ can be recycled and reused.

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During this research period, I have worked with a great number of people whose contribution in assorted ways to the success of my research and the completion of this report deserves special mention. It is a pleasure to convey my gratitude to them all in my humble acknowledgment.

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I cannot end without thanking my friends and family, on whose constant encouragement and love I have relied throughout my time in completing this research. Their unflinching courage and conviction will always inspire me. It is to them that I dedicate the success of my research.

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ABBREVATIONS AND NOMENCLATURES

Nanocrystalline Cellulose…………………………………... NCC

Microcrystalline Cellulose………………………………….. MCC

1-butyl-3-methylimidazolium hydrogen sulphate…………. BMIM HSO_4

1-butyl-3-methylimidazolium chloride…………………….. BMIM Cl

1-allyl-3-methylimidazolium chloride……………………… AMIM Cl

Field Emission Scanning Electron Microscope…………….. FESEM

X-Ray Diffraction…………………………………………... XRD

Fourier Transform Infrared Spectroscopy…………………. FTIR

CHAPTER1: INTRODUCTION

1.1   BACKGROUND OF PROJECT

Cellulose is the most abundant bio-renewable material on earth. Current cellulose dissolution processes uses acid hydrolysis technique which is cumbersome, expensive, requires the use of hazardous chemicals and creates pollution (Swatloski et al., 2004). Thus, there is a need to use green technology in order to prevent pollution and waste production from harmful chemicals. Such green technology is the usage of ionic liquid in cellulose dissolution. Ionic liquid is thermally stable, non-volatile and less harmful (Swatloski et al., 2004). Ionic liquid can also be regenerated and recycled due to the low or near zero vapor pressure (Gmehling, 2009). Starting material of cellulose used in this project is Microcrystalline Cellulose (MCC). Chloride-containing ionic liquids have constantly been used in MCC dissolution by researchers as it appears to be the most effective solvents by solubilizing cellulose through forming hydrogen bonding from hydroxyl functions of cellulose to the anions of the solvent (Hubbe et al., 2007). However, since only cellulose can be obtained through dissolution of MCC in Chloride containing ionic liquid, this experiment would investigate dissolution of MCC in ionic liquid 1-butyl-3-methylimidazolium hydrogen sulfate (BMIM HSO_4) to obtain nanocrystalline cellulose (NCC). The objective of this experiment is to study the development of NCC using MCC as starting material via dissolution in BMIM HSO_4. The characteristics of the regenerated NCC using ionic liquid are also studied in this experiment. NCC that is generated can be used to make biodegradable polymer or used as biofillers in polymer composites to reduce the use of synthetic polymers which are non-biodegradable. The usage of NCC as fillers is more advantageous as compared to microfillers as it has larger surface area per unit volume and also large aspect ratio. Thus, the reinforcement of polymers with NCC can yield polymer with higher mechanical strength and increase the rate of biodegradation (Hubbe et al., 2007). Therefore,

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this experiment can replace acid hydrolysis and yield NCC that can produce biodegradable polymer composite with high mechanical strength.

1.2 PROBLEM STATEMENT

Problem Statement is divided into two sections: Problem Identification and Significance of the Project. In Problem Identification, the need to substitute plastic polymers with biodegradable polymer is established. Then, on a second level, the disadvantages of the acid hydrolysis which is currently used to produce NCC are explicitly mentioned. In the Significance of Project section, the significance of substituting acid hydrolysis with dissolution using Ionic Liquid is highlighted in terms of four aspects: Economy, Environment, Product and Process.

1.2.1 Problem Identification

Non-biodegradability of plastic polymers

Plastic polymers produced in the market right now are non-biodegradable and causes a serious threat of non-biodegradable waste production. Plastics are durable and degrade very slowly; the molecular bonds that make plastic so durable make it equally resistant to natural processes of degradation (Weisman, 2007). Since the 1950s, one billion tons of plastic has been discarded and may persist for hundreds or even thousands of years (Weisman, 2007). In some cases, burning plastic can release toxic fumes. Burning the plastic polyvinyl chloride (PVC) may create dioxin. Also, the manufacturing of plastics often creates large quantities of chemical pollutants (Weisman, 2007).

Thus, other alternatives of plastic polymers, which include biodegradable polymer with from NCC or biodegradable polymers reinforced

with NCC, are being investigated. NCC can be obtained from cellulose and used in producing polymer materials.

Disadvantages of Acid Hydrolysis

Current methods of obtaining NCC using acid hydrolysis are cumbersome, expensive and require the use of hazardous chemicals at relatively harsh conditions at above 200 °C (Swatloski et al., 2004). Moreover, these processes sometimes cause serious environmental problems because these solvents cannot be recovered and reused (Swatloski et al., 2004). There is a need to use green technology in order to prevent pollution and waste production from these harmful chemicals. Therefore, to make full use of cellulose resources, it is necessary to develop green cellulose extraction methods and suitable cellulose dissolution approaches (Zhu & Wu, 2006). Usage of ionic liquids to substitute traditionally volatile organic solvents can minimize atmospheric solvent loss and flammability hazard through its minuscule vapor pressure as it is composed entirely of ions. Ionic liquid used in cellulose dissolution is also thermally stable, non-volatile and less harmful (Zhu & Wu, 2006).

1.2.2 Significance of Project

This project is significant in terms of four aspects, which are in terms of economy, environment, process and product.

Economical Aspect

This project utilizes microcrystalline cellulose (MCC) and dissolves it to obtain nanocrystalline cellulose (NCC), which can be further used to produce polymer composites. The techniques and development from this project can then be used to dissolve biomass to obtain NCC. Thus, production of these polymer composites can be viewed as an economical source to Malaysia and would create a sustainable industry. Besides that, the usage of

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NCC to produced polymer composites can reduce dependency on plastic based polymers.

Environment Aspect

Environment aspect compares the usage of acid in acid hydrolysis and usage of ionic liquid in dissolution of MCC. Usage of acid in acid hydrolysis posses environmental threat due to discharge of these acidic substance into effluent streams. With increasing governmental regulations in industry, the need to implement 'green' processes in order to prevent pollution and waste production is becoming increasingly important (Anastas & Warner, 1998). Usage of ionic liquid altogether eliminates waste production and pollution problem. Ionic liquid can also be recycled completely, thus also reducing solvent consumption (Zhu & Wu, 2006).

Process Aspect

The third aspect that proves this project to be significant is the process aspect. In this experiment, ionic liquid is used to dissolve MCC to obtain NCC. Current commercial method of dissolving cellulose is using acid hydrolysis. On a large scale application of bio-refinery, prolonged usage of acid may corrode the reactor and other equipments. Thus, in terms of the process, usage of ionic liquid is more beneficial than usage of acid in dissolving cellulose.

Product Aspect

In terms of product, the NCC obtained can be used to develop biodegradable polymer composite. By developing polymers from NCC, or using NCC as fillers in polymer, polymers become more biodegradable and the problem of non-biodegradable plastic polymers can be largely reduced. They can be broken down into CO_2 and water by microorganisms (Weisman, 2007). The usage of NCC can also improve polymer composites in terms of

improved mechanical properties, strength issues and more light weight high performance structure.

Polymer reinforced with NCC is more advantageous as compared to polymer reinforced with cellulose. NCC has larger surface area per unit volume and large aspect ratio. Thus, the reinforcement of polymers with NCC can yield polymer with higher mechanical strength and increase the rate of biodegradation (Hubbe et al., 2007).

1.3 OBJECTIVES OF STUDY

The objectives of this research project are:

i)   To study the dissolution of cellulose from Microcrystalline Cellulose (MCC) to obtain Nanocrystalline Cellulose (NCC) using ionic liquid: 1-butyl-3-methylimidazolium hydrogen sulfate (BMIM HSO_4)

ii)   To investigate the effect of dissolution time and dissolution temperature on size and crystallinity of NCC obtained

iii)   To study and compare the characteristics of NCC obtained with MCC

iv)   To find viable alternative in replacing acid hydrolysis in obtaining NCC from MCC

1.4 SCOPE OF STUDY

First stage of study is dissolution of MCC in BMIM HSO_4 using stirrer heating plate at dissolution temperature of 70 °C, 80 °C, and 90 °C, and at a dissolution time of 30 minutes and 1 hour respectively.

Second stage of the study is to produce NCC from the dissolved MCC solution by addition of water. Then, the solution is ultrasonificated and centrifuged to obtain NCC by removing the BMIM HSO_4 and water from the NCC. Then, the NCC is dried in freeze drier at -40 °C for 2 days.

In the third stage of the study, NCC obtained is examined using Fourier Transform Infrared analysis (FTIR), X-Ray Diffraction (XRD) Analysis and Field Emission Scanning Electron Microscope (FESEM).

1.5 RELEVANCY OF THE PROJECT

The project is relevant to be conducted as it involves further experimentation and research in the area of NCC and biopolymer, which is an integral part of Chemical Engineering.

Careful engineering of the nano-scale components of cellulosic structures has the potential to achieve materials properties and end-uses such as medical applications, bio-nanocomposites, food applications and oil recovery applications. Besides the advantages that can be derived from NCC, this project aims to find a viable alternative of replacing acid hydrolysis in cellulose dissolution by using green solvents, which are ionic liquid. Since many researches nowadays are also focused towards developing greener technologies, this research project is relevant to be conducted.

CHAPTER 2: LITERATURE REVIEW

The literature review is done on cellulose and its structure. Then, information on Nanocrystalline Cellulose (NCC) and its potential applications are also provided. The second part of the literature review focuses on the current technology of producing NCC from cellulose which is acid hydrolysis. Thirdly, this section also provides information on ionic liquid and dissolution of MCC using ionic liquid.

2.1   CELLULOSE

Cellulose is composed of monomers of glucose, a hexose sugar, linked by $\beta(1,4)$-glycosidic bonds. The structure of cellulose is shown in Figure 1 (Williams, 2006).
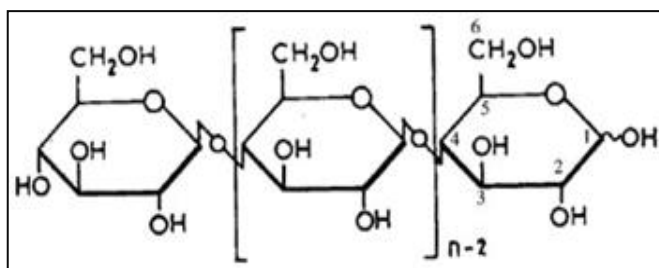
Figure 1: Cellulose structure
Source: Williams (2006)

Each repeating unit of cellulose contains three hydroxyl (-OH) groups. This hydroxyl group and their ability to form hydrogen bonds play a major role in directing the crystal packing and also governing the physical properties of cellulose. In cellulosic plant fiber, cellulose is present in an amorphous state, but also associates to crystalline domains through both inter-molecular and intra-molecular hydrogen bonding (Klemm et al., 2005). The multiple hydroxyl groups on the glucose residues from one chain form hydrogen bonds with oxygen molecules on the same or on a neighbor chain, holding the chains firmly

together side-by-side and forming microfibrils with high tensile strength (Klemm et al., 2005).

Solubility is an important issue especially in the case of cellulose as these tightly packed structures prevent the intrusion of solvents and reagents, thus making celullose a particularly difficult material to transform chemically (Krzan, Kunaver, & Tisler, 2005).

2.2 SOURCE MATERIAL FOR CELLULOSE

In principle, almost any cellulosic material could be considered as a potential source for the isolation of cellulosic structures. The main sources of cellulose are wood, grass, agriculture byproduct materials and cellulose from non-vegetable sources and explained as below:

2.2.1 Wood

Woods are mainly composed of cellulose, lignin and hemicelluloses. Generally, there are 2 types of wood: (1) hard wood and (2) soft wood. The hard woods are composed of closely packed cells with thick walls. While the soft wood composed of larges cells with thin walls (Mishra, 2005). Because of its great abundance, wood has been considered as an attractive starting material for making cellulose.

2.2.2 Grasses

Grasses and straw are another important source of cellulose (Mishra, 2005). The examples of grasses and straw are sabai grass, cereal straw, rice straw, wheat straw and espato grass.

2.2.3 Agricultural Waste

Cellulose is the major component of plant cell wall. Thus, the residual wastes from plants form a huge potential source of cellulose. The crushed stalk of sugar cane, corn cubs, rice halls, grains and seed hulls, and soyabean stems are source of cellulose from agricultural waste (Mishra, 2005). Cotton also has been used as a source material, taking advantage of its relatively low lignin and hemicellulose content, as compared to wood (Hubbe et al., 2007).

2.2.4 Non-Vegetable Sources

Cellulose is also found in animal and mineral kingdom. It occurs in fossil woods, peat, lignite, mineral cellulose (sapperite), and animal cellulose like tunicin (Mishra, 2005).

2.3 MICROCRYSTALLINE CELLULOSE (MCC)

Microcrystalline Cellulose (MCC) is cellulose that is derived from high quality wood pulp. While cellulose is the most abundant organic material, MCC can only be derived from a special grade of alpha cellulose (LeMoigne M.N., 2008).

MCC is comprised of glucose units connected by $\beta(1,4)$ glycosidic bonds. These linear cellulose chains are bundled together as microfibril spiraled together in the walls of plant cell. Each microfibril exhibits a high degree of three-dimensional internal bonding resulting in a crystalline structure that is insoluble in water and resistant to reagents. There are, however, relatively weak segments of the microfibril with weaker internal bonding. These are called amorphous regions. The crystalline region is isolated to produce MCC.

Figure 2 below shows the representation of the microfibril spiraled together in the walls of plant cell.
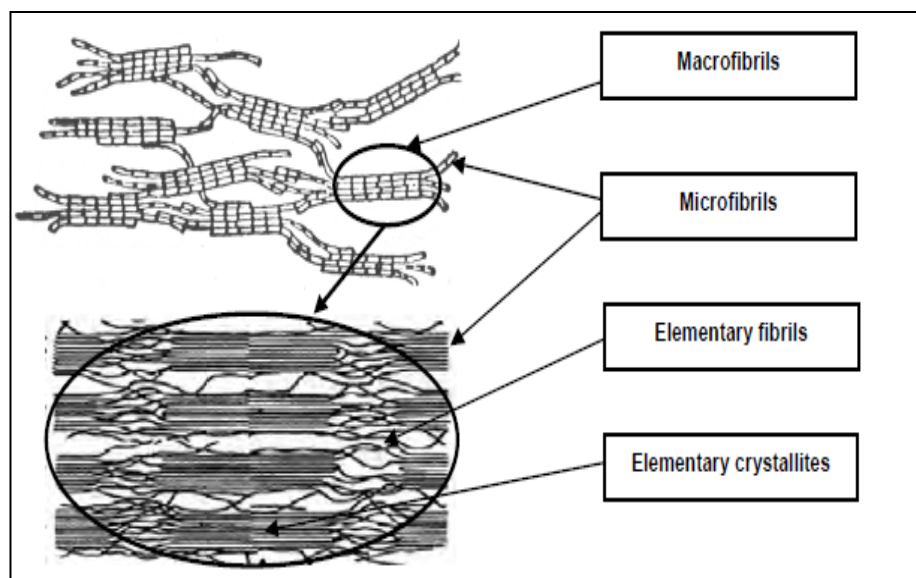
Figure 2: Representation of the microfibril of the fiber structure

Source: LeMoigne M.N. (2008)

Most researchers have used MCC from which most of lignin and substantial amount of hemicelluloses have already been removed (Hubbe et al., 2007).

2.4   NANOCRYSTALLINE CELLULOSE (NCC)

2.4.1   Definition of NCC

The supramolecular structure of NCC includes amorphous and crystalline regions. The crystalline regions are up to 100-200 nm long and below 100 nm wide (Hubbe et al, 2007). Because of their dimensions (high aspect ratio) they can be regarded as nano-whiskers. It is further possible to isolate these NCC in the form of independent particles. The size of the NCC is controlled by the size of the crystalline regions in the cellulose and therefore by the cellulose sources (Hubbe et al, 2007).
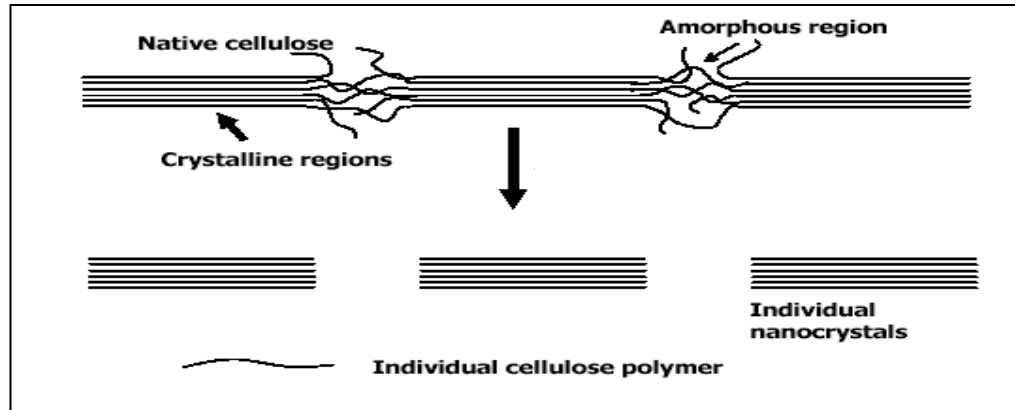
Figure 3: Isolation of NCC from cellulose
Source: *LeMoigne M.N. (2008)*

Nanocrystalline cellulose (NCC) whiskers have been separated from various sources such as wheat straws and tunicin, and have been used as reinforcements in polymer matrices. In order to utilize NCC as a reinforcement, the strong hydrogen bonds between cellulose crystals must be separated and the cellulose crystals must be well dispersed in the polymer matrices (Cyras et al., 2007).

2.4.2 Advantages of NCC

Nanocelluose is expected to show high stiffness since the Young's modulus of the cellulose crystal is as high as 134 GPa. The tensile strength of the NCC crystal structure was assessed to be approximately 0.8 up to 10 GPa (Lee & Mohan et al., 2008). NCC reinforcements in the polymer matrix may provide the value-added materials with superior performance and extensive applications (Lee & Mohan et al., 2008).

Nano cellulose can provide additional property improvement and unique characteristics. As an example, presence of finely fibrillated cellulose is able to prevent the development of micro-cracks in a composite. The other reason is the inherent nature of macroscopic cellulosic fibers (Zavrel et al, 2008). The cellulose in typical wood derived fibers can contain about 25 to 40% of non-

crystalline material. This is the amorphous region of the native cellulose. This material renders the cellulose fibers quite susceptible to dimensional changes when the moisture changes (Zavrel et al, 2008). Even if the continuous phase of a cellulose fiber-filled composite is a hydrophobic plastic material, the cellulosic fibers that are used as reinforcing agents can be expected to allow moisture into the interior of the composite structure, eventually leading to decay and loss of strength. In principle, it is possible to avoid such problems by using only non-porous crystalline cellulosic structures, and these are presently available in the nano-scale, which is nano cellulose (Zavrel et al, 2008).

2.4.3 Application of Cellulosic Nanocomposite

There are many application of cellulosic nanocomposite as below:

Polymer Composites

NCC can be used as a reinforcing filler to prepare composites with solutions of water-soluble polymers, as well as with acrylic and other latex to change the viscocity and to increase the mechanical properties of dry composites. Of great importance has been the addition of nano-cellulose to biodegradable polymers, permitting both the improvement of mechanical properties and acceleration in the rate of biodegradation. Epoxy resins and Polyvinyl Alcohol are some of the common polymers used to prepare polymer composites (Hubbe et al., 2007).

Medical Applications

Pure NCC is harmless and it is biocompatible. Therefore, it can be used for health care applications, such as personal hygiene products, cosmetics, and biomedicine. One of the simplest application of NCC dispersion is its use for stabilization of medical suspensions against phase separation and sedimentation of heavy ingredients. Chemically modified cellulose can be a promising carrier for immobilization of enzymes and other drugs. Due to its nano size, such a carrier-drug complex can penetrate through skin pores and treat skin diseases.

Moreover, it can be used as a gentle, but active peeling agent in cosmetics (Hubbe et al., 2007).

Nanocomposite Manufacture for Optical Effect

Current research formulates strong but transparent composite materials from cellulosic nano-composites. Improvements are obtained in both strength and transparency by isolating nano-fibrillated cellulosic fibers, and taking steps to improve the distribution of the nanofibers in the matrix. An organic display system is also developed from nano-cellulose. This type of product can be expected to bring a transformative change in the different sectors of electronics and telecommunication (Hubbe et al., 2007).

Barrier Films

NCC may have potential use in various kinds of barrier films. Such applications are clearly of interest for paper products and packaging industries. Preparation of edible films can serve as a protective coating of the food itself. Most cellulosic nanomaterials consists of thin fibrils, either alone or attached together in bunches. Thus, the shape is not ideal for inhibiting the passage of gases or moisture through a film. Another research that evaluated MCC-containing poly(lactic acid) composites, there were no significant improvement in resistance to oxygen permeability in comparison to the matrix polymer by itself. Much better oxygen barrier performance could be achieved by incorporating very thin particles such as montmorillonite (bentonite) platelets into the matrix (Hubbe et al., 2007).

Nanocomposites with conductive features

Cellulosic materials are not electrically or thermally conductive. However, some published studies suggest that it may be feasible to prepare cellulosic nanocomposites that have conductive characters. It is possible to assemble alternating layers of oppositely charged polyelectrolyte of cellulosic fibers, thus, increasing the electrical conductivity. Though the cited work was

focused on the use of millimeter-sized fibers for the preparation of paper, it is conceivable that a similar approach could be applied to more finely divided cellulosic elements. A related approach was applied in the case of cellulosic whiskers using used pi-conjugated polymers to achieve conductive cellulosic surfaces. The resulting nanocomposite films had enhanced conductivity, which increased according to the amount of conductive nanofibers that were used (Hubbe et al., 2007).

2.5   CURRENT TECHNOLOGY OF PRODUCING NCC

2.5.1   Mechanism of Acid Hydrolysis to produce NCC

Acid hydrolytic processes are also used to degrade amorphous cellulose in forming cellulose nanofibers. Traditionally, cellulose crystallites from cellulosic materials were prepared using hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) hydrolysis, and cellulose whiskers were also obtained from microfibrils by acid hydrolysis (Lee & Mohan et al., 2008). Acid-catalyzed cellulose hydrolysis is a complex heterogeneous reaction. It involves physical factors as well as the hydrolytic chemical reaction.
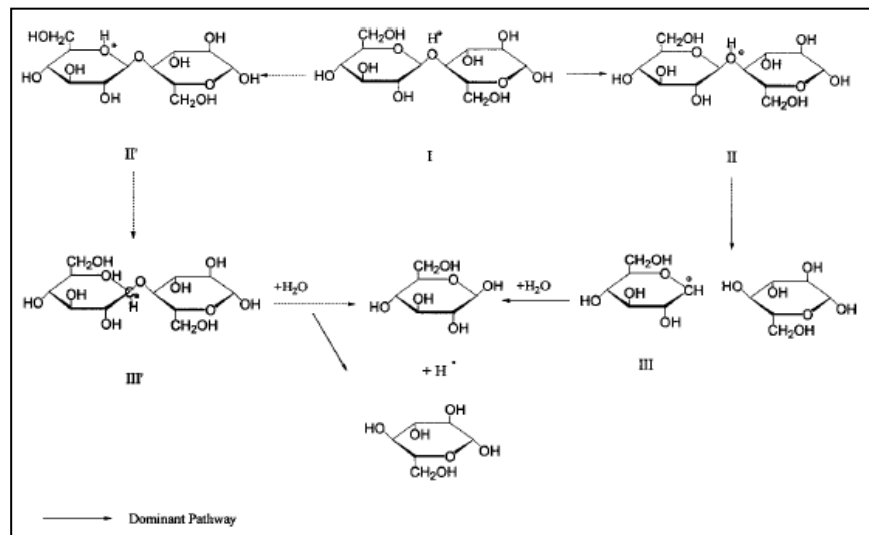
Figure 4: Mechanism of acid catalyzed hydrolysis of cellulose
Source: Fengel et al., (2004)

The molecular mechanism of acid-catalyzed hydrolysis of cellulose (cleavage of β-1-4-glycosidic bond) follows the pattern outlined in Fig.ure 4. Acid hydrolysis proceeds in three steps. The reaction starts with a proton from acid interacting rapidly with the glycosidic oxygen linking two sugar units, forming a conjugate acid (Feng et al., 2004). The cleavage of the C-O bond and breakdown of the conjugate acid to the cyclic carbonium ion then takes place, which adopts a half-chair conformation. After a rapid addition of water, free sugar and a proton are liberated. The formation of the intermediate carbonium ion takes place more rapidly at the end than in the middle of the polysaccharide chain (Feng et al., 2004). In accordance with this, the yield of monosaccharides after partial hydrolysis is higher than that calculated on the basis of a random bond cleavage (Feng et al., 2004).

2.5.2   Process of Acid Hydrolysis to produce NCC

There are several variations of hydrolyzing cellulose using acids to obtain NCC. In general such methods have involved one of the two approaches: dilute acid treatment at high temperatures (> 200 °C) and pressures and concentrated acid pre-treatment (Ong, 2004). Dilute acid processes are conducted at high temperature under pressure (for example, using 1% sulphuric acid at 237 °C). Concentrated acid processing typically starts with an initial acid concentration of 10%, which is raised to 70% through dewatering at 100 °C and ambient pressure (Ong, 2004). Different types of acid such as sulphuric, hydrochloric, hydrofluoric and nitric acids can be used (Ong, 2004).

2.5.3   Disadvantages of Acid Hydrolysis

Chemical and mechanical treatments of the cellulose fibrils used to produce NCC results in chemical and mechanical changes on the NCC fibers and surface, which affects the properties of the fiber nanocomposites (Lee & Mohan et al., 2008). Besides that, usage of acid in acid hydrolysis posses environmental threat due to discharge of these acidic substance into effluent streams. Acid

hydrolysis method creates pollution and waste production, which is not favorable to the environment, what more with the increasing governmental regulations (Anastas & Warner, 1998). Besides that, in terms of the dissolution of cellulose process in a bio-refinery, usage of acid increases the risk of reactor corrosion.

2.6   IONIC LIQUID

2.6.1   Properties of Ionic Liquid

An ionic liquid is a salt in which the ions are poorly coordinated, which results in these solvents being liquid below 100°C, or even at room temperature. Aqueous salts are the example of ionic liquid. At least one ion has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice (Gmehling, 2009). Ionic liquid is electrically conductive and has low vapor pressure.

Due to their unique properties such as chemical and thermal stability, non-flammability, immeasurable low vapor pressure and ease of recycling, ionic liquid seem to be an attractive alternative to conventional volatile organic solvents such as acid in the dissolution of cellulose (Swatloski et al., 2004). Ionic liquid are also called ''green solvents'' because of these properties (Swatloski et al., 2004). The advantages of these properties are discussed as below:

Table 1: Properties of Ionic Liquid and its respective advantages

Properties	Advantages
Low or near zero vapor pressure	Ionic liquid can almost entirely be regenerated and recycled because it is not easily vaporized. Atmospheric solvent loss and thus, flammability hazard is reduced. Solvent consumption is also reduced.
Large liquid range and thermal stability	Ionic liquid would always exist as liquid phase during the dissolution process either at low temperature or high temperature

Possible to design physical and chemical properties	Properties such as melting point, viscosity, density, and hydrophobicity can be varied by simple changes to the structure of the ions (Earlc & Seddon, 2000)
Excellent dissolution characteristics	Able to solubilize cellulose through hydrogen-bonding from hydroxyl functions of cellulose to the solvent

2.6.2 Dissolution of Cellulose in Halide Containing Ionic Liquid

Ionic liquids containing chloride anions have been shown to be strongly hydrogen-bonding. Ionic liquids can be used as nonderivitizing solvents for cellulose (Swatloski et al., 2004). Cellulose can be dissolved in ionic liquids without derivitization in high concentrations, up to 30 wt% is possible although solutions containing 5 wt% cellulose in ionic liquid are more easy to prepare and handle. The greatest solubility was obtained using 1-butyl-3-methylimidazolium chloride (BMIM Cl, molecular formula: $C_8H_{15}ClN_2$) as the solvent (Swatloski et al., 2004).

Dissolution of cellulose in ionic liquid was attributed to their ability to break the extensive network of hydrogen bonds existing in cellulose. In the case of alkylimidazolium chloride; examples include 1-butyl-3-methylimidazolium choride (BMIM Cl) and 1-allyl-3-methylimidazolium chloride (AMIM Cl), the high chloride concentration in the ionic liquid enhances its ability to disrupt hydrogen bonding (Swatloski et al., 2004). The ability of the ionic liquids to dissolve cellulose varies significantly with the size and polarizability of the anion present, and also with the nature of the cation. Chloride-containing ionic liquids appear to be the most effective solvents, presumably solubilizing cellulose through hydrogen-bonding from hydroxyl functions to the anions of the solvent (Swatloski et al., 2004). The molecular structure of BMIM Cl is provided in the following figure:
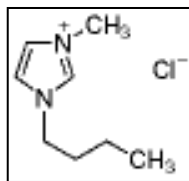
Figure 5: Molecular structure of BMIM Cl
Source: Swatloski et al., (2004)

As an example, a possible mechanism of cellulose dissolution in AmimCl is shown in Figure 6. Above the critical temperature, the ion pairs in AmimCl dissociates to individual Cl− and Amim+ ions. Then free Cl− ions associates with cellulose hydroxyl proton, and free cations complexes with cellulose hydroxyl oxygen, which disrupted hydrogen bonding in cellulose and lead to the dissolution of cellulose (Swatloski et al., 2004).
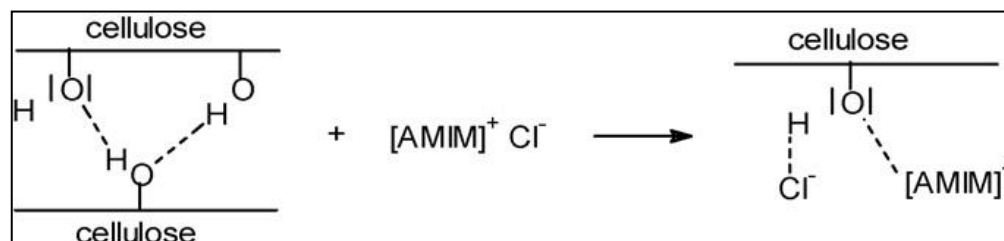
Figure 6: Possible dissolution mechanism of cellulose in AmimCl
Source: Swatloski et al., (2004)

2.6.3   Dissolution of Cellulose in Acidic Ionic Liquid

Previous works on cellulose dissolution using chloride containing ionic liquid such as 1-butyl-3-methylimidazolium Chloride (BMIM Cl) have shown that only cellulose can be regenerated from dissolution of MCC in these ionic liquids. Thus, this experiment aims to investigate the ability of ionic liquid, BMIM HSO$_4$ in producing NCC through dissolution of MCC. Previous works that have been done in dissolution of cellulose in acidic ionic liquid has been reported by Owereh and Amarasekara. In this work, Bronsted acidic ionic liquid of 1-(1-propylsulfonic)-3-methylimidazolium chloride and 1-(1-butylsulfonic)-3-

methylimidazolium chloride has been used for the dissolution and hydrolysis of cellulose (Owereh & Amarasekara, 2009). However, dissolution of cellulose in these ionic liquids yields glucose and total reducing sugar (Owereh & Amarasekara, 2009). In this work, the usage of 1-butyl-3-methylimidazolium hydrogen sulfate, BMIM HSO_4 in dissolving MCC to produce NCC is investigated.

BMIM HSO_4 can behave as the solvent and catalyst as well, additionally, no neutralization and separation of the acidic ionic liquid is required, and there is no waste BMIM HSO_4, as BMIM HSO_4 is the solvent itself (Owereh & Amarasekara, 2009). Furthermore, a higher concentration of $-SO_3H$ active sites in BMIM HSO_4 is expected to accelerate the reaction and lower the operating temperature, thus saving energy (Owereh & Amarasekara, 2009). The following depicts a diagram of BMIM HSO_4:
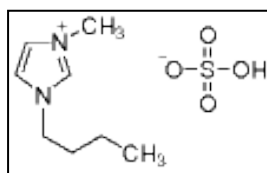
Figure 7: Molecular structure of BMIM HSO_4
Source: Swatloski et al., (2004)

2.6.4   Regeneration of Cellulose from Ionic Liquid

Cellulose in the ionic liquid solution can be easily precipitated by addition of water. As an example, 1-butyl-3-methylimidazolium chloride (BMIM Cl) is completely miscible with water in any ratio, thus the regenerated cellulose materials can be easily obtained by coagulation. The ions of the ionic liquid are extracted into the aqueous phase through hydrogen bonding, dipolar and Coulombic forces (Zavrel et al., 2008). Water molecules form hydrodynamic shells around the ions of the ionic liquid. Therefore, the direct interactions of ionic liquid ions to the cellulose are shielded. Thus, intra- and inter-molecular

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hydrogen bonds are re-built and cellulose precipitates (Zavrel et al., 2008). The regenerated cellulose has almost the same degree of polymerization and polydispersity as the initial one, but its morphology is significantly changed and its microfibrils are fused into a relatively homogeneous macrostructure as in Figure 8 (Zavrel et al., 2008).

To obtain cellulose films, ionic liquid cellulose solution is cast onto a glass plate and then coagulated in water. After removing ionic liquid and water, and drying completely, a transparent cellulose film is obtained. The cellulose fibers regenerated from ionic liquid can be prepared easily by either wet spinning or dry jet-wet spinning process and coagulated with water (Zavrel et al., 2008). Other methods include drying it in the oven.
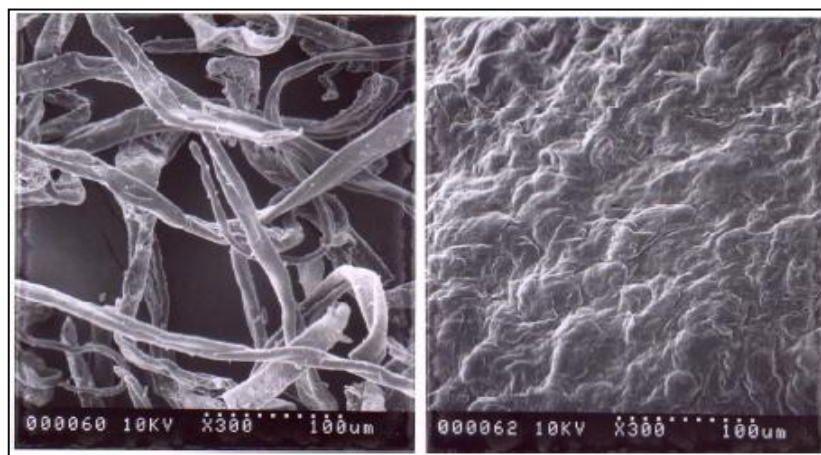
Figure 8: Electron micrograph of fibrous cellulose before (left), and after (right), dissolution and regeneration from the ionic liquid
Source: Zavrel et al., (2008)

2.6.5   Recovery of Ionic Liquid

Recovery and recycling of ionic liquids is normally done after the regeneration of cellulose. The cellulose is filtered out first, and then the residual ionic liquid in the filtrate is recovered by evaporation, giving a clean ionic liquid (Cao & Jin Wu, 2009). Recovery of ionic liquid from mixture of water-ionic

liquid can be done by taking advantage of the difference in boiling point of the two liquids. Boiling point for water is at 100°C while boiling point for ionic liquid is often above 200°C (Appendix A). Water-ionic liquid solution contains large excess of water that is used to precipitate the cellulose after dissolution.

The residual ionic liquid can also be recovered by reducing the pressure and subsequently distilling water away. The purity of recovered ionic liquid should be above 99%, as confirmed by H NMR spectroscopy (Cao & JinWu, 2009). Compared with the fresh ionic liquid, the recycled ionic liquid exhibits the similar dissolving capability for cellulose. However, for the future industrial applications on a large scale, it has been suggested that other methods for removal of water may be more practical. These alternative methods include nanofiltration, reverse osmosis, pervaporation, and salting out of the ionic liquid. Apparently, the advantages of easy recycling of ionic liquid will promote their industrial application in this field (Cao & JinWu, 2009).

CHAPTER 3: METHODOLOGY

3.1   RESEARCH METHODOLOGY

Research methodology taken for research is as below:

```
┌─────────────────────────────────────────────────────┐
│  Defining the problem: Current method of acid        │
│  hydrolysis to dissolve cellulose to produce NCC     │
└─────────────────────────────────────────────────────┘
                         │
                         ▼
┌─────────────────────────────────────────────────────┐
│  Defining the objectives and scope of study:  To     │
│  investigate dissolution of MCC using BMIM HSO4      │
└─────────────────────────────────────────────────────┘
                         │
                         ▼
┌─────────────────────────────────────────────────────┐
│  Conducting literature review on cellulose,          │
│  nanocrystalline cellulose and ionic liquid          │
└─────────────────────────────────────────────────────┘
                         │
                         ▼
┌─────────────────────────────────────────────────────┐
│  Conducting the experiment: Experiment parameters    │
│  of dissolution temperature, T = 70, 80, 90 °C and   │◄───┐
│  dissolution time, t = 30 minutes and 1 hour         │    │
│  with stirring                                       │    │
└─────────────────────────────────────────────────────┘    │
                         │                                  │
                         ▼                                  │
┌─────────────────────────────────────────────────────┐    │
│  Performing characteristics studies on regenerated   │    │
│  NCC                                         ┌──────┐│    │
│  -  Fourier Transform Infrared Analyzer (FTIR)│  NO  ││    │
│  -  Scanning Electron Microscopy (SEM)       └──────┘│    │
│  -  X-Ray Diffraction Analysis (XRD)                 │    │
└─────────────────────────────────────────────────────┘    │
                         │                                  │
                         ▼                                  │
              ◇ Is NCC Obtained? ◇────────────────────────────┘
                         │
                    ┌────────┐
                    │  YES   │
                    └────────┘
                         │
                         ▼
┌─────────────────────────────────────────────────────┐
│  Performing Results and Discussion and drawing        │
│  Conclusion                                           │
└─────────────────────────────────────────────────────┘
```

3.2   RAW MATERIALS AND EQUIPMENTS USED

The raw materials used in this experiment are:

- Microcrystalline Cellulose
- 1-butyl-3-methylimidazolium hydrogen sulphate
- Deionized water

The equipments, analyzers, and tools used in this experiment are:

Equipments: 1) Ultrasonic Bath (Transsonic Digital, Elma)

2) Centrifuge (Medium Speed Centrifuge, Sigma)

3) Stirrer Heater

4) Freeze Drier

Apparatus: 1) 30 ml glass vial, 2) magnetic stirrer

Analyzers: 1) Field Emission Scanning Electron Microscope (Carl Zeiss)

2) X-Ray Diffractometer (Bruker AXS)

3) Fourier Transform Infrared Analyzer (Shimadzu FTIR)

3.3   DISSOLUTION OF MICROCRYSTALLINE CELLULOSE (MCC) IN BMIM HSO$_4$

MCC (0.3 gm, 1.85 mmol) is mixed into 3 g of BMIM HSO$_4$ in a 30 ml container. Container is immersed in silicon oil bath at a temperature of 70 °C. Magnetic stirrer is put in the container to provide stirring effects to the solution and sample are left in the oil bath for 30 minutes. The heater is put to off and let to cool.   Procedure is repeated for manipulated variables of dissolution temperature of 80 °C and 90 °C and dissolution time of 1 hour.
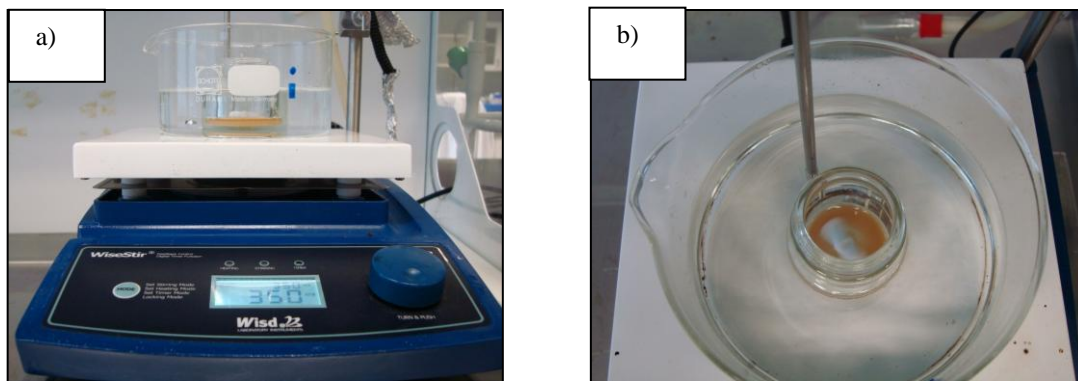
Figure 9: a) Frontal view and b) Top view of equipment setup for dissolution of MCC in BMIM HSO$_4$

3.4   REGENERATION OF NCC

NCC can be precipitated from ionic BMIM HSO$_4$ by admixing the MCC containing BMIM HSO$_4$ with water. 20 mL deionized water is filled into the glass vial containing MCC dissolved in BMIM HSO$_4$. Solution is then left to stir for 30 minutes. Formation of powdery flock can be observed in this stage.

3.5   ULTRASONIFICATION OF NCC

Ultrasonification bath is prepared at a temperature of 35° C. Polystyrene sheet is used to float the glass vial containing the regenerated NCC in the ultrasonification bath.   The container is left in the ultrasonification bath for 1 hour with intensity of 120 %.

3.6   CENTRIFUGATION OF NCC

The content of 30 mL glass vial containing NCC, water and BMIM HSO$_4$ is transferred into 50 mL centrifugation tube. Deionized water is added until the 50 mL mark and is well mixed by shaking the centrifugation tube using hands. Initial pH reading is taken using pH meter. Centrifugation is done using 7500 rpm for 30 minutes interval. Centrifugation is until a pH of 7 is obtained, usually requiring 6 washing. The solution that is removed from the first two washing

contains mostly BMIM HSO$_4$ is kept separately and would be used to regenerate BMIM HSO$_4$.
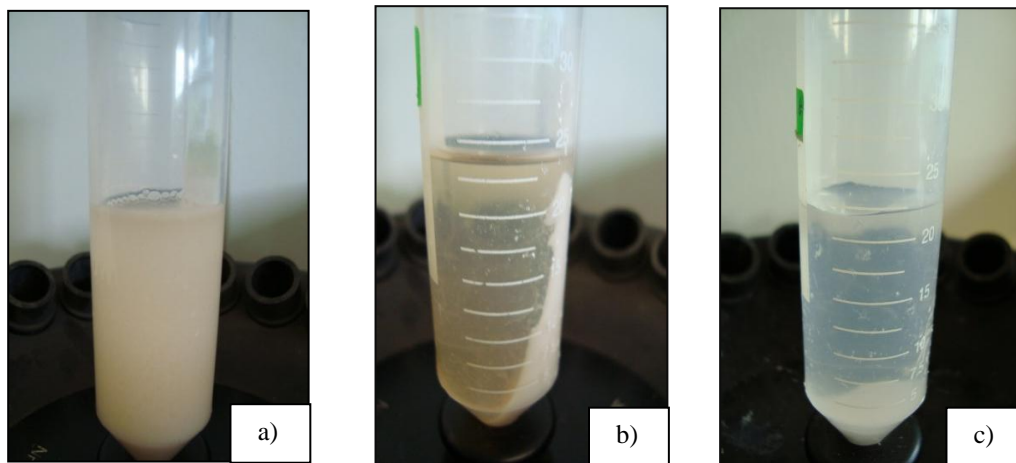
Figure 10: Centrifugation of MCC dissolved in BMIM HSO$_4$ for T = 90 °C and t = 1 hour treatment a) before 1st washing, b) after 1st washing, c) after 6th washing

3.7 CHARACTERISTICS STUDIES ON EXTRACTED CELLULOSE

Regenerated NCC is characterized by using Field Emission Scanning Electron Microscopy (FESEM), X-Ray Diffraction (XRD), Fourier Transform Infrared Analyzer (FTIR).

3.7.1 Sample preparation

For FESEM, droplet suspension of NCC supernatant is diluted to 0.01 vol % and placed on FESEM pellets and allowed to dry at 40 °C overnight. For XRD and FTIR, the NCC supernatant is left to dry in the freeze drier at -40 °C for 2 days.

3.7.2 Field Electron Scanning Electron Microscope (FESEM) Observation

Equipments needed: 1) Field Electron Scanning Electron Microscope Carl Zeiss

FESEM is used to observe the bulk structure and average particle size of MCC and NCC. MCC is observed under SEM at magnification of 500 X. Regenerated NCC is observed under SEM at magnification of 500 X. Differences in micrographies of MCC and NCC are observed.

3.7.3 X-Ray Diffraction Analysis

Equipments and materials needed: 1) Bruker AXS XRD

XRD is used to determine the increase in degree of crystallinity (X_c) of the regenerated NCC as compared to MCC. MCC and regenerated NCC are analyzed at angle 2θ between $2°$ and $80°$. Difference in peak between MCC and NCC is analyzed. Crystallinity Index, CrI is calculated as Eqn (1) below (Lee et al., 2008)

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \tag{1}$$

where: I_{002} is the overall intensity of the peak at 2θ

I_{am} is the intensity of the baseline at 2θ

3.7.4 Fourier Transform Infrared (FTIR) Analysis

Equipment needed: 1) Shimadzu FTIR Analyzer

FTIR spectroscopy can be used to examine any changes in the functional group of MCC after the chemical treatment using BMIM HSO_4. MCC is grinded and mixed with Kalium Bromite, KBr. Mixtures are pressed into transparent thin pellets. Spectral Output is obtained in the range of 4000-600 cm^{-1} and recorded

in transmittance mode as a function of wave number. Procedure is repeated for all the regenerated NCC samples.

3.8 REGENERATION OF BMIM HSO$_4$

BMIM HSO$_4$ is regenerated by removing water from the solution obtained from the first two washing during centrifugation of NCC using vacuum evaporation at 55 °C. Vacuum evaporation removes water and leaves only BMIM HSO$_4$ in the solution because BMIM HSO$_4$ does not evaporate.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 EFFECTS OF BMIM HSO$_4$ DISSOLUTION ON STRUCTURE OF MCC

To date, no models have been proposed for dissolution of MCC in BMIM HSO$_4$ as BMIM HSO$_4$'s dissolution capability is not widely investigated (Swatloski et al., 2004). However, since BMIM HSO$_4$ is able to dissolve MCC and yield NCC, it is expected that BMIM HSO$_4$ diffuses preferentially into the amorphous region of the cellulose and dissolves the accessible C-O-C bonds in the amorphous region. Then, more easily accessible C-O-C bonds in the cellulose chain are broken, leaving only shorter crystalline region in nano size range. The proposed model for cleavage of the C-O-C bond through BMIM HSO$_4$ dissolution is shown as below:
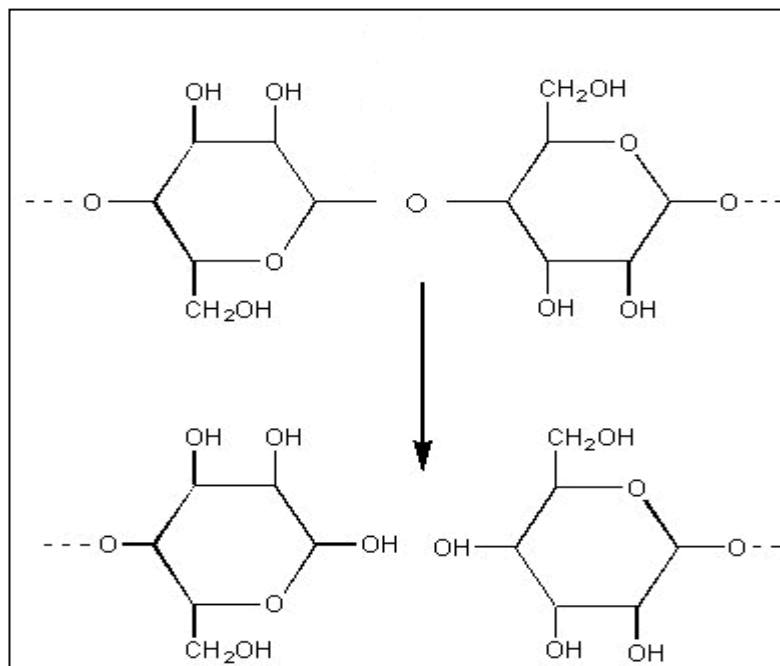

Figure 11: Cleavage of C-O-C bond in MCC

4.2 RESULTS FOR MCC AND REGENERATED NCC

The MCC and regenerated NCC are characterized by using: Field Emission Scanning Electron Microscope (FESEM), X-Ray Diffraction (XRD), and Fourier Transform Infrared Analyzer (FTIR). The analysis of the results obtained and concept of BMIM HSO_4 dissolution is explained as following:

4.2.1 Digital Microscopic Image of MCC Dissolution in BMIM HSO_4

The digital microscopic image of MCC dissolved in BMIM HSO_4 as dissolution time progresses is presented as an example in Figure 12 for dissolution at 90 °C for 1 hour. The images were captured using DinoLite Digital Microscope at a magnification of 20 X.

At time t= 0, the MCC is put into a glass vial containing 3 gm BMIM HSO_4 in a 30 mL glass vial. Then, the solution is heated and stirred for 60 minutes. At 10 minutes, some of the particles have already been dissolved. Coarse particles are still present, indicating dissolution is incomplete. At 20 minutes, presence of coarse particles can still be detected, however the size of un-dissolved particles were relatively smaller than at t= 10 minutes. The amount of MCC particles which are not dissolved yet is significantly reduced at 30 minutes.

At 40 minutes, the microscopic image shows that all the MCC has already been dissolved. The solution became clearer as time increases from 40 minutes to 50 minutes and 60 minutes respectively. The microscopic image of MCC dissolved at t= 60 minutes shows a completely dissolved MCC in BMIM HSO_4 without any presence of MCC particles.

t= 0 min   t = 10 min   t = 20 min

t = 30 min   t = 40 min   t = 50 min
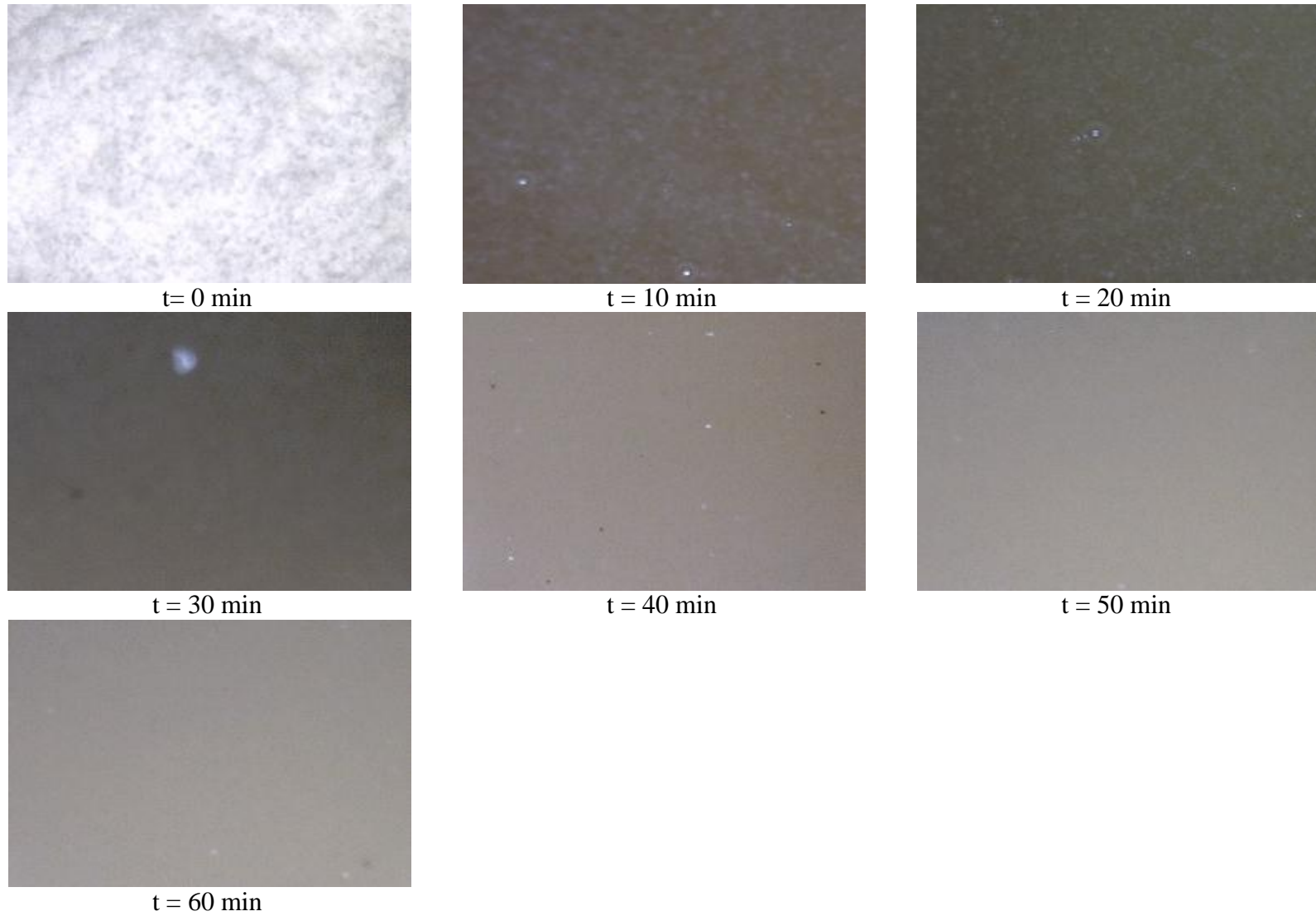
t = 60 min

Figure 12: Optical Microscope Image of MCC dissolution at 90 °C for at time, t= 0, 10, 20, 30, 40, 50 and 60 minutes

4.2.2 Morphological Properties - Field Emission Scanning Electron Microscope (FESEM) Image

FESEM can be used to obtain micrographies of the original MCC and the micrographies of the regenerated NCC obtained through BMIM HSO_4 dissolution. Figure below shows FESEM images of untreated MCC before dissolution.
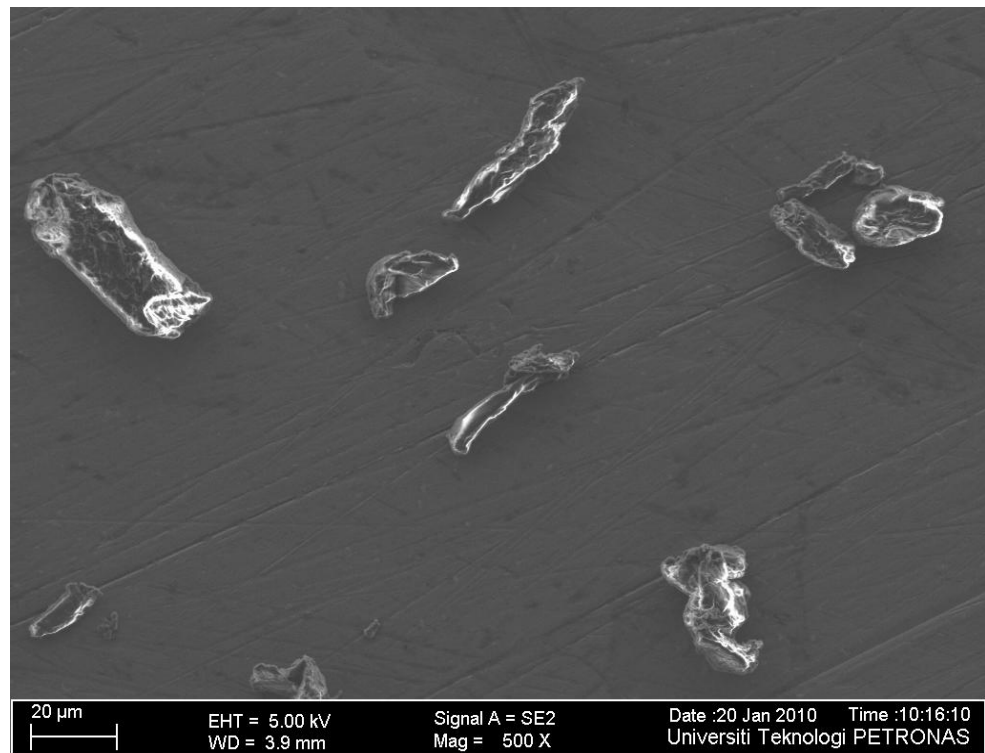
Figure 13: FESEM Image of MCC before dissolution in BMIM HSO_4

Figure 13 clearly shows the shape and size distribution of the micron size celluloses in MCC. These well separated microfibrils have diameters ranging from 5-40 μm. MCC fibers does not have uniform size, diameter and length.

Figures 14, 15 and 16 show the FESEM images of NCC obtained through MCC's dissolution in BMIM HSO_4.
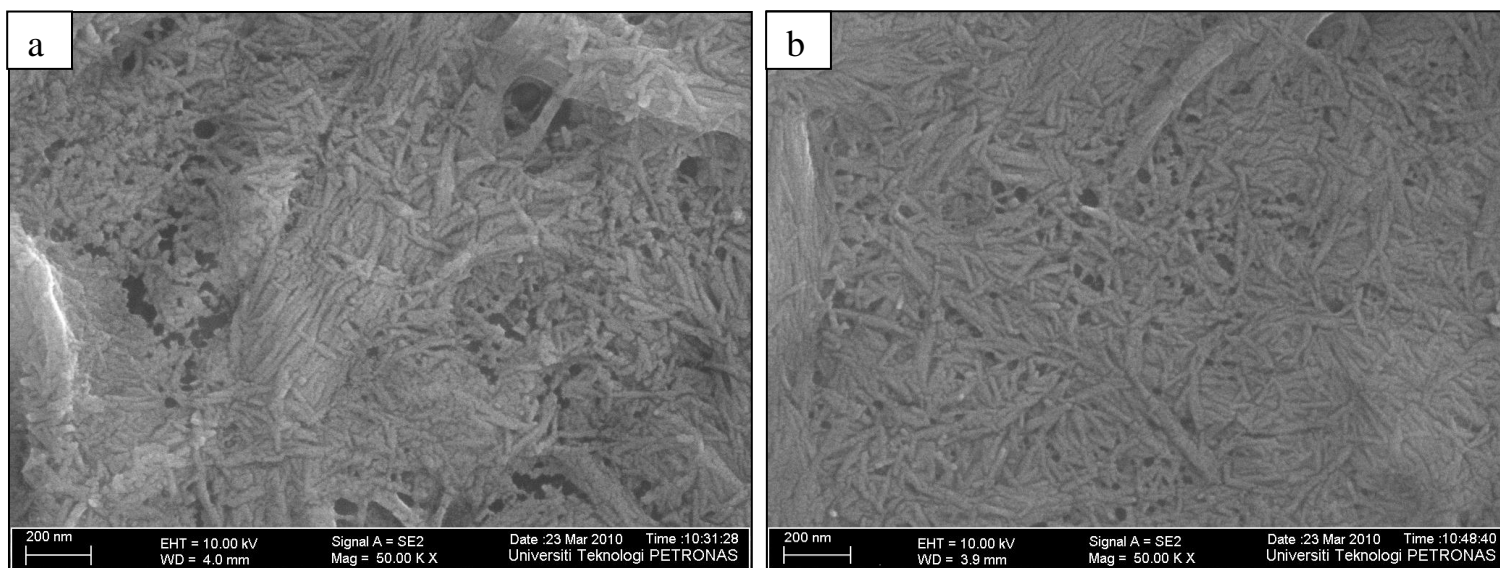
Figure 14: FESEM Image for Dissoluton Conditions of a) T = 70 °C, t = 30 minutes, b) T = 70 °C, t = 1 hour
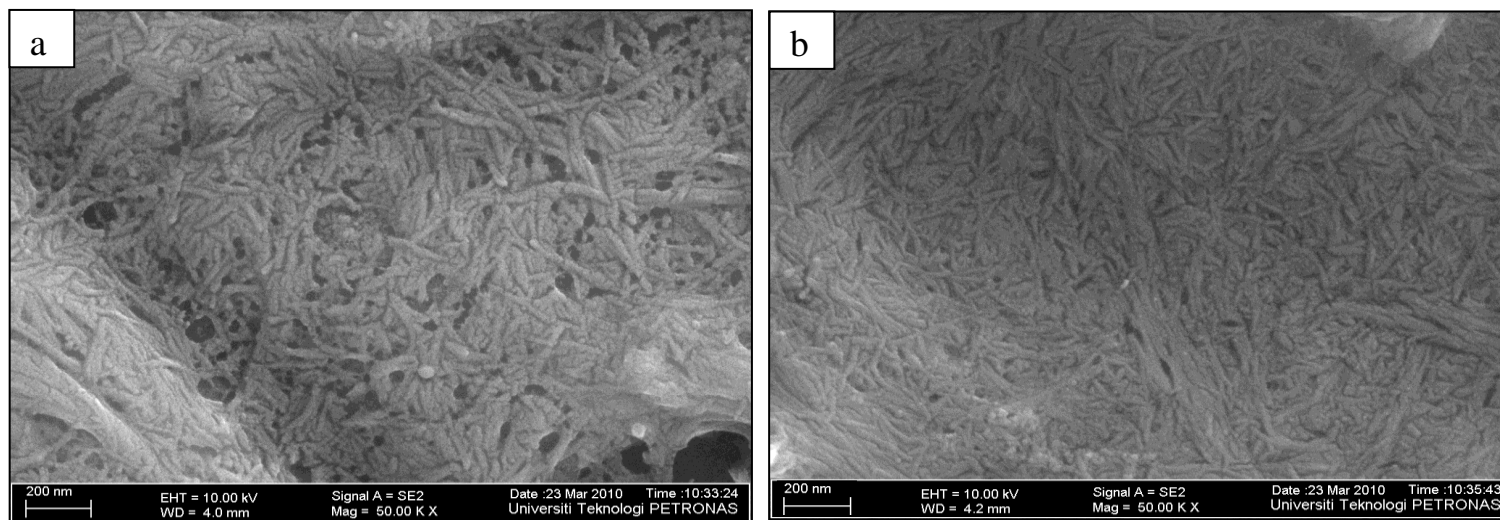
Figure 15: FESEM Image for Dissoluton Conditions of a) T = 80 °C, t = 30 minutes, b) T = 80 °C, t = 1 hour
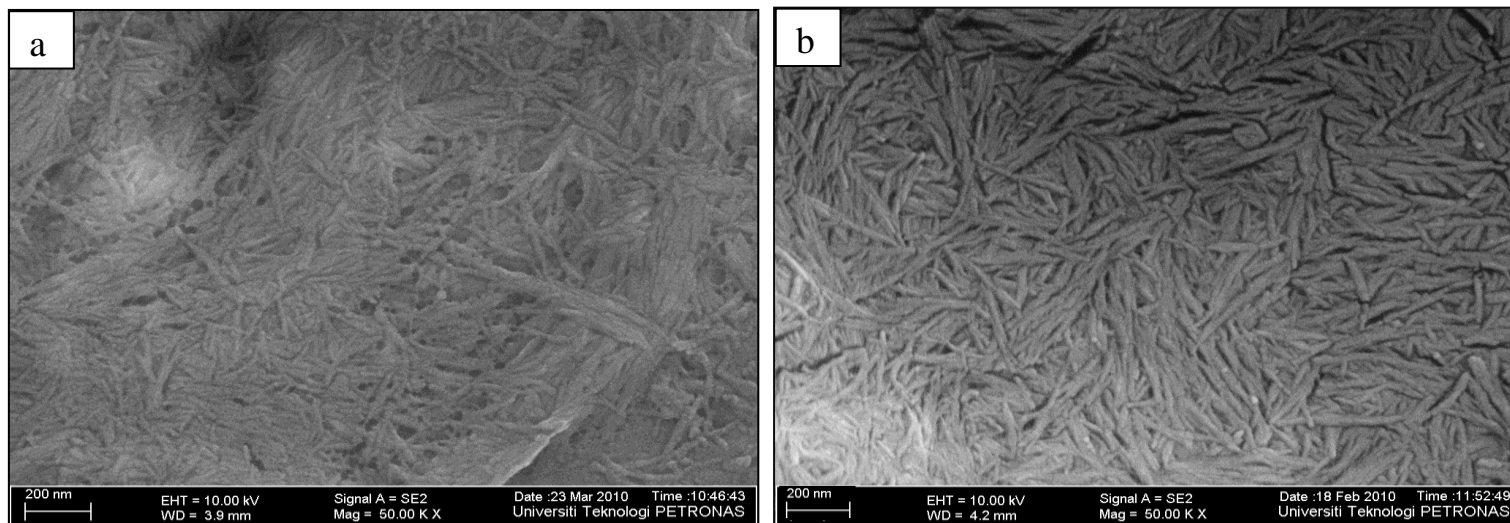
Figure 16: FESEM Image for Dissoluton Conditions of a) T = 90 °C, t = 30 minutes, b) T = 90 °C, t = 1 hour

As shown in Figure 14, 15 and 16, regenerated NCC are isolated into individual crystallites and dispersed showing a needle shaped structure. Reduction of length and diameters of MCC after dissolution using BMIM HSO_4 is clearly detected. The average range of particle diameter is 5-45 nm for all NCC samples obtained.

However, although the NCC has smaller diameter and are dispersed into individual crystallites, it is not dispersed uniformly as agglomeration of NCC is still present. This problem can be traced to sample preparation, where the NCC sample prepared is not dilute enough. Dilution of NCC sample with more water is important as the presence of water molecules suspends the NCC in suspension form and hinders the NCC from agglomerating together (Cao et al., 2008).

As a comparison of particle size, the following figure shows diameter distribution of MCC before dissolution in BMIM HSO$_4$ and for NCC obtained through dissolution of MCC in BMIM HSO$_4$ at a temperature of 90 °C for 1 hour. The diameters of the particles are measured from FESEM images. The range of diameter distribution for MCC is from 5-40 μm and the range of diameter of NCC that is obtained has been reduced to 5-45 nm, which is within nano-particle size (Hubbe et al, 2007).
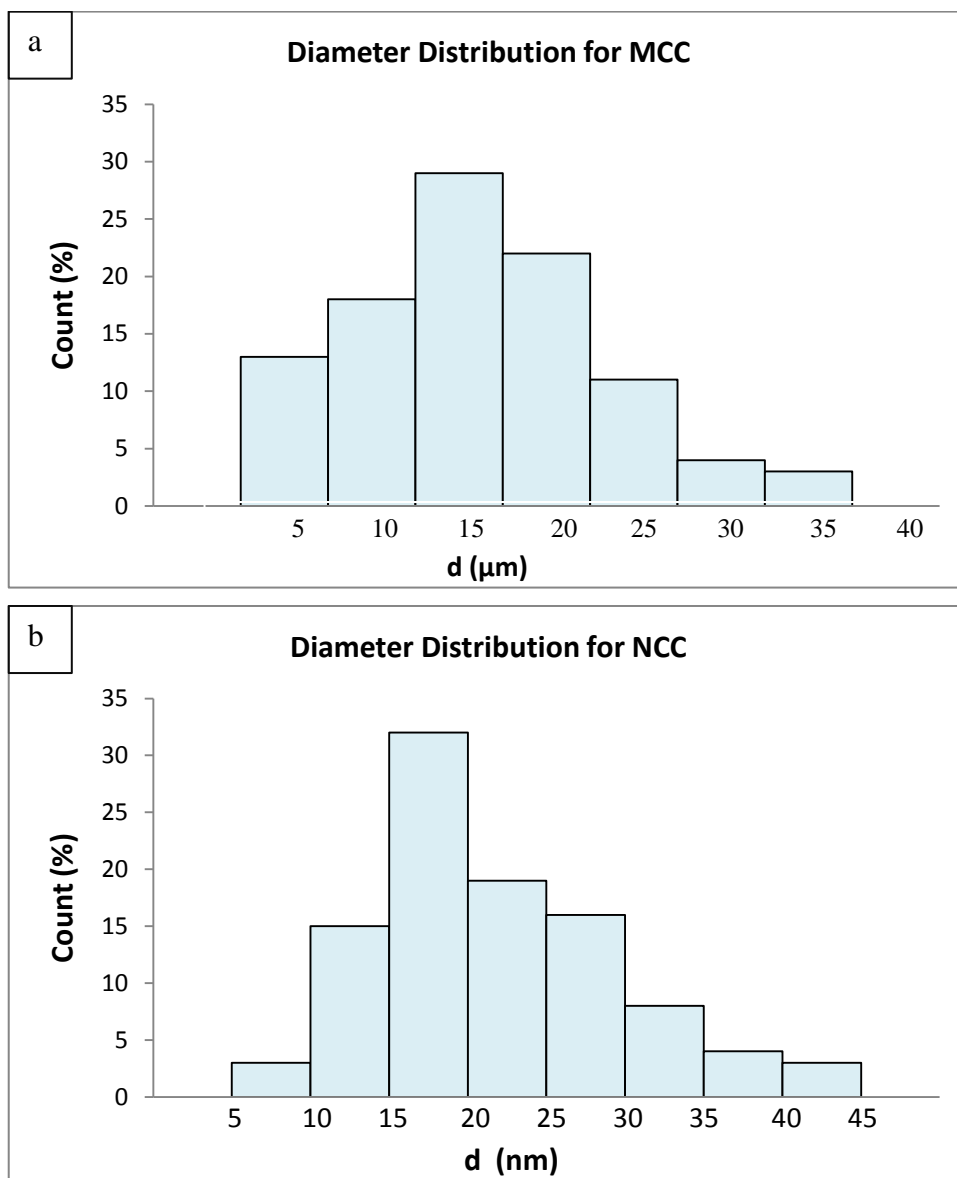
Figure 17: Diameter distribution for a) MCC and b) NCC sample for dissolution condition T= 90 °C, t = 1 hr

4.2.3 X-Ray Diffraction Analysis (XRD)

The structure and crystallinity, (X_c) of NCC obtained through this experiment was studied using XRD. Microcrystalline cellulose (MCC) is also subjected to XRD analysis to obtain qualitative comparison of the increase in crystallinity when MCC is subjected to dissolution using BMIM HSO_4. The XRD patterns for MCC and NCC obtained through BMIM HSO_4 are shown as below:

Analysis for Effect of Dissolution Time
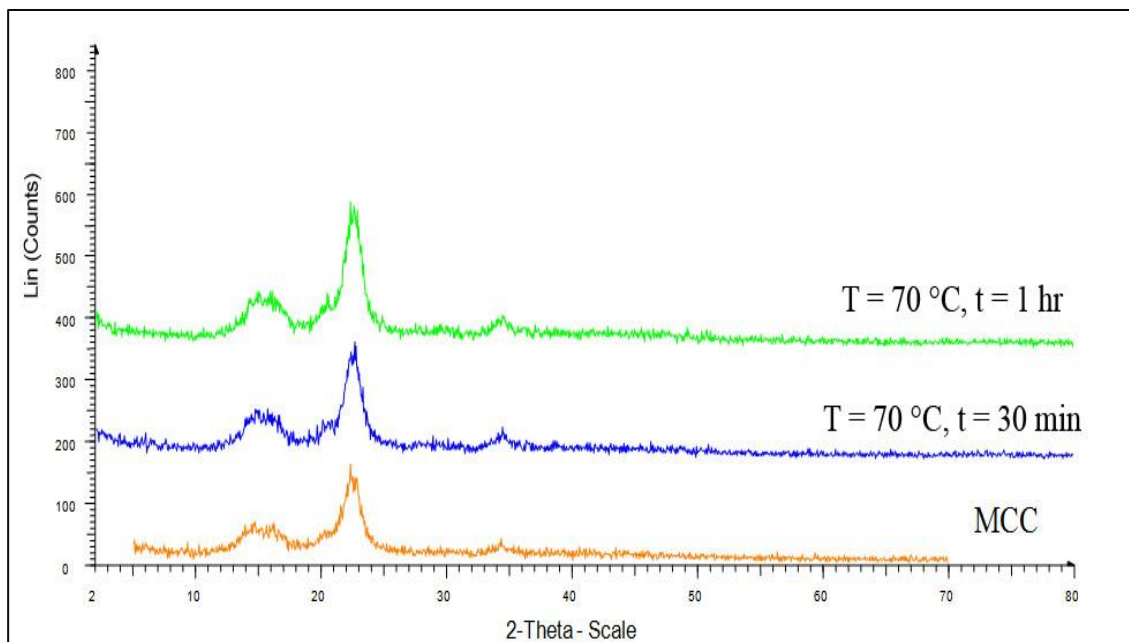
a) Temperature = 70 °C
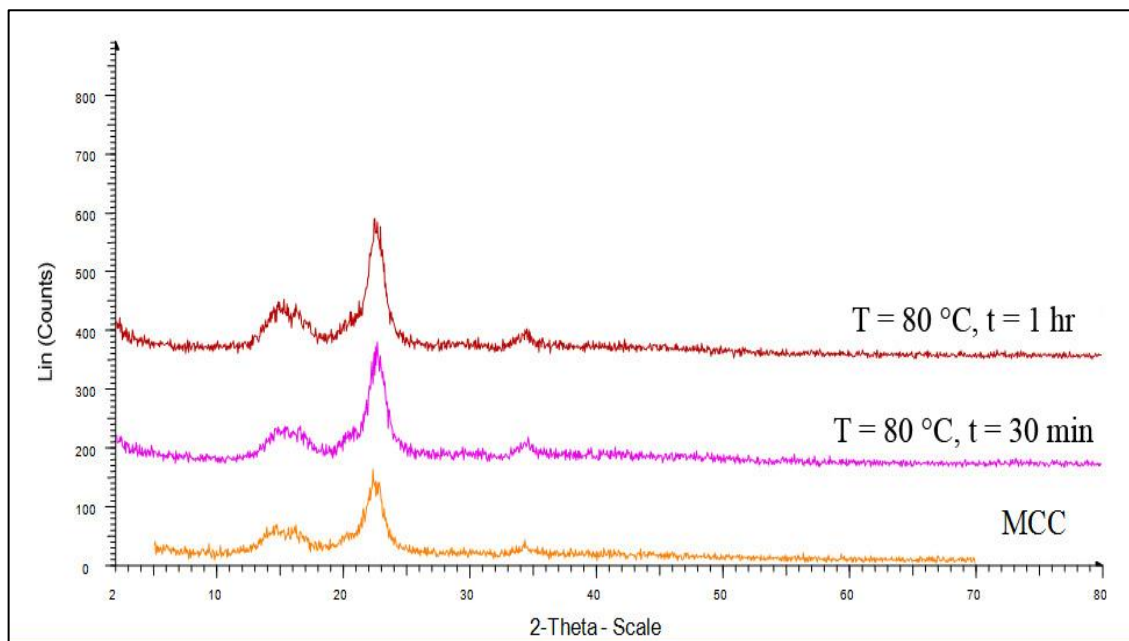
b) Temperature = 80 °C
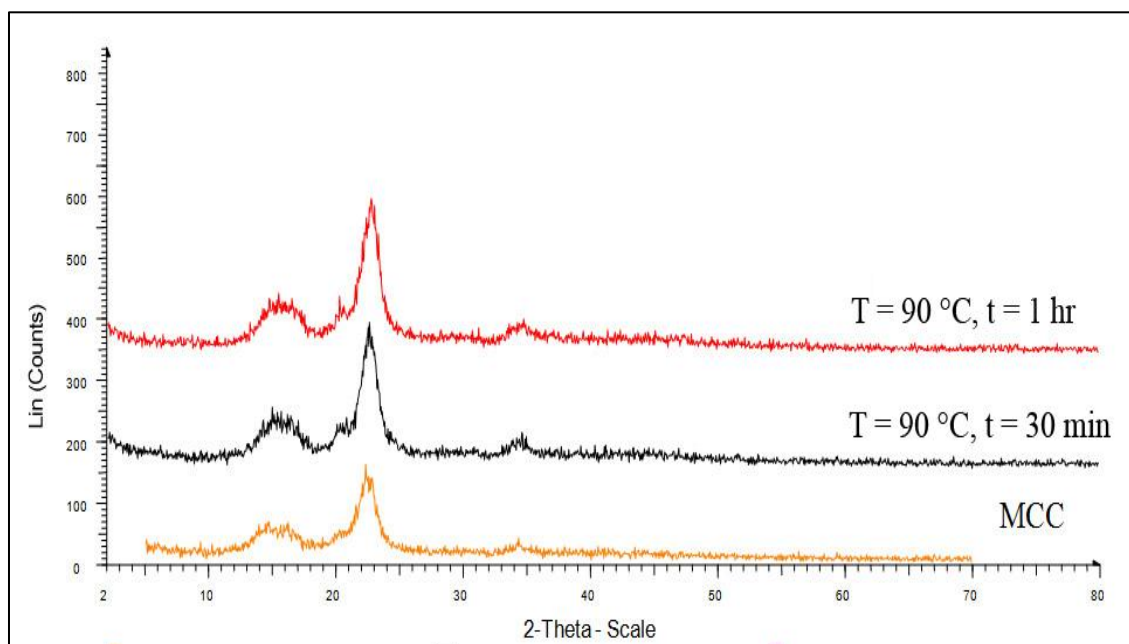
c) Temperature = 90 °C

Figure 18: XRD Data for Effect of Dissolution Time (30 minutes, 1 hour) for MCC dissolved in BMIM HSO$_4$ at Dissolution Temperature a) 70 °C, b) 80 °C, c) 90 °C

Table 2: Crystallinity Index (X_c) of MCC before and after dissolution (Effect of Dissolution Time of 30 minutes and 1 hour at constant Dissolution Temperature of 70 °C, 80 °C, and 90 °C)

Systems	X_c (%)
MCC	75.02
Dissolution Temperature = 70 °C	
Dissolution Time t= 30 minutes	82.29
Dissolution Time t= 1 hour	89.08
Dissolution Temperature = 80 °C	
Dissolution Time t= 30 minutes	84.05
Dissolution Time t= 1 hour	90.02
Dissolution Temperature = 90 °C	
Dissolution Time t= 30 minutes	87.23
Dissolution Time t= 1 hour	91.21
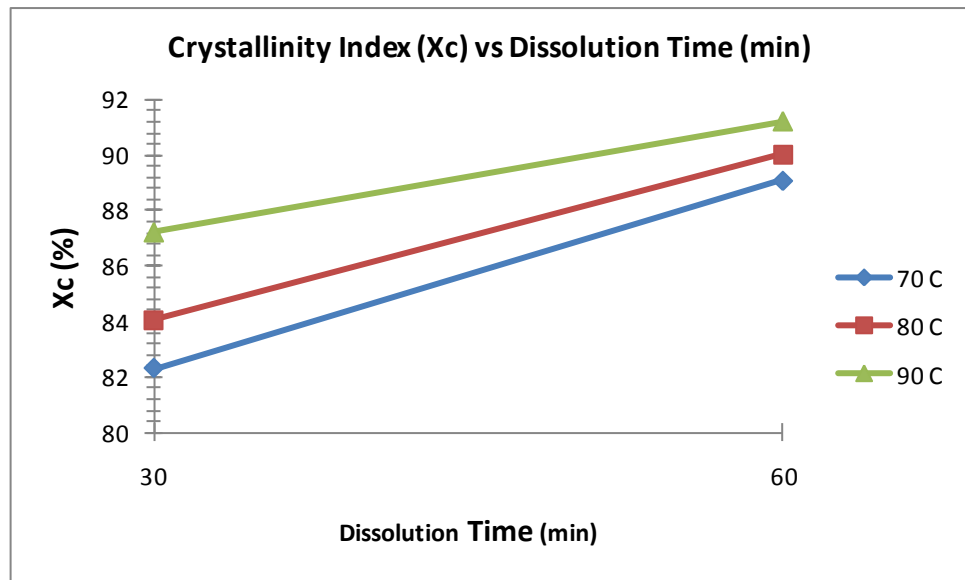
Figure 19: Cyrstallinity Index vs Dissolution Time for Dissolution Temperature of 70 °C, 80 °C, and 90 °C

As can be seen from Figure 18, the intensity of the peaks is higher for NCC as compared to MCC, showing that NCC is more crystalline than MCC. After the dissolution using BMIM HSO_4, the X_c of MCC showed a significant increase. This result indicates that when MCC is subjected to BMIM HSO_4 dissolution, accessible amorphous region is dissolved, and the crystalline region remains (Lee & Mohan et al., 2008).

Table 2 shows the crystallinity index (X_c) of MCC before and after dissolution in studying the effect of dissolution time. The crystallinity index is calculated as per Equation (1) in Section 3.7.3. Figure 19 shows the increase in crystallinity index (X_c) as dissolution time increases from 30 minutes to 1 hour (60 minutes). NCC produced from dissolution of MCC in BMIM HSO_4 for 1 hour is more crystalline than NCC sample prepared by dissolution for 30 minutes for all temperatures of 70 °C, 80 °C and 90 °C.

Dissolution time of nearly 1 hour is needed to effectively dissolve the MCC, which is also evident from the microscope image of MCC dissolution in BMIM HSO_4 as per section 4.2.1. The crystallinity index (X_c) is lesser for NCC obtained through dissolution for 30 minutes because of incomplete dissolution due to short dissolution time. Thus, only when MCC is subjected to adequate dissolution time, more accessible amorphous region of cellulose can be dissolved to yield more crystalline NCC. Therefore, the crystallinity index is higher for NCC obtained through dissolution at 1 hour as compared to 30 minutes.

Analysis for Effect of Dissolution Temperature
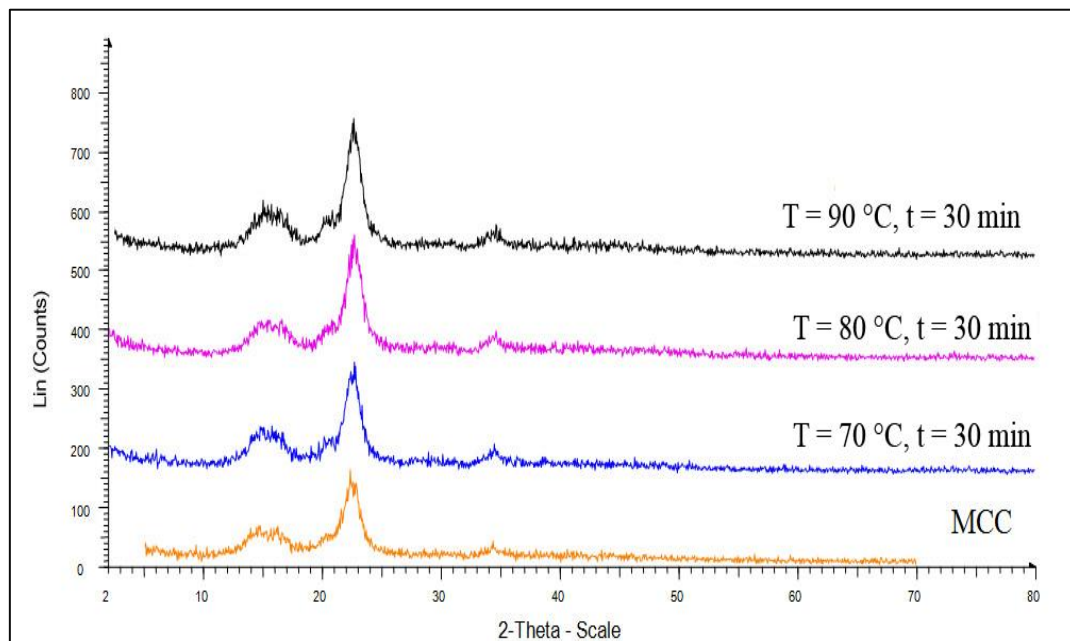
a) Time = 30 minutes

b) Time = 1 hour
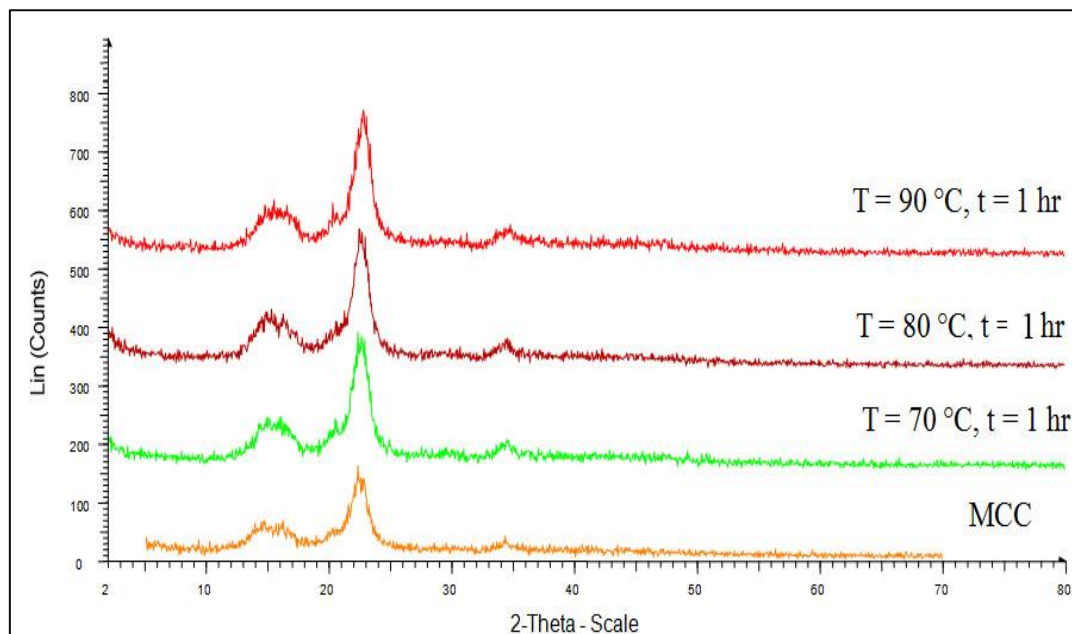
Figure 20: XRD Data for Effect of Dissolution Temperature (70 °C, 80 °C, 90 °C,) for MCC dissolved in BMIM HSO_4 at Dissolution Time a) 30 minutes, b) 1 hour

Table 3: Crystallinity Index (X_c) of MCC before and after dissolution (Effect of Dissolution Temperature of 70°C, 80 °C, and 90 °C at constant Dissolution Time of 30 minutes, and 1 hour)

Systems	X_c (%)
MCC	75.02
Dissolution Time t= 30 minutes	
Dissolution Temperature = 70 °C	82.29
Dissolution Temperature = 80 °C	84.05
Dissolution Temperature = 90 °C	87.23
Dissolution Time t= 1 hour	
Dissolution Temperature = 70 °C	89.08
Dissolution Temperature = 80 °C	90.02
Dissolution Temperature = 90 °C	91.21
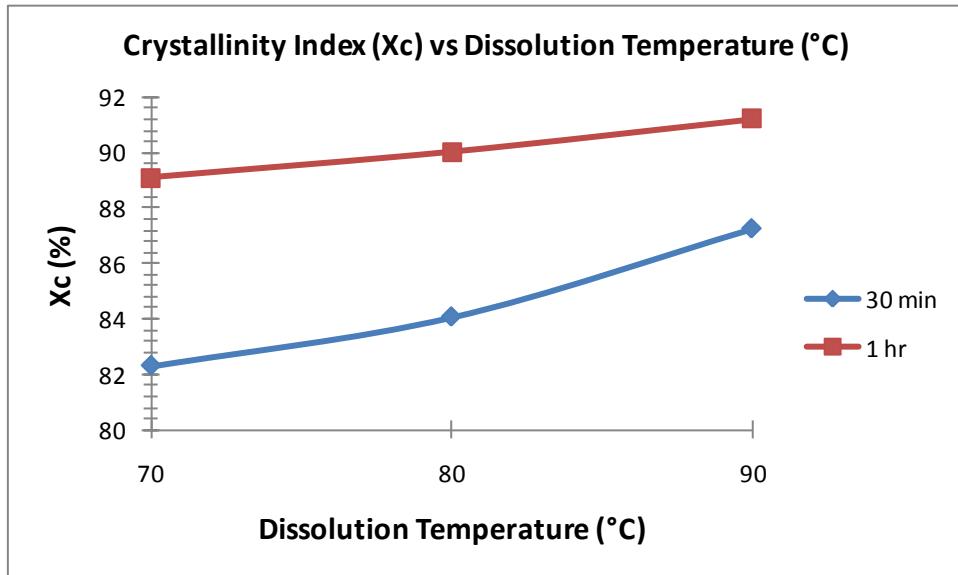
Figure 21: Crystallinity Index vs Dissolution Temperature for Dissolution Time of 30 minutes, and 1 hour

As can be seen from Figure 20, the intensity of the peaks is higher for regenerated NCC than MCC, showing that NCC is more crystalline than MCC. After the dissolution using BMIM HSO_4, the X_c of MCC showed a significant increase. This result indicates that when MCC is subjected to BMIM HSO_4 dissolution, accessible amorphous region is dissolved, and the crystalline region remains (Lee & Mohan et al., 2008).

Table 3 shows the crystallinity index (X_c) of MCC before and after dissolution in studying the effect of dissolution temperature. Figure 21 shows the increase in crystallinity as dissolution temperature increases from 70 °C, to 80 °C and 90 °C. NCC produced from dissolution of MCC in BMIM HSO_4 at 90 °C is more crystalline than the NCC sample prepared by dissolution for 80 °C and 70 °C respectively for dissolution at both 30 minutes and 1 hour. Thus, it can be concluded that the higher the dissolution temperature of MCC in BMIM HSO_4, the more crystalline the NCC produced.

This is due to the increase in dissolution rate as the dissolution temperature increases. As the dissolution rate increases at higher temperatures, more accessible amorphous region of cellulose is dissolved to yield more crystalline NCC. Therefore, the crystallinity index (X_c) is higher for NCC obtained through dissolution at higher temperature. However, care should be maintained in order not to exceed the dissolution temperature at which NCC samples degrade.

4.2.4 Fourier Transform Infrared Analyzer (FTIR)

Samples analyzed are MCC and regenerated NCC obtained in this experiment. The FTIR helps characterize the chemical structure by identifying the functional groups present in each sample.

The samples are expected to produce absorbance region. The infrared spectra for cellulose are studied from literature (Cyras et al., 2007). The typical functional groups and the corresponding wave number for cellulose are shown in Table 4 below:

Table 4: Absorption bands for functional groups of cellulose (Cyras et al., 2007)

Fiber Component	Wave Number (cm$^-$1)	Functional groups	Compounds
Cellulose	4000-2995	OH	Acid, methanol
	2890	H–C–H	Alkyl, aliphatic
	1640	Fiber-OH	Adsorbed water
	1270-1232	C–O–C	Aryl-alkyl ether

The results of FTIR conducted for all the regenerated NCC sample and MCC are as in the following page, where wavelength corresponding each functional group has been labelled.

Separate graphs has been used to compare the effect of dissolution time on functional group present and the effect of dissolution temperature on the functional group present, as presented in Figure 22 and Figure 23 respectively.

Analysis for Effect of Dissolution Time
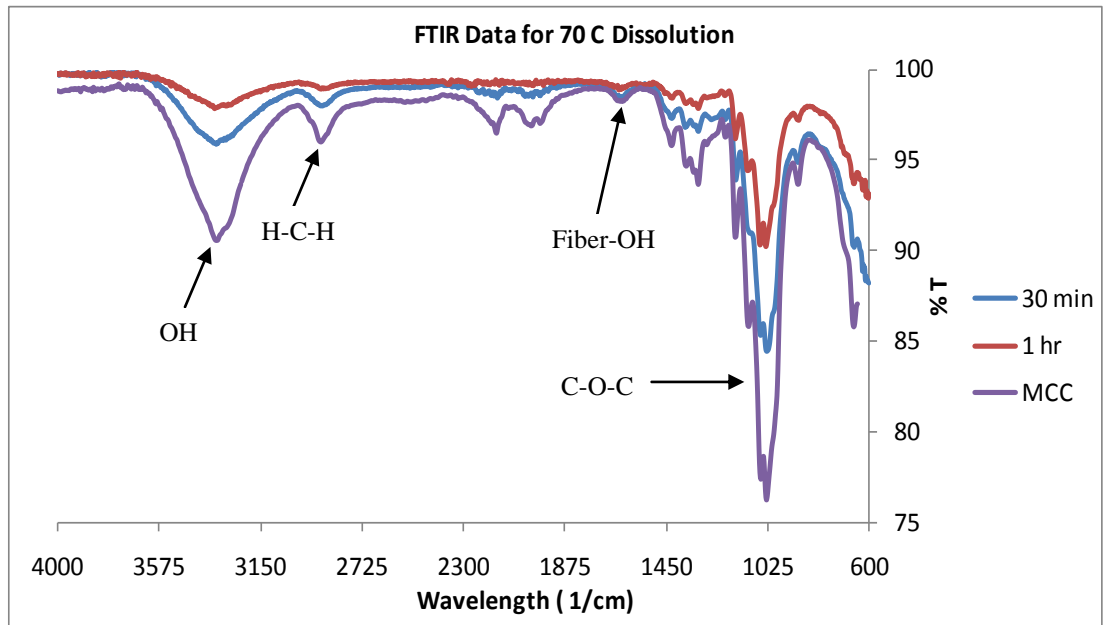
a) Temperature = 70 °C
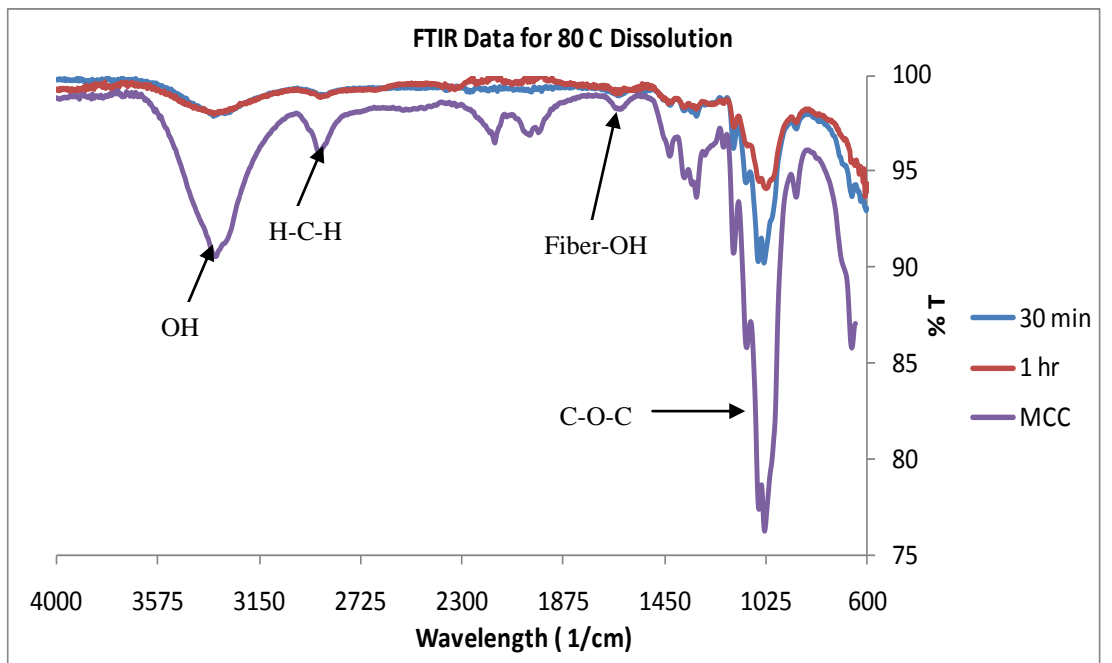
b) Temperature = 80 °C
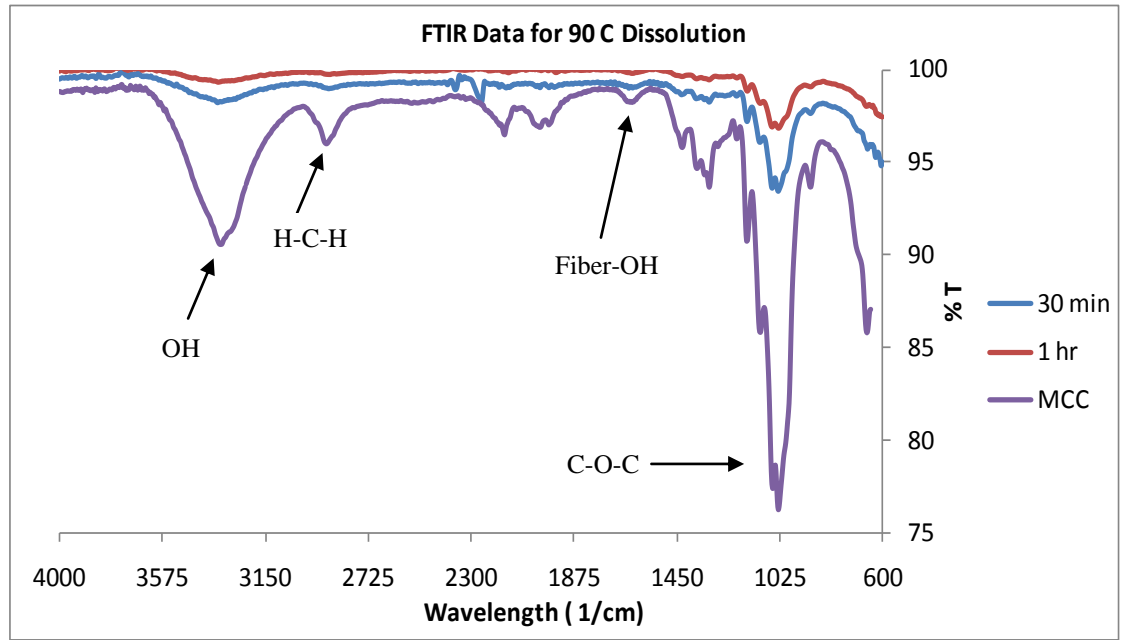
c) Temperature = 90 °C

Figure 22: FTIR Data for Effect of Dissolution Time (30 minutes, 1 hour)
for MCC dissolved in BMIM HSO_4 at Dissolution Temperature
a) 70 °C, b) 80 °C, c) 90 °C

Analysis for Effect of Dissolution Temperature

a) Time = 30 minutes

b) Time = 1 hour

FTIR Data for 1 hour dissolution
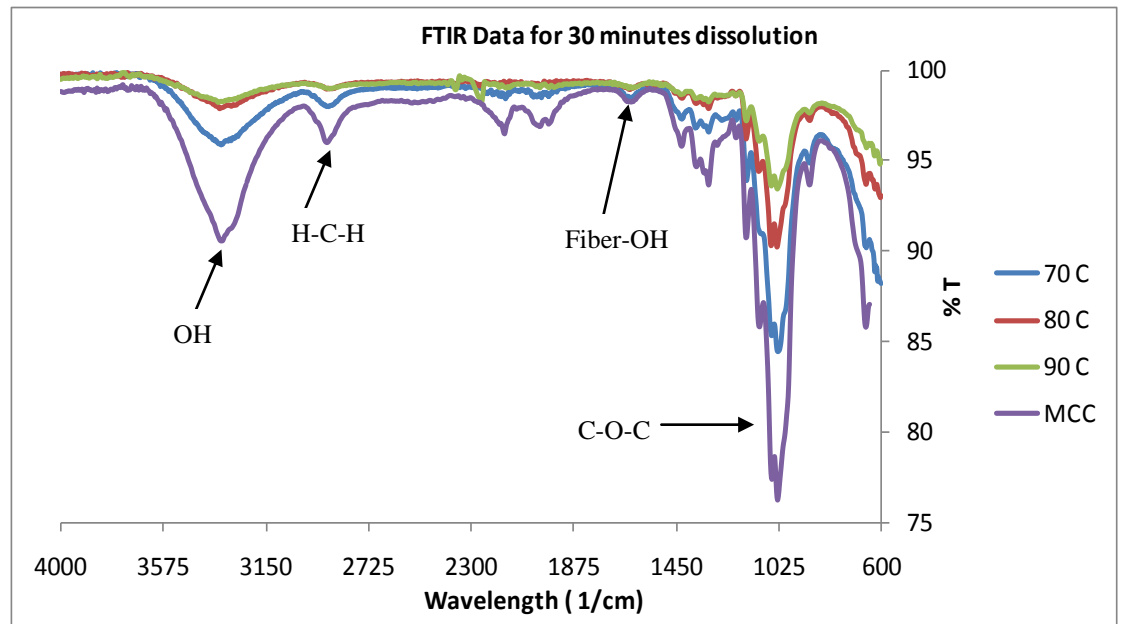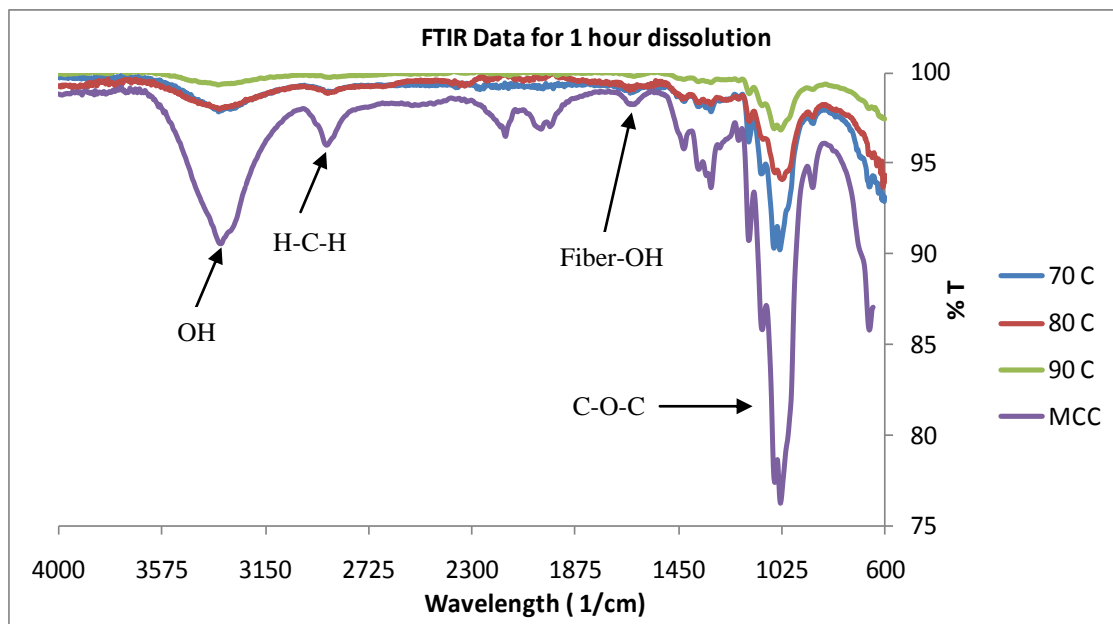
Figure 23 :FTIR Data for Effect of Dissolution Temperature (70 °C, 80 °C, 90 °C) for MCC dissolved in BMIM HSO$_4$ at Dissolution Time a) 30 minutes, b) 1 hour

All samples presented two main absorbance regions. The first one at low wavelength 1500-600 cm^{-1}, and the second one at higher wavelength corresponding to the range of 3700–2995 cm^{-1} approximately. However, specific absorption peaks can be identified for each sample.

As can be seen from Figure 22 and Figure 23, the characteristics peak for the MCC and NCC include the absorbance region from 3700-2995 cm^{-1}, corresponding to OH group that are present in cellulose (Cyras et al., 2007). This is because cellulose absorbs water content. Although sample has been dried in freeze drier for 2 days, there is still water content present in cellulose, which is even more obvious for MCC samples (Cyras et al., 2007).

An absorbance region (between 2800 cm^{-1} to 3000 cm^{-1}) is also shown for both MCC and NCC, indicating H-C-H bond (corresponding to 2890 cm^{-1}

from Table 4). Besides that, Fiber-OH absorbance region of wavelength around ~1640 cm$^-$1 is shown by both MCC and NCC obtained.

Both MCC and NCC also exhibits absorbance region in between 1270-1232 cm$^-$1, indicating C-O-C bond (Cyras et al., 2007). In both Figure 22 and Figure 23, the FTIR curve for MCC has lower % transmittance (% T) for C-O-C bond as compared to FTIR curve for NCC. Lower % transmittance for C-O-C bond indicates higher intensity of C-O-C bond in the particle. The intensity of C-O-C bond is lesser in NCC due to the reduction and breakage of C-O-C bond that occurs during BMIM HSO$_4$ dissolution, as discussed in Section 4.1.

The C-O-C bond is lesser for NCC obtained though dissolution for 1 hour as compared to 30 minutes dissolution for all three dissolution temperatures of 70 °C, 80 °C, and 90 °C (Figure 22). Thus, dissolution time of 1 hour can more effectively cause cleavage of C-O-C bonds in the amorphous region and cleavage of other easily accessible C-O-C bonds. NCC obtained through 30 minutes dissolution has higher intensity of C-O-C due to incomplete dissolution.

The C-O-C bond is lesser for NCC obtained through dissolution at 90 °C, followed by 80 °C and 70 °C respectively, for both dissolution time of 30 minutes and 1 hour (Figure 23). Thus, the most effective dissolution occurs at 90 °C. At higher temperatures, the dissolution rate increases, causing more C-O-C bonds in the amorphous region and other easily accessible C-O-C bond to be broken.

The data obtained from FTIR analysis on the most effective dissolution temperature and time supports finding from XRD. In short, all absorbance regions (wave number) that are listed in Table 4 are exhibited by both MCC and NCC. This shows that the NCC generated from BMIM HSO$_4$ dissolution has the same chemical bonds as MCC. MCC's dissolution in BMIM HSO$_4$ does not change the chemical bond that is present in cellulose.

4.3   REGENERATION OF IONIC LIQUID

A FTIR analysis is subjected to the regenerated BMIM HSO_4 and compared to the unused BMIM HSO_4. The wave number absorbance region corresponding to each of the functional group present in BMIM HSO_4 is as table following (Socrates G, 2005).

Table 5: Absorbance Region for bonds present in BMIM HSO_4 (Socrates G, 2005)

Functional group	Wave number (cm^{-1})
CH_2- C-CH_3	~910
Straight Chain Alkane	1105-1020
Bisulphate Ion, HSO_4^-	1190-1160
Tertiary aromatic Amine	1380- 1265
C=C	1540-1510
C=N	1690-1640
N^+-CH_3	2820-2810
CH_2	2870- 2840
CH_3	2885-2865
O-H	3550-3230

The functional groups (bond) presented in Table above are shown in the BMIM HSO_4 structure in Figure 24:
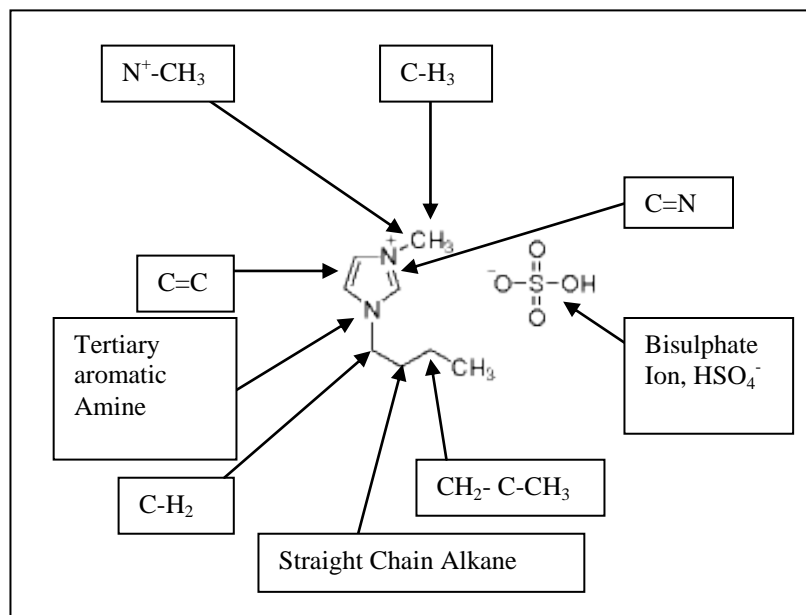
Figure 24: Different types of bond in BMIM HSO_4

Comparison of FTIR Data for unused BMIM HSO_4 and regenerated BMIM HSO_4 is shown as below:
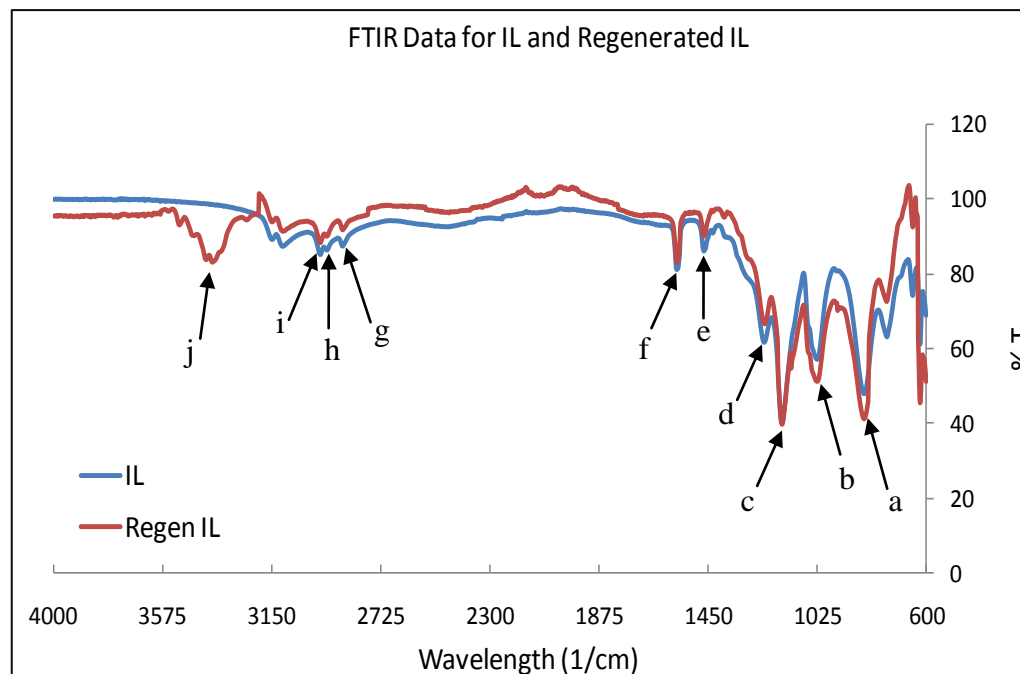
Figure 25: FTIR data for BMIM HSO_4 and Regenerated BMIM HSO_4 where a) CH_2- C-CH_3, b) Straight Chain Alkane, c) Bisulphate Ion, HSO_4^-, d) Tertiary aromatic Amine, e) C=C, f) C=N, g) N^+-CH_3, h) CH_2, i) CH_3, j) OH bond

FTIR spectrum is observed at ~3400 cm^{-1} only for regenerated BMIM HSO_4. This falls perfectly into the absorbance region of -OH within $3550 - 3220$ cm^{-1} as per Table 5 (Socrates G, 2005). This spectrum corresponds to -OH bond that is present in water due to water absorption by BMIM HSO_4 (Yang et al., 2007).

Besides the presence of absorbance region for -OH in regenerated BMIM HSO_4, Figure 25 shows that both the regenerated BMIM HSO_4 and the unused BMIM HSO_4 have the same functional groups, observed from the similar absorbance region. This shows that the chemical structure of BMIM HSO_4 remains unchanged even after the dissolution.

This result has significant importance as it shows that BMIM HSO_4 can be regenerated and recycled after the dissolution of MCC. BMIM HSO_4 can be regenerated using vacuum evaporation, which takes advantages of the distinct boiling point differences of water and BMIM HSO_4. Water has a boiling point of 100°C at standard conditions, while the boiling point of BMIM HSO_4 is above 200°C (Cao & Jin Wu, 2009). Thus, when BMIM HSO_4-water solution is subjected to vacuum evaporation, water evaporates from ionic liquid-water solution leaving BMIM HSO_4.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1   RECOMMENDATIONS

This project has good potential to be developed further. Some of the areas that can still be explored are included in this recommendation section:

5.1.1   Sample Preparation

Due to unavailability of a dialysis unit, NCC obtained after centrifugation was not subjected to dialysis. NCC sample for XRD, FTIR, and FESEM is supposed to be prepared by subjecting the supernatant collected from centrifugation to dialysis until the pH remains constant (Oksman K., Mathew A., et al, 2006). Dialysis would help obtain smaller particle size of NCC and help segregate the supernatant further from precipitate formed.

5.1.2   Identification of best method to recover BMIM HSO$_4$

One of the significant properties of Ionic Liquid is that is recyclable. The current project uses vacuum evaporation at vacuum condition and 50°C to recover BMIM HSO$_4$. One recommendation would include identification of the best method to recover BMIM HSO$_4$ at the end of the dissolution process.

This might include membrane separation process. Given the prospect of development of a bio-plant to generate NCC using BMIM HSO$_4$, this study on the best method is important so as to find the most economical and feasible method of recovering BMIM HSO$_4$.

5.1.3 Dissolution using other sources of cellulose

There are many cellulose sources such as grass, Empty Fruit Bunch (EFB), rice grains, and kapuk cotton. Thus, further studies can also include identification of other cellulose sources that yields high generation of NCC when dissolved using BMIM HSO$_4$. This identification of alternative cellulose sources also needs to take into consideration factors such as availability in Malaysia and raw material price so that it is economically feasible to generate NCC from this sources.

On the next level, comparison studies can be done by comparing the structure and crystallinity of NCC generated from MCC and this other cellulose sources.

5.1.4 Performing Comparison studies between Dissolution using Ionic Liquid and Acid Hydrolysis

This study uses BMIM HSO$_4$ to dissolve cellulose sources as opposed to current method of using Acid Hydrolysis. Thus, a comparison study can be performed between the structure, strength, and crystallinity of NCC generated using both of these methods.

5.2   CONCLUSION

Conclusion can be drawn for three major aspects which are as listed below:

1) Cellulose can be dissolved from Microcrystalline Cellulose (MCC) using 1-butyl-3-methylimidazolium hydrogen sulfate (BMIM HSO$_4$) to obtain Nanocrystalline Cellulose (NCC).

2) Dissolution temperature of 90°C produces more crystalline NCC and more cleavage of C-O-C bond than dissolution temperature of 80°C, followed by 70 °C. Dissolution time of 1 hour produces more crystalline NCC and more cleavage of C-O-C bond than dissolution time of 30 minutes. Most crystalline NCC is obtained at a dissolution temperature of 90 °C and dissolution time of 1 hour.

3) NCC is more crystalline than MCC and has smaller particle size in the range of 5-45 nm. NCC has all the chemical bonds that are present in MCC.

4) BMIM HSO$_4$ can be used to dissolve MCC to obtain NCC. Thus, BMIM HSO$_4$ dissolution can be used to replace acid hydrolysis process.

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APPENDIX A: IMPORTANT PROPERTIES OF IONIC LIQUID

Table 6: Properties of Ionic Liquid (Johnson, 2007)

A salt	Cation and or anion quite large
Liquidus range	Often > 200°C
Thermal stability	Usually high
Viscosity	Normally < 100 cP, workable
Dielectric constant	Implied < 30
Polarity	Moderate
Specific conductivity	Usually < 10 mScm-1, "Good"
Molar conductivity	< 10 Scm2 mol-1
Electrochemical window	> 2V even 4.5 V, except for Brønsted acidic systems
Solvent and/or catalyst	Excellent for many organic reactions
Vapor pressure	Usually negligible

APPENDIX B: PROJECT ACTIVITIES OF THE RESEARCH

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┌─────────────────────────────────────────────────────┐
│     PREPARATION OF IONIC LIQUID BMIM HSO₄            │
└─────────────────────────────────────────────────────┘
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┌─────────────────────────────────────────────────────┐
│        DISSOLUTION OF MCC IN BMIM HSO₄              │
└─────────────────────────────────────────────────────┘
                          │
                          ▼
┌─────────────────────────────────────────────────────┐
│       REGENERATION OF NANOCRYSTALLINE               │
│              CELLULOSE (NCC)                        │
└─────────────────────────────────────────────────────┘
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┌─────────────────────────────────────────────────────┐
│      ULTRASONIFICATION AND CENTRIFUGATION           │
└─────────────────────────────────────────────────────┘
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┌─────────────────────────────────────────────────────┐
│     CHARACTERISTICS STUDIES ON EXTRACTED            │
│                  CELLULOSE                          │
│                                                     │
│   -  Fourier Transform Infrared Analyzer (FTIR)     │
│   -  Field Emission Scanning Electron Microscopy    │
│      (FESEM)                                        │
│   -  X-Ray Diffraction Analysis (XRD)               │
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┌─────────────────────────────────────────────────────┐
│          REGENERATION OF BMIM HSO₄                  │
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PREPARATION OF IONIC LIQUID BMIM HSO$_4$

DISSOLUTION OF MCC IN BMIM HSO$_4$

REGENERATION OF NANOCRYSTALLINE CELLULOSE (NCC)

ULTRASONIFICATION AND CENTRIFUGATION

CHARACTERISTICS STUDIES ON EXTRACTED CELLULOSE

- Fourier Transform Infrared Analyzer (FTIR)
- Field Emission Scanning Electron Microscopy (FESEM)
- X-Ray Diffraction Analysis (XRD)

REGENERATION OF BMIM HSO$_4$

APPENDIX C: MILESTONE OF RESEARCH PROJECT

No.	Detail/ Week	1	2	3	4	5	6	7	8	9		10	11	12	13	14	18	19	14
	Date	25-Jan	01-Feb	08-Feb	15-Feb	22-Feb	28-Feb	01-Mac	08-Mac	15-Mac		22-Mac	29-Mac	####	12-Apr	19-Apr	26-Apr	24-Mei	04-Jun	11-Jun
1	Preparation of NCC	■	■	■	■	■	■	■	■										
	1. Ionic Liquid Dissolution																		
	2. Centrifugation																		
	3. Ultrasonification																		
	4. Freeze drying																		
2	Submission of Progress Report 1						■												
3	NCC characterization				■	■	■	■	■			■	■	■	■				
	1. FTIR analysis																		
	2. XRD analysis																		
	3. FESEM analysis																		
4	Submission of Progress Report 2												■						
5	Pre-EDX (Poster Presentation)													■					
6	Project work continues											■	■	■	■				
	1.Preparation of Nanocomposites																		
	2.Mechanical testing																		
7	Submission of Final Report																■		
8	Documentation	■	■	■	■	■	■	■	■			■	■	■	■	■	■	■	■
9	Final Oral Presentation																■	■	
10	Submission of hardbound																		■

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