1-METHYL-3-PROPIONITRILE IMIDAZOLIUM STUDIES FOR SAGO WASTE DISSOLUTION

by

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CERTIFICATION OF APPROVAL

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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 person

ADI AIZAT BIN RAZALI

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ABSTRACT

Biomass is one of the most redundant biorenewable resources available, with a long and well-established technological base. With the current crucial concern, the energy crisis, a numbers or Research and Development in developing the substitute materials of petroleum and other depleting natural fuel resources is in progress. A substantial research effort is underway that focused on degrading biomass into smaller constituents by using a variety of physical, chemical and biological processes. Ionic liquid can be considered as the best alternative in dissolution of biomass because of its advantageous properties and it can also be a medium for efficient dissolution of a variety of materials. By synthesizing various types of ionic lLiquids having different anion, the best ionic liquids for **Sago Waste** can be analyze and evaluate.

CHAPTER 1

1. INTRODUCTION

1.1. BACKGROUND OF STUDY

The depletion of petroleum-based resources has increased the worldwide interest for finding the alternative resources. One of the most sought after criteria is renewable resources. Recently, there are tremendous increases of interest in cellulosic biomass for production of biofuels. However, to take the Nature's abundant biopolymers: cellulose, hemicellulose and lignin, to separate and create a monomeric fuel, is very difficult.

The current biorefinery concept only emphasize on other value-added chemicals other than fuels. Basically, cellulose and hemicellulose will be used to produced paper, fibers, membranes, and other commodity materials and chemicals, while lignin is usually burned for energy. The full potential of cellulose has still not yet been utilized because of four main reasons:

1. Historical shift to petroleum-based polymers from 1940s onward.
2. The lack of an environmental-friendly method in extracting the cellulose from its primitive resources.
3. The difficulty in modifying the cellulose properties.
4. Limited number of common solvents that readily dissolve cellulose.

(ShengdongZhu et. al. 2006)

Various types of solvents have been used for processing of cellulose. In paper making, wood is treated with alkaline solution and in the preparation of cellulose xanthate carbon disulphide as the solvent (N. Muhammad et. al., 2010). However, they suffered from problems related to volatility, generation of toxic gas and also difficulty in recovery for recycle gas. The processes are also often cumbersome or expensive and require the use of unusual solvents, with high ionic strength and use relatively harsh conditions (Shengdong Zhu et. al. 2006).

There are also some available ionic liquid commercially available, however most of them also suffered from disadvantages such as for [Bim]Ac, which is difficult to synthesize and [Bim]Cl, which very unstable.

To date, most of the reactions have been carried out in with molecular a solvents which are problematic. One of the most advantageous criteria for ionic liquids is it can act as a "green solvent" because of their benign properties, such as chemical and thermal stability, non-flammability and immeasurably low vapor pressure. Their properties make them of fundamental interest to all chemists, since both thermodynamic and kinetics of reactions in ionic liquid are different to those in molecular solvents, then the chemistry is different and unpredictable at our current state of knowledge (M. J. Earle and K. R. Seddon, 2000).

1.2. PROBLEM STATEMENTS

The current and widely used technology, which uses molecular solvents for biomass dissolution has several limitations and also disadvantages:

- The chemistry is different and unpredictable.
- Emit volatile organic compounds (VOCs).
- High volatility.
- Difficulties in recovery for recycle use.
- Generation of toxic gas.
- For Plant Biomass, difficult to dissolve due to the three dimensional network structures of lignin which binds the plant cells together.

1.3. OBJECTIVE

The **primary objective** of this project is **to provide comprehensive feasibility evaluation and thorough research of using a novel class compound, ionic liquids for biomass dissolution.**

1.4. SCOPES OF DUTY

The study conducted regarding the chosen topic will cover the following scopes of duty:

- Producing a range of ionic liquid solvent for further evaluation and research.
- Determining the unique property set of each of the Ionic Liquid solvents that can provide new options based upon different chemical and physical properties.
- Determining the fundamental factors which can influence the dissolution of the biomass material.

CHAPTER 2

2. LITERATURE REVIEW

2.1. IONIC LIQUIDS

Generally, ionic liquids are salts that are liquid at low temperature (<100°C) and represent a new class of solvents with non-molecular, ionic character. One of the most significant properties is the low vapour pressures in most instances which is contrast of the environmental problems of volatile organic solvents. The molarity if the liquid is important regarding kinetic measurements, including conductivities. Ionic liquids are made up of at least two components which can be varied, the inorganic, polyatomic anion and organic cation. Some simple physical properties of the ionic liquids that make them interesting as potential solvents for synthesis are the following:

(1) They are good solvents for a wide range of both inorganic and organic materials, and unusual combinations of reagents can be brought into the same phase.

(2) They are often composed of poorly coordinating ions, so they have the potential to be highly polar yet noncoordinating solvents.

(3) They are immiscible with a number of organic solvents and provide a nonaqueous, polar alternative for two-phase systems. Hydrophobic ionic liquids can also be used as immiscible polar phases with water.

(4) Ionic liquids are nonvolatile, hence they may be used in high-vacuum systems and eliminate many containment problems.

The figure below shows some of the common cation and anion:

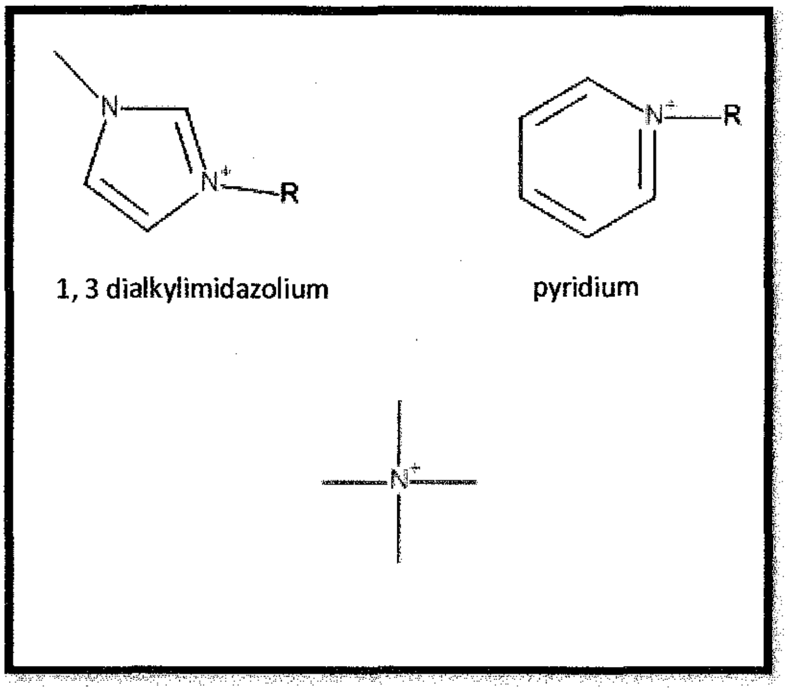


Figure 1: Common structure of cation

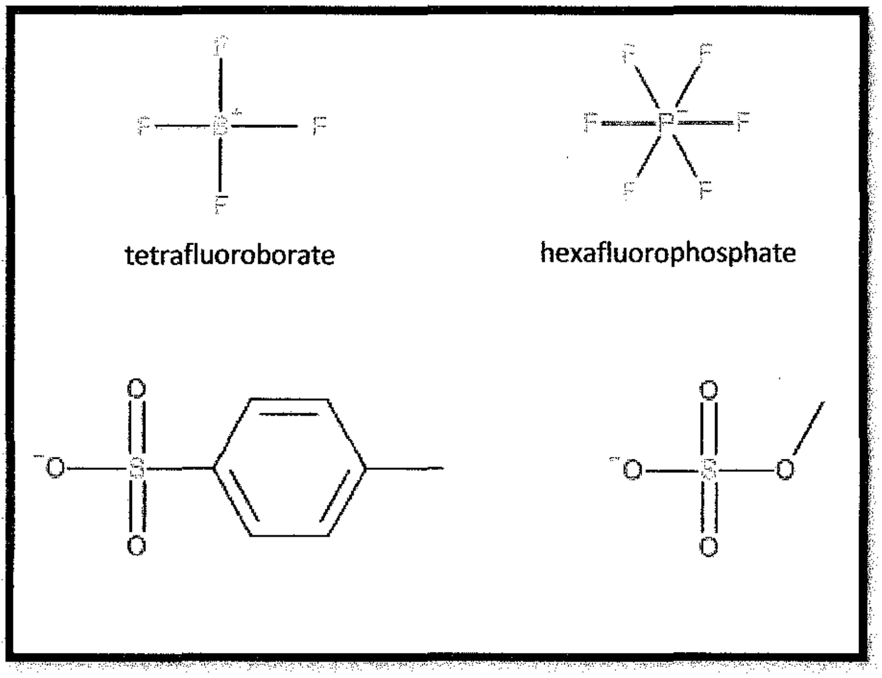


Figure 2: Common structure of anion

2.1.1. History of Ionic Liquids

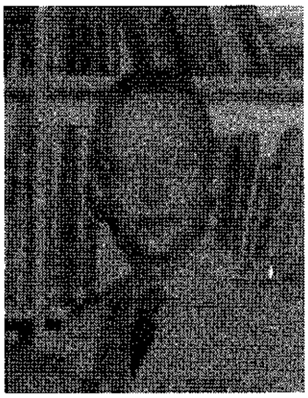


Figure 3: Dr. Lowell A. King

The earliest material that meet current definition of an ionic liquid was observed in Friedel–Crafts reactions in the mid-19th century as a separate liquid phase called the "red oil." The fact that red oil was a salt was determined more recently, when NMR spectroscopy becomes a commonly available tool. During early 20th century,there are some alkylammonium nitrate salts were found to be liquid, and more recently liquid gun propellants based on binary nitrate ionic liquids have been developed.

1960s – John Yoke at Oregon State University reported that mixtures of copper(I) chloride and alkylammonium chlorides were often liquids.

1970s – Jerry Atwood at the University of Alabama discovered an unusual class of liquid salts he termed "liquid clathrates". These were composed of a salt combined with an aluminium alkyl, which then formed an inclusion compound with one or more aromatic molecules. A formula for the ionicportion is M[Al2(CH3)6X], where M is an inorganic or organic cation and X is a halide.

In 1953, Major (Dr,) Lowell A. King initiated a research project at the U.S. Air Force Academy, which aimed at finding replacement for LiCl/KCL molten salt electrolyte used in thermal batteries. Even though the LiCl/KCl eutectic mixture has a low melting temperature (355 °C) for an inorganic salt, the temperature causes materials problems inside the battery, and incompatibilities with nearby devices.

With three principal investigators: King, John Wilkes and Richard Carlin, a continuous molten salt/ionic liquids research program has been established. The class of molten salts known as chloroaluminates, which are mixtures of alkali halides and aluminium chloride, have melting temperatures much lower than nearly all other inorganic eutectic salts. In fact NaCl/AlCl3 has a eutectic composition with a melting point of 107 °C, very nearly an ionic liquid by our definition.

Early in their work, the researchers surveyed the aluminium electroplating literature for electrolyte baths that might be suitable for a battery with an aluminium metal anode and chlorine cathode. They found a 1948's patent describing ionically conductive mixtures of AlCl3 and 1-ethylpyridinium halides, mainly bromides. Subsequently, the salt 1-butylpyridinium chloride/AlCl3 was found to be better behaved than the earlier halide system. So, the chemical and physical properties were measured and published. This is the start of the modern era for ionic liquids, as a wider audience of chemist started to take interest in these totally ionic, completely no aqueous new solvents.

According to Dr. King, we should take heed of with the newer ionic liquids: if a new material is to be accepted as a technically useful material, the chemists must present reliable data on the chemical and physical properties needed by engineers to design processes and devices.

(P. Wasserscheid and T. Welton, 2002)

2.1.2. Characteristic Properties of Ionic Liquid

Ionic liquids are made up of at least two components which can be varied, the inorganic, polyatomic anion and organic cation. The term "designer solvents' is given to them because; the solvents can be designed with particular end use in mind, or to possess a particular set of properties. So, the unique property set of each of the ionic liquid materials can provide new options based upon different chemical and physical properties. Since there are many known and potential cations and anions, the potential number of ionic liquids is huge.

Understanding basic thermophysical properties of ILs is vital for design and evaluation. For instance, melting points, glass-transition temperatures, and thermal decomposition temperatures are needed to set the feasible temperature operating range for a particular fluid. Density (as a function of temperature) is needed for equipment sizing. Heat capacities are needed to estimate heating and cooling requirements as well as heat-storage capacity. Table 1 below shows the summarized properties of modern ionic liquid:

Table 1 : Modern Ionic Liquids Properties

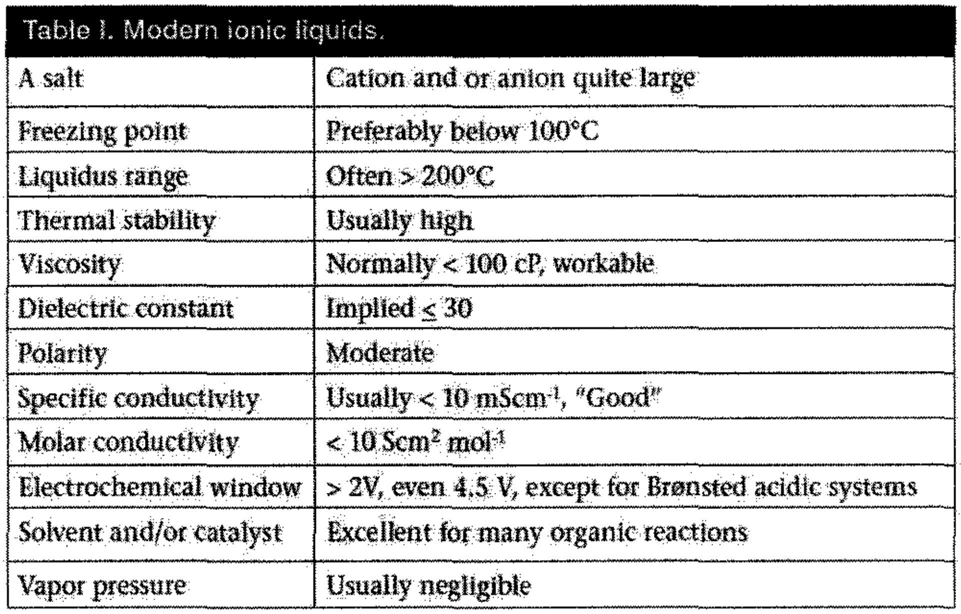


Table 1. Modern ionic liquids.

A salt	Cation and or anion quite large
Freezing point	Preferably below 100°C
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	$< 10\ Scm^{2}\ mol^{-1}$
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

(Keith E. Johnson, 2007)

2.1.2.1. Melting Point

For the cation, because of the low symmetry, the intermolecular interaction is weak, thus making the melting significantly lower. And also, the good distribution of charge also contributes to the low melting point of the ionic liquid. Ionic liquids also have high range of temperature (-90°C to 150°C). The quantitative structure property relationship (QSPR) method has previously been employed to relate the structure and melting points of a variety of ionic liquids, since sufficient melting point data were available to execute such correlations

2.1.2.2. Colour

For a high quality ionic liquids, consists of $[bmim]^+$ cation and a variety of anion (such as [PF6]-, [BF4]- and [CF3SO3]-), even though they are not entirely pure, there are report saying that they happen to be colourless. Typically, for a less pure ionic liquid, the colour ranges between yellowish to orange. The colour of ionic liquids is affected by the material used as a start, or also excessive heating during the formation of imidazolium salt. For $[mmim]^+$ cation, the colour can range from slightly yellow to yellow depending on the anion used.

2.1.2.3. Vapour Pressure and Thermal Stability

Ionic liquids have significantly low and negligible vapor pressure. This had been main advantage that drives the interest of all research regarding the ionic liquids. They have small and non-measurable vapour pressure. Having low vapor pressure will ensure that the ionic liquids will emit no volatile organic compounds (VOCs) which are the problem for most organic solvents. For the thermal stability, it depends on the anion for the ionic liquids. Generally, the thermal stability of ionic liquids is limited by the strength of their heteroatom-carbon and their heteroatom-hydrogen bonds. The thermal stability increases with increasing anion size, and heat capacities increase with temperature and increasing number of atoms in the IL.

2.1.2.4. Density

As the bulkiness of an ionic liquid increase, the densities of the comparable ionic liquids are also increase. Density decreases as the length of the alkyl chain on the cation increases. For a given cation, the density increases as the molecular weight of the anion increases for the anions studied here

2.1.2.5. Viscosity

The viscosity of ionic liquids relied on the tendency to form hydrogen bonding and also the strength of the Van der Waals interaction. Typically, the viscosity will vary from the range of 200 to 3000 cP. Viscosity measurement will indicates that ionic liquid will become less viscous with increase of water content.

2.1.2.6. Hygroscopy

Some of the characteristics of the ionic liquids which makes them so sensitive is very hygroscopy towards water. Handling of the ionic liquid is very important especially after finishing the synthesis. An ionic liquid will greatly attract moisture even from the environment and absorb it, causing higher water content. Great precautions are required in handling the ionic liquid, for example to keep it in vacuum line to prevent water from coming in, especially when the ionic liquid is still hot. Viscosity measurement indicates that ionic liquids became less viscous with increasing water content.

Probably one of the most appealing features of using ionic liquids is their potential to be custom-made with pre-selected characteristics (e.g. moisture stability, viscosity, density, miscibility with other co-solvents), by careful selection of the cation, anion, or both. Basically, to discover a new ionic liquid is relatively easy, but to determine its usefulness as a solvent will requires a much more substantial investment in determination of physical and chemical properties. Despite their 'designer solvent' classification, ionic liquids research is still a relatively new field with insufficient physical property data available to conveniently allow their bespoke preparation.

2.1.3. Synthesis of the Ionic Liquids

The synthesis of ionic liquid can be split into two sections: formation of the desired cation, and anion exchange where necessary to form desired product. The first step of Ionic Liquids synthesis is the **quartenization** of and amine or phosphane for example, to form cation: imidazolium ion, pyridium ion, ammonium ion and phosphonium ion. In the case the desired anion is not possible to be form directly, a further **anion exchange** step are required:

- Metathesis of halide salt with, for instance, a silver, group 1 metal or ammonium salt of desired anion.
- Acid-base neutralization reaction

(Zuraifah Anuar, Evaluation on Ionic Liquid for CO2 Absorption, 2007)

Simplified diagram of ionic liquid synthesis:

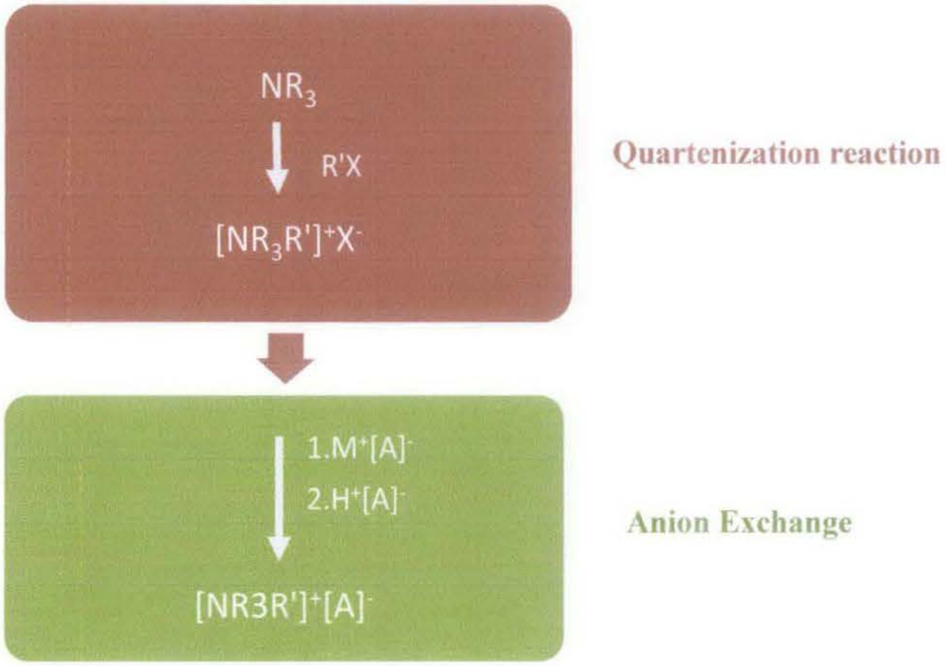


Figure 4: Simplified Diagram of Ionic Liquids Synthesis

Many alkylammonium halides are commercially available or they can be prepared simply by the reaction of the appropriate halogenoalkane and amine. Preparation of the pyridinium and imidazolium halides can be achieved similarly. For volatile halogenoalkanes, the low boiling points lead to preparations requiring either a sealed tube, such as in the synthesis of [emim]Cl (where [emim]+ is the 1-ethyl-3-

methylimidazolium cation), or an elaborate reaction still. Hence, the use of salts with longer chain substituents, such as [bmim]Cl (where [bmim]+ is the 1-butyl-3-methylimidazolium cation), that can be prepared in conventional glassware by heating under reflux has become popular.

The formation of the cations may be carried out either by protonation with a free acid as noted above, or by **quaternization** of an amine or a phosphine, most commonly with a haloalkane. According to P. Wasserscheid and T. Welton (Eds.), the quartenization process possesses the advantages that (a) a wide range of cheap haloalkanes are available, and (b) the substitution reactions generally occur smoothly at reasonable temperatures. Furthermore, the halide salts formed can easily be converted into salts with other anions. The reaction may be carried out with chloroalkanes, bromoalkanes, and iodoalkanes. The reaction conditions required becoming steadily more gentle in the order Cl → Br → I, as expected for nucleophilic substitution reactions. Fluoride salts cannot be formed in this manner.

The quaternization reactions are: the amine (or phosphine) is mixed with the desired haloalkane, and the mixture is then stirred and heated in nitrogen environment. In the case of bromoalkanes, great care must be taken with large-scale reactions, as when the reaction rate increase, a strong exotherm can occur. Besides the safety implications, the excess heat generated can result in discoloration of the final product. The reaction with iodoalkanes can often be carried out at room temperature, but the iodide salts formed are light-sensitive, requiring shielding of the reaction vessel from bright light.

Most quartenization use a simple round-bottomed flask/reflux condenser experimental setup. The reaction should be carried out under nitrogen atmosphere or some other inert gas in order to exclude water and oxygen during the quaternization. Exclusion of oxygen is particularly important if a colorless halide salt is required. After reaction is complete and the solvent is decanted, it is necessary to remove all excess solvent and starting material by heating the salt under vacuum. Overheating the product can cause reversal of the quartenization reaction. So, care should be taken at this stage. It is preferably not to heat the product to temperature greater than 80°C.

Examples of the cation that can be produced are imidazolium ion, pyridinium ion, ammonium ion and phosphonium ion. The followings are the example of synthesizing **propanenitrile imidazole** from **imidazole** and **acrylonitrite** mixed in methanol. To synthesize a particular anion, the next step which is Anion Exchange is necessary.

In case where it is not possible to form desired anion directly, anion exchange or **metathesis** step is required. By doing anion exchange with the component RX, which R and X can be derived from above component, different Ionic Liquids with different Anion can be obtained as shown as in Figure 4 above. The purpose of metathesis is the formation of the desired ionic liquid uncontaminated with unwanted cations or anions, a task that is easier for water-immiscible ionic liquids. Because of the preparation for water-immiscible ionic liquid is quite straightforward, these methods is favored first than that of water-soluble analogues. The water solubility of ionic liquids depends on the anion and cation present. By increasing the organic character of the cation, the water solubility will decrease.

The common approach for the preparation of water immiscible ionic liquids is first to prepare the aqueous solution of a halide salt of desired cation. The anion exchange is then carried out either with the free acid of the appropriate anion, or else with a metal or ammonium salt.

The preparation of water-miscible ionic liquids can be a more demanding process, as separation of the desired and undesired salts may be complex. The common approach is to carry out the exchange in aqueous solution with either the free acid of the appropriate anion, the ammonium salt or an alkali metal salt. It is very important to isolate the ionic liquid from the contamination of unwanted halide-containing byproducts.

Alternatively, the metathesis reaction may be carried out entirely in an organic solvent such as CH_2Cl_2 or acetone. In both systems, the starting materials are not fully soluble in the reaction solvent, so the reaction is carried out with a suspension. Thus, when this method is employed it is important that the extracts be washed with water or ethyl acetate to minimize the halide content of the final product. This approach clearly results in a lowering of the yield of the final product, so care must be taken that the volume of solvent used to carry out the washing is low.

Some of the example is **1-Methyl-3-Propionitrile Imidazole Chloride** that will undergo anion exchange with **Sodium Dihexylsulfosuccinate** and **Sodium Dioctylsulfosuccinate.** The resulting metathesis will produce **1-Methyl-3-Propionitrile Imidazole Dihexylsulfosuccinate** and **1-Methyl-3-Propionitrile Imidazole Dioctylsulfosuccinate** respectively. The metathesis reaction will also produce side reaction which is **Sodium Chloride** which will precipitate after the reaction and will be filtered out.

2.1.4. Current Application of the Ionic Liquids

Because of ionic liquids' properties, which do not exhibit measurable vapor pressure, hence it can also emit no volatile organic compounds (VOCs). It is the perfect candidate in replacing the volatile organic solvents. ILs have been considered as solvents for reactions, as absorption media for gas separations, as the separating agent in extractive distillation, as heat transfer fluids, for processing biomass, and as the working fluid in a variety of electrochemical applications. Some of the examples of current application of ionic liquids are:

2.1.4.1. Homogeneous and Heterogeneous Catalyst

Because of ionic liquids can be immiscible with the reactants and products but dissolve the catalysts, thus for some applications, ionic liquids can offer the advantage of both homogeneous and heterogeneous catalysts. The French Petroleum Institute, in Paris, have commercially licensed an ionic liquids-based process that uses these properties for preparing polybutene dimers used in plastics, automobile tires, and related materials.

2.1.4.2. Biological Reactions Media

Biological reactions will involve the use of enzymes, for example in the synthesis of pharmaceuticals product. Thus, it will required a stable media to ensure smooth reaction. Enzymes are stable in ionic liquids. This opens the possibility for ionic liquids to be used in biological reactions. Previous study in 2000, from University of Pittsburgh, used enzymes in an ionic liquid to synthesize Z-aspartame, a precursor of artificial sweetener.

2.1.4.3. Solar Thermal Energy

Ionic liquids have potential as a heat transfer and storage medium in solar thermal energy systems. Concentrating solar thermal facilities focus the sun's energy onto a receiver which can generate temperatures of around 600 °C. This heat can then generate electricity in a steam or other cycle. For buffering during cloudy periods or to enable generation overnight, energy can be stored by heating an intermediate fluid. Nitrate salts is the previous choice since 1980s, however the freeze at 220°C and require heating to prevent solidification. Ionic liquids such as [C4mim][BF4] have more favorable liquid-phase temperature ranges (-75 to 459 °C) and could therefore be excellent liquid thermal storage media and heat transfer fluids.

2.1.5. New Application of the Ionic Liquids

2.1.5.1. Purification of Gases

It has been found that many gases, including CO2, are highly soluble in ionic liquids. Simulations have been conducted to investigate this, and results indicate that the anion is primarily responsible for high CO2 solubility. Previous experiment had shown conclusive results.

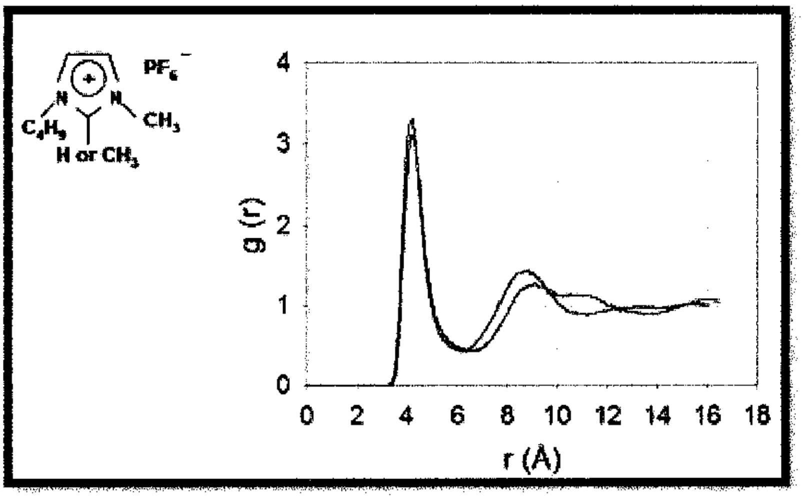


Figure 5: Radial distribution function for CO2 associating with the PF6 anion in 1-n-butyl-2(H/CH3)-3-methylimidazolium PF6

Figure above shows the calculations from the paper by Cadena et al. show the radial distribution function for CO2 associating with the PF6 anion in 1-n-butyl-2(H/CH3)-3-methylimidazolium PF6. The blue curve shows the anion-CO2 g(r) for the case when the carbon at the 2-position on the ring is bonded to a hydrogen, and the red curve shows when this group is a methyl group. Some theory suggests that the cation plays a relatively minor role in controlling CO2 solubility.

Ionic liquid can be found to preferentially dissolve certain gaseous species, then it can be used in conventional gas absorption applications. Ionic liquid is the best candidate as separating agents. The non-volatile nature of ionic liquids plays two important roles. First, there will be no cross-contamination of the gas stream by the solvent during operation. This means no solvent loss and no air pollution. Second, regeneration of the solvent is easy. A simple flash or mild distillation step is all that is required to remove the gas from the solvent, again with no cross-contamination.

2.1.5.2. Hg^{2+} and Cd^{2+} removal from waste water

For metal ions in [Cnmim][PF6]/aqueous systems, the distribution ratios are below 1, indicating their hydrated nature and preference for the aqueous phase (e.g., the distribution ratios for Hg^{2+} and Cd^{2+} in [C4mim][PF6]/ water systems are 0.84 and 0.03, respectively). In traditional solvent extraction, increasing the metal ion partitioning to the more hydrophobic phase is accomplished by adding extractants that reside quantitatively in the extracting phase. The extractant molecules serve to dehydrate the metal ions and to offer a more hydrophobic environment that enables their transport to the extracting phase.

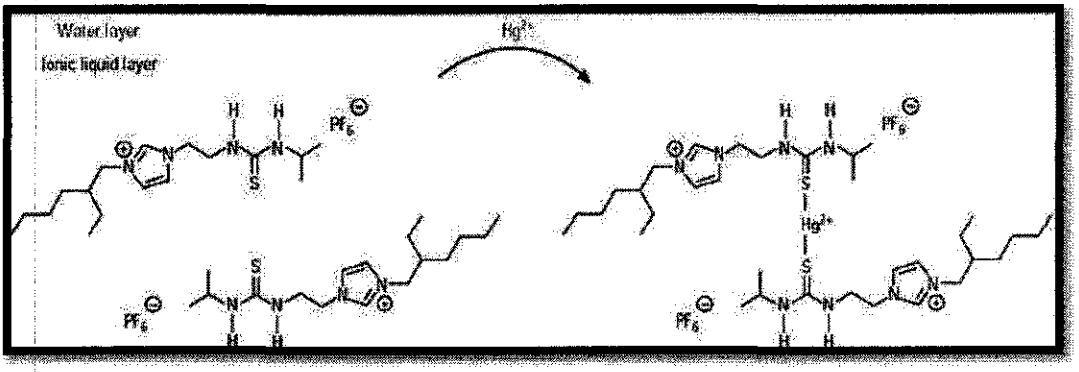


Figure 6 : Proposed reaction for mercury cation removal from water

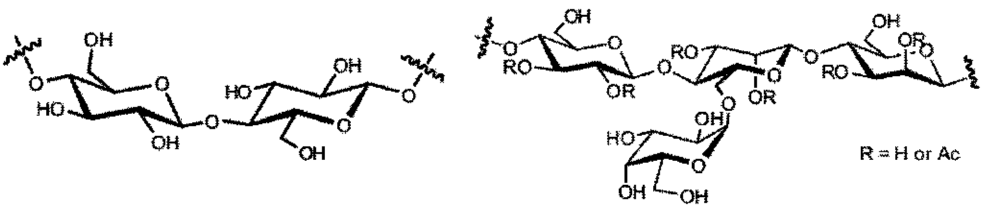
Attaching a metal ion coordinating group directly to the imidazolium cation makes the extractant an integral part of the hydrophobic phase and greatly diminishes the chance for loss to the aqueous phase. Figure above shows two or more ionic liquid cations with electron rich thiourea groups bind Hg^{2+} cations and sequester them in ionic liquid phase. Other reports confirm that acidic conditions can be sufficient to induce Hg^{2+} and Cd^{2+} stripping from thiourea and thioether-based extractants.

2.2. BIOMASS

Biomass is the organic materials produced by plants. In some cases, microbial and animal metabolic wastes are also considered biomass. The term "biomass" is intended to refer to materials that do not directly go into foods or consumer products but may have alternative industrial uses. Throughout the project, the biomass chosen to be tested is **Sago Waste** because of the availability of the waste obtained from Sabah.

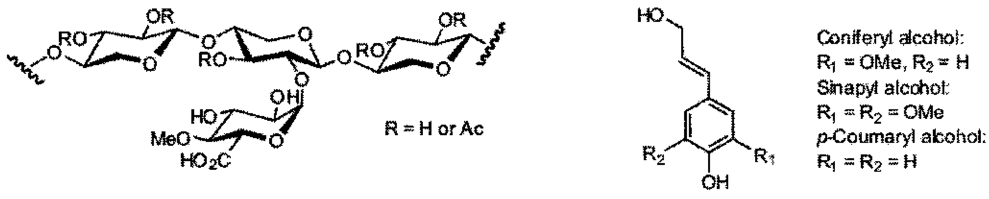
2.2.1. Sago Waste

Biomass chosen is **Sago Waste** (Fiqure 1) which is a **Plant Biomass**. The main components of plant biomass are cellulose, lignin and hemicelluloses. Cellulose, the main part of wood, constitutes 45-50%, Hemicellulose constitutes 15-25% and lignin constitutes 23-33% in softwood and 16-25% in hardwoods (N. Muhammad et. al., 2010). According to I. Kilpelainen et al (*Dissolution of Wood in Ionic liquids, 2007*), the lignin binds the plant cells together, providing wood with mechanical strength and rigidity to resist external forces, such as wind, and forming barrier against microbial attack. Due to the three dimensional network structures of lignin which binds the plant cells together, it is thought to be practically impossible to dissolve it.



A: Cellulose

B: Galactoglucomannans (major hemicellulose in softwood)



C : Glucuronoxylan (major hemicellulose in hardwood)

D: Three building blocks of lignin

Figure 7: The structures of three major biopolymers (A-D) of the plant cell walls

(Nan Jiang and Arthur J Ragauskas, 2010)

2.2.2. Dissolution of Cellulose

Cellulose is the major carbohydrate produced by plant photosynthesis, therefore is the most abundant organic polymer on earth. Cellulose can be used as a 'green' polymer for fabricating new and attractive materials, by chemical modification or mixing with other components. Cellulose consists of linear chains of 1,4-linked b-D-glucose units, so that its biodegradation has a great impact on the recovery of natural resources, as well as the production of electrochemical energy by bio-fuel cells. It should be noted here that the total energy needed to produce useful energy from biomass is very important. Accordingly, its treatment with low energy should be important. Cellulose is hardly soluble in conventional solvents because of its many intermolecular hydrogen bonds. (Yukinobu Fukaya et. al. 2007)

Dissolution of cellulose, the main component of the wood is based on the disruption of the inter- and intramolecular hydrogen bonding of cellulose and the formation of new hydrogen bonds between the carbohydrate hydroxyl protons and the anions of the ionic liquids. Figure 3 below demonstrate that the solvation of cellulose by the ionic liquid (IL) 1-*n*-butyl-3-methylimidazolium chloride ([C_4mim]Cl) involves hydrogen-bonding between the carbohydrate hydroxyl protons and the IL chloride ions:

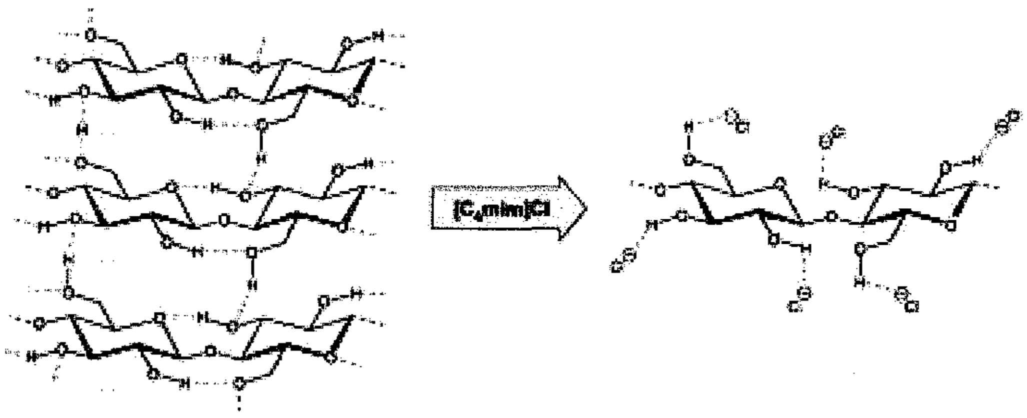
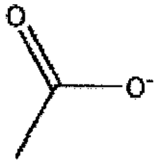


Figure 8: Hydrogen-bonding between the carbohydrate hydroxyl protons and the IL chloride ions

(Richard C. Remsing et. al., 2006)

Some of the anion had undergone research and experiment to justify the ability to dissolve biomass. They have also research undergone for them. Below is some of the examples of anion that had recently been studied regarding the dissolution of cellulose:

Table 2: Anions for Biomass Dissolution

Ionic Name	Ionic Structure	References
Acetate		Ning sun et. al. "Complete Dissolution and Pertial Delignification of wood in ionic liquid 1-ethyl-3-methylimidazolium acetate", Green Chemistry, 2009
Bromide	Br^-	Haibo Xie et. al. "Ionic Liquid as Novel Solvents for the Dissolution and Blending of Wool Keratin Fibers", Green Chemistry, 2005
Chloride	Cl^-	Shengdong Zhu et. al. "Dissolution of Cellulose With Ionic Liquids and Its Application: a mini-review" Green Chemistry, 2006

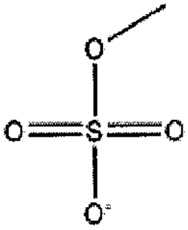
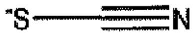
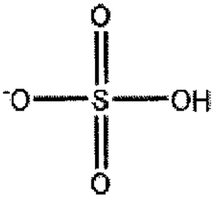
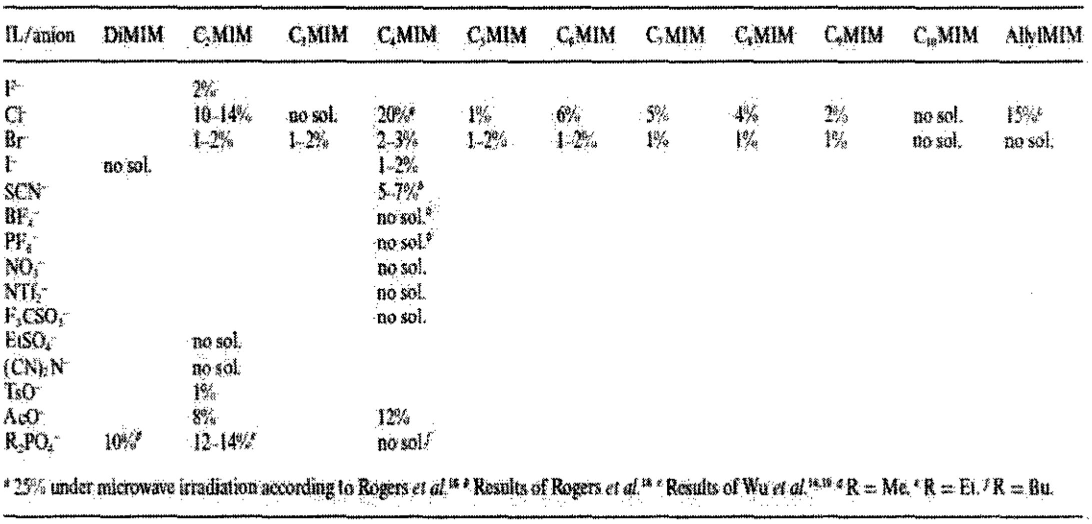
Methyl Sulfate		Yukinobu Fukaya et. al. "Cellulose Dissolution with Polar Ionic Liquids Under Mild Conditions: required factors for anions", Green Chemistry, 2007
Thiocyanate		Richard P. Swatloski et. al. "Dissolution of Cellose with Ionic Liquids" JACS Communication, 2002
HydrogenSulfate		N. Muhammad et. al., "Dissolution of Bamboo (*Gigantochloa scortechinii)* Using Ionic iquids", Universiti Teknologi PETRONAS, Perak, 2010.

Table 3: Overview of the Results from the dissolutions studies for imidazolium based ILs



IL/anion	DiMIM	C_2MIM	C_3MIM	C_4MIM	C_5MIM	C_6MIM	C_7MIM	C_8MIM	C_9MIM	$C_{10}MIM$	AllylMIM
F^-		2%									
Cl^-		10-14%	no sol.	20%[a]	1%	6%	5%	4%	2%	no sol.	15%[c]
Br^-		1-2%	1-2%	2-3%	1-2%	1-2%	1%	1%	1%	no sol.	no sol.
I^-	no sol.			1-2%							
SCN^-				5-7%[b]							
BF_4^-				no sol.[b]							
PF_6^-				no sol.[b]							
NO_3^-				no sol.							
NTf_2^-				no sol.							
$F_3CSO_3^-$				no sol.							
$EtSO_4^-$		no sol.									
$(CN)_2N^-$		no sol.									
TsO^-		1%									
AcO^-		8%		12%							
$R_2PO_4^-$	10%[d]	12-14%[e]		no sol[f]							

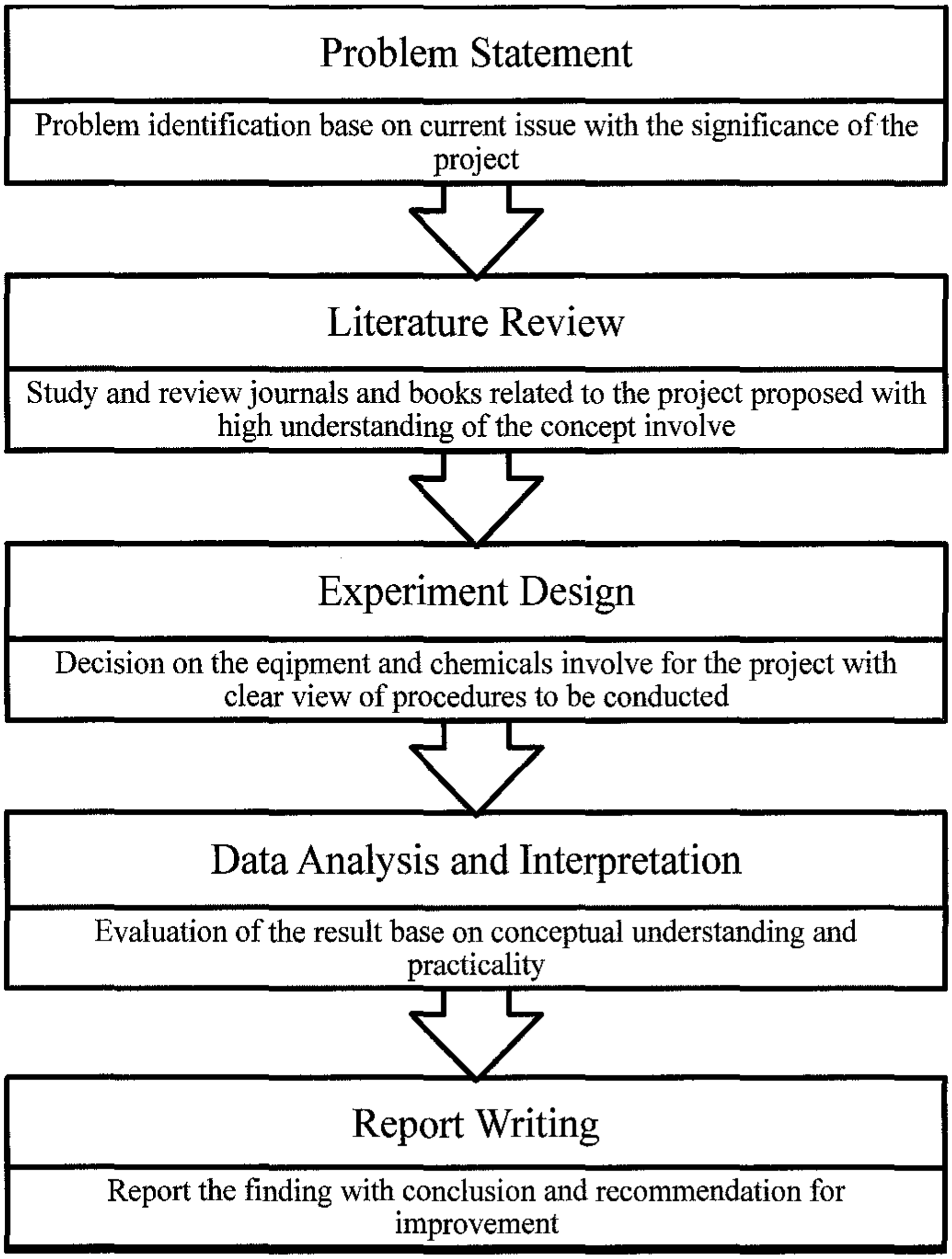
[a] 25% under microwave irradiation according to Rogers *et al.*[18] [b] Results of Rogers *et al.*[18] [c] Results of Wu *et al.*[16,19] [d] R = Me. [e] R = Et. [f] R = Bu.

Jurgen Vitz et. al. "Extended Dissolution Studies of Cellulose in imidazolium based ILs" 2009

CHAPTER 3

3. METHODOLOGY

3.1. RESEARCH METHODOLOGY



Problem Statement

Problem identification base on current issue with the significance of the project

Literature Review

Study and review journals and books related to the project proposed with high understanding of the concept involve

Experiment Design

Decision on the eqipment and chemicals involve for the project with clear view of procedures to be conducted

Data Analysis and Interpretation

Evaluation of the result base on conceptual understanding and practicality

Report Writing

Report the finding with conclusion and recommendation for improvement

3.2. EXPERIMENTAL SECTION

For this experiment, one cation is used with two different anions to have variety of ionic liquids with different data and analysis. The cation and anion that will be used is shown in the figure below:

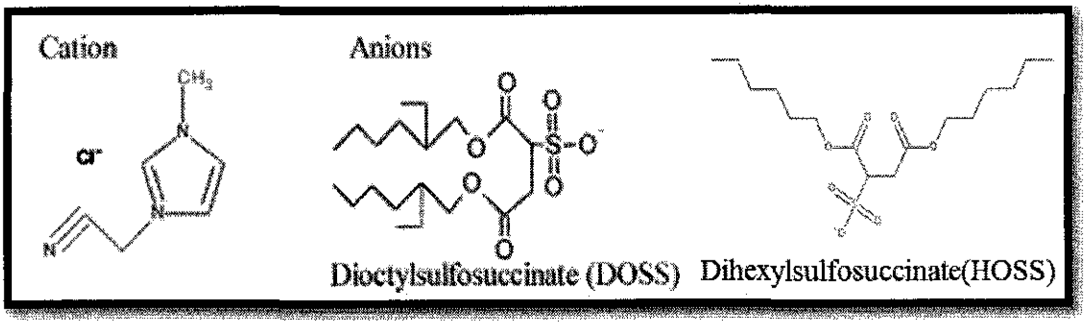


Figure 9 : Cation and Anions that will be used

The ionic liquids that had been synthesized are:

- 1-Methyl-3-Propionitrile Imidazole Diocylsulfosuccinate (DOSS)
- 1-Methyl-3-Propionitrile Imidazole Dihexylsulfosuccinate (HOSS)

3.2.1. Equipments and Materials

Equipment: Round-bottomed flask equipped with a heating oil bath, nitrogen inlet adapter, magnetic stirrer, reflux condenser flushed with dry nitrogen, vacuum oven, volumetric flask, rotary evaporator, Karl Fischer Titrator

Materials: Methylimidazole, 3-chloropropionitrile, methanol, Nitrogen gas, , sodium dioctyl sulfosuccinate, sodium dihexylsulfosuccinate (HOSS), acetone, ethyl acetate, diethyl ether, deionized water, dimethyl sulfoxide

3.2.2. Ionic Liquid Synthesis

These procedures are based on basic procedure outline in the journal **Densities, viscosities, and Refractive Index of 1-Hexyl-3-propanetrile Imidazolium Ionic Liquids Incorporated with Sulfonate-Based Anion** (Abobakr K. Ziyada *et al.* 2011). During the planning of the experiment, the procedures are based on the journal. The original procedures and planning can be divided into three main sections, which are:

- **SECTION 1:** Alkylation reaction – Preparation of Propanetrile Imidazole
- **SECTION 2:** Quartenization Reaction – Preparation of 1-Butyl-3-Propanetrile Imidazole Bromide.
- **SECTION 3:** Metathesis Reaction – Preparation of 1-Butyl-3-Propanetrile Imidazole DOSS, 1-Butyl-3-Propanetrile Imidazole DDS, 1-Butyl-3-Propanetrile Imidazole BS, 1-Butyl-3-Propanetrile Imidazole BMA, 1-Butyl-3-Propanetrile Imidazole TFMS.

However, during the start of the experiment, because insufficient chemical and limited time, the route have to be changed. The current synthesis consists of:

- **SECTION 1:** Quartenization Reaction – Preparation of 1-Methyl-3-Propionitrile Imidazole Chloride.
- **SECTION 2:** Metathesis Reaction – Preparation of 1-Methyl-3-Propionitrile Imidazole DOSS, 1-Methyl-3-Propionitrile Imidazole HOSS

Below are the detailed methodologies including the observation throughout the experiment:

SECTION 1: Quartenization Reaction – Preparation of 1-Methyl-3-Propionitrile Imidazole Chloride

1. The chemical involved is measured to the calculated volume (15ml of 3-Chloropropionitrile and 15.23ml of methylimidazole). The calculation is shown in the **appendix section** by assuming equimolar reaction. 30 ml methanol also measured which act as solvent for both chemical. The solubility test is required to ensure both of the chemical dissolved.
2. The reflux equipment is prepared
3. Both 3-chloropropionitrile and methylimidazole are dissolved in the methanol before mix them in the reflux.
4. 3-chloropropionitrile which already dissolved in the solvent, is inserted inside the reflux.
5. The reflux equipment is flushed with nitrogen gas to ensure that no air left inside. Ensure the water for condenser is flowing.
6. Methylimidazole which already dissolved in the solvent is inserted into the reflux by using syringe to prevent air from coming in to the reflux.
7. The solution is heated under reflux and nitrogen atmosphere at 50-55°C for 24 hours to ensure complete reaction.
8. The resulting compound is cooled to room temperature.
9. The resulting compound is washed with ethyl acetate for three times.
10. The remaining solvent is removed at 80°C by using Rotary Evaporator (Rotavap). The method of handling the Rotavap will be discussed in the discussion section.
11. The resulting compound is dried in vacuum oven for 72 hours to give **1-methyl-3-propionitrile imidazolium chloride [C_2CN Mim]Cl.**

SECTION 3: Metathesis Reaction – Anion Exchange

i. Preparation of 1-Methyl-3-Propionitrile Imidazole Dioctylsulfosuccinate (DOSS)

1. 13.34 g of Sodium DOSS (0.03 mole) and 5.15 g of [C_2CN Mim]Cl (0.03 mole) are measured.
2. Both chemical are dissolved in acetone. Before dissolving, ensured that both chemical dissolved in acetone by doing the solubility test.
3. The 1-methyl-3-propionitrile imidazolium chloride, [C_2CN Mim]Cl and sodium dioctylsulfosuccinate is mixed.
4. The mixture is stirred at room temperature for 48 hours.
5. The solid precipitate (NaCl) is separated by using filter paper.
6. The remaining solvent is removed by using Rotavap.
7. The remaining solvent is removed under vacuum at 80^{o}C for 24 hours.
8. The remaining solvent is washed by using ethyl acetate and diethyl ether.
9. The remaining solvent is removed under vacuum at 80^{o}C for 48 hours.
10. The product is 1-Methyl-3-Propionitrile Imidazole DOSS. The product are required to be sealed and put inside vacuum line to prevent water from dissolving into the ionic liquid.

ii. Preparation of 1-Butyl-3-Propanetrile Imidazole Dihexylsulfosuccinate (HOSS)

1. 4.53g of Sodium HOSS (0.012 mole) and 2 g of [C_2CN Mim]Cl (0.012 mole) are measured.
2. Both chemical are dissolved in methanol. Before dissolving, ensured that both chemical dissolved in methanol by doing the solubility test.
3. The 1-methyl-3-propionitrile imidazolium chloride, [C_2CN Mim]Cl and sodium HOSS is mixed.
4. The mixture is stirred at room temperature for 48 hours.
5. The solid precipitate (NaCl) is separated by using filter paper.

6. The remaining solvent is removed by using Rotavap.
7. The remaining solvent is removed under vacuum at 80°C for 24 hours.
8. The remaining solvent is washed by using ethyl acetate and diethyl ether.
9. The remaining solvent is removed under vacuum at 80°C for 48 hours.
10. The product is 1-Methyl-3-Propionitrile Imidazole DOSS. The product is required to be sealed and put inside vacuum line to prevent water from dissolving into the ionic liquid.

3.2.3. Observation and Discussion of the Ionic Liquids Synthesis

Mr. Zulhaziman, post graduate student under Dr. Cecilia, guided us throughout our experiment to ensure correct understanding of the method and also proper way to use the equipment. According to him, synthesis of the ionic liquids will require a long time to ensure that all the chemicals react and formed the bond properly. Ionic liquids are very sensitive especially to water because it can dissolve with water even with air droplet in the atmosphere very fast. So extra caution need to be taken into consideration especially after vacuum oven.

The basic calculation to calculate the amount of chemical used is:

$$\rho = \frac{M}{V}$$

$$mole = \frac{M}{MW} = \frac{\rho V}{MW}$$

ρ = Density g/cm^3

M = Mass, g

V = Volume, mL

MW = Molecular weight

1cm^3 = 1ml

The reaction is equimolar reaction where 1 mole of reactant will react with another 1 mole of other reactant. The calculation is very important in estimating chemical required and also the product. The detail calculation for the synthesis is shown in the **Appendix Section**.

Before starting the experiment, the first aspect that been stress out is safety in lab and handling the equipment. Before proceeding with the experiment, safety briefing is held by En Yusoff that touches all the important aspect of safety. Because the lab contains lot of hazardous material, safety is very important.

The first equipment used during the quartenization is Reflux. Reflux is important in order to ensure the reaction is under Nitrogen atmosphere and also prevent the loss of solvent. The nitrogen inlet provide continuous supply of nitrogen and condenser is to condense solvent which vaporize because of the heat used.

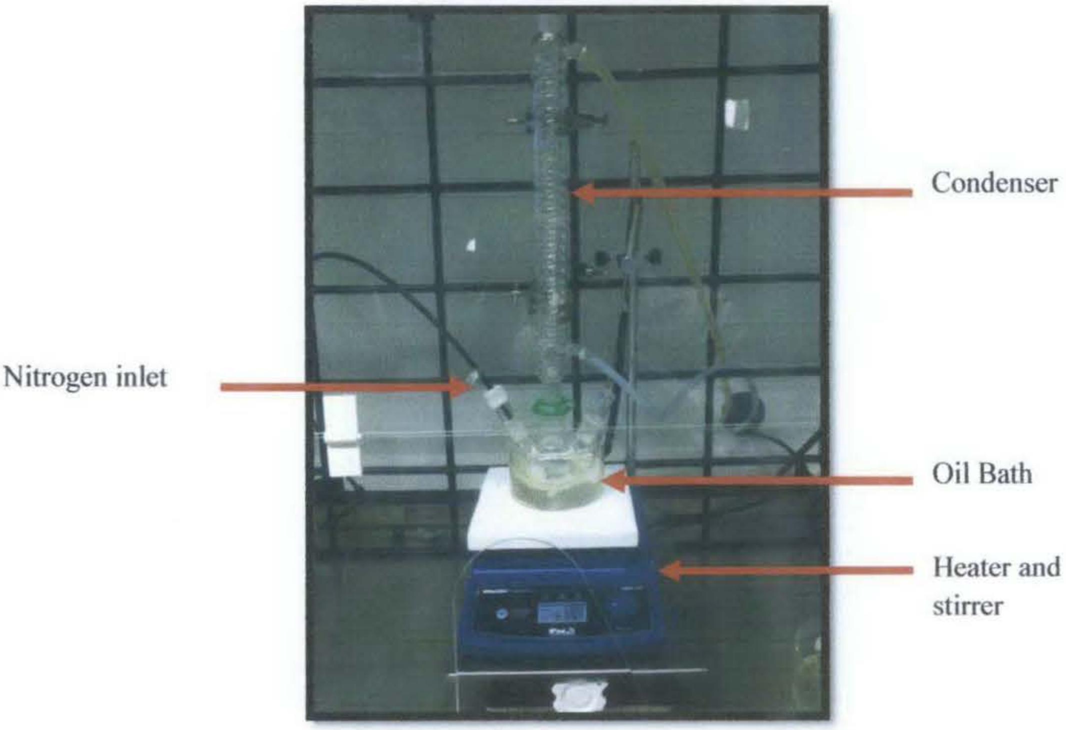


Figure: Reflux

Some of the important details that we need to take into consideration during quartenization are:

1. Heat the oil slowly and change the temperature one step at a time. Do not put straight away put the final temperature. This is because of the time taken for the oil bath to slow in case of overheating as heat capacity of oil is quite large.
2. Ensure that the thermal sensor is dipped inside the oil bath. If the thermal sensor is not dipped in the water, it will sense the air temperature. This will result in the continuous heating and may cause fire.
3. Do not use high flow for the water in the condenser. Because of small diameter tube is used, high flow will result in the water spilling from the pipe.

After leaving the reflux overnight, the 1-methyl-3-propionitrile imidazolium chloride, [C_2CN Mim]Cl is synthesized. However, the compound is not pure because of the leftover solvent during the quartenization. To remove all the solvent left, first, it needs to be washed by ethyl acetate. Then to fully remove the solvent, Rotary Evaporation (Rotavap) is used.

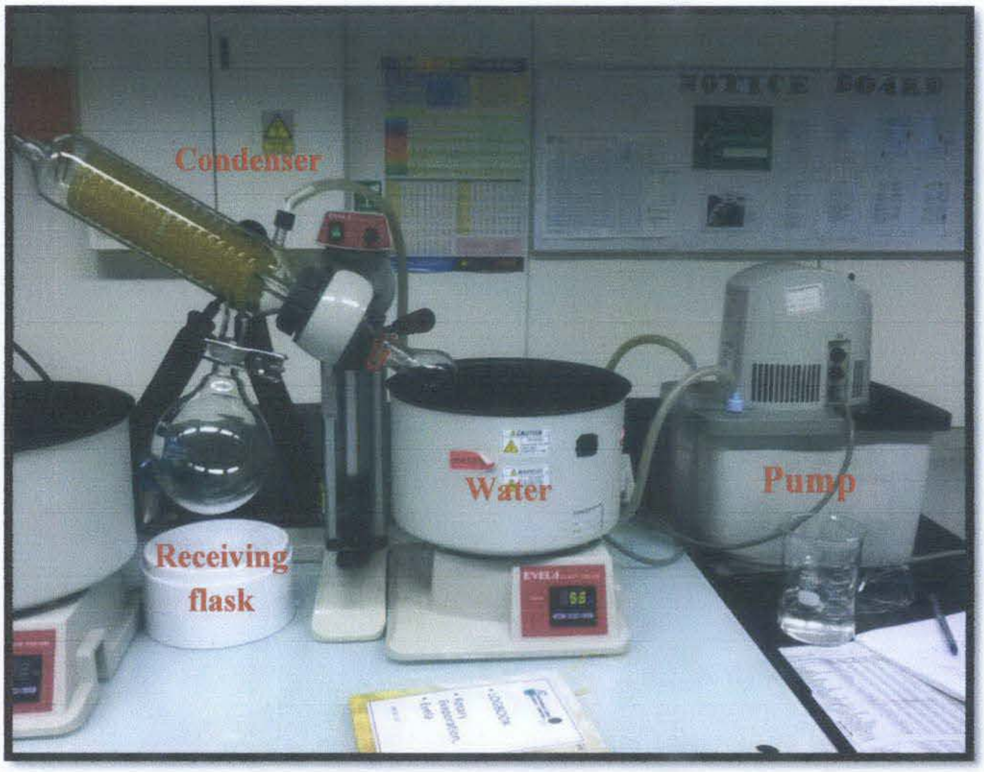


Figure 10: Rotary Evaporation

The functions of the equipment are explained below:

Water: Provide sufficient heat to evaporate solvent

Pump: To provide vacuum atmosphere for the solution

Condenser: To condense solvent that evaporated to become liquid form

Receiving Flask: Receive liquefied solvent after condenser

Rotary Evaporation uses the concept of different boiling point in separating the chemical. Because of low boiling point for solvent, whereas the boiling point of ionic liquids is high, it is easier to separate while retaining the desired product.

There are some important details that need to be taken into consideration in using this equipment:

1. Do not reduce the pressure very sudden to low pressure. Reduce the pressure step by step. By reducing the pressure very sudden, it will cause the compound to boil vigorously, causing the compound to enter the condenser.

2. Use clip to hold the round flask. Even though when the pump is on, the vacuum atmosphere prevent the flask from falling down, however, using clip will act as precaution to prevent worst case scenario.
3. When pulling out the flask, ensure that the pump is close or the valve is released. And pull the flask carefully, as it may be quite tight to pull.

The resulting ionic liquid is 1-methyl-3-propionitrile imidazolium chloride, [C_2CN Mim]Cl. It is viscous liquid and yellowish in colour. The compound can already be characterized as ionic liquid and have the characteristic of an ionic liquid.

Figure 11 : 1-methyl-3-propionitrile imidazolium chloride

The ionic liquid is the dried by putting it in the vacuum oven. This is to ensure all water is gone before we start the metathesis. The next step is metathesis or anion exchange

Figure 12 : Metathesis in progress

Metathesis is quite simple and easy to do. The first part is, to ensure that the ionic liquid and the Sodium DOSS and Sodium HOSS dissolve with the solvent. For the first metathesis, which used Sodium DOSS, acetone was chosen because it can dissolve both ionic liquid and the salt. Moreover, the solvent will not dissolve the precipitate that will come up after the metathesis. The chemical is than dissolved and mix. The mixture is then stirred for 48 hours to ensure full reaction occurred. Precipitate will come out resulting from the anion exchange which then produced NaCl or Sodium Chloride. To filter out the salt, filter paper is used to separate the ionic liquid and the salt. The apparatus is shown below:

Figure 13 : Filtering remaining NaCl

After filtering, the remaining compound still has the solvent that being used for the metathesis. To remove the remaining solvent, Rotavap is used. Then the compound is placed inside the vacuum oven to remove all the water content. After 24 hours, the compound is washed with ethyl acetate to ensure all the solvent is removed before placing it back in vacuum oven for 48 hours.

Figure 14 : 1-methyl-3-propionitrile imidazolium DOSS

The products of metathesis are **1-Methyl-3-Propionitrile Imidazole Dioctylsulfosuccinate (DOSS)** and **1-Methyl-3-Propionitrile Imidazole Dihexylsulfosuccinate (HOSS).** The ionic liquid for the first metathesis is yellowish and very viscous. For the second metathesis, it is still on going because of several problems met in synthesizing the ionic liquid.

3.2.4. Characterization and Properties Measurement

The methods for characterizing and properties measurement are also highlighted in the journal by Abobakr K. Ziyada *et. al* (2011). It is also based on the availability of the equipment in University Technology PETRONAS's Ionic Liquids Laboratory.

i. FTIR-ATR, NMR and Elemental Analysis

The synthesized ionic liquids are characterized by using Fourier transformation infrared (FTIR) spectra. The then are recorded in Shimadzu FTIR-8400S Fourier Transform Infrared Spectrometer (FTIR) in mid region (4000 cm-1 to 400 cm-1) using Attenuated Total Reflectance (MIRacle ATR) measurement mode. To determine the individual percentage of elements, a CHNS-932 (LECO instruments) elemental analyzer will be used. For determining the 1H NMR spectra of the ionic liquids, a Bruker Avance 300 spectrophotometer is used.

ii. Water and Chloride Content

For determining water content of the ionic liquids, a coulometric Karl Fisher titrator (DL 39 Mettler Toledo) with CombiCoulomat fritless Karl Fischer reagent (Merck) is used. The measurement for each ionic liquid will be made in triplicate, and average values will be reported.

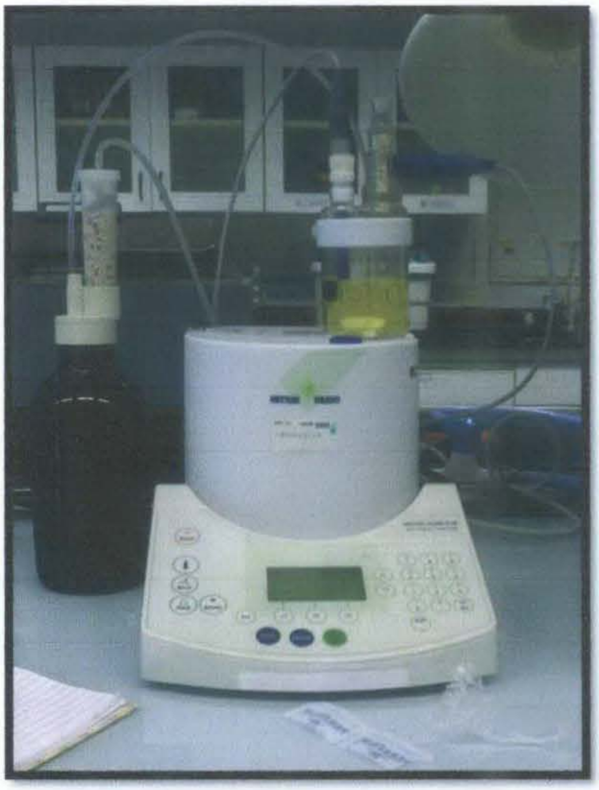


Figure 15 : Karl Fischer Titrator

For the time being, the characterization that managed to be done is the water content measurement. Small droplet of ionic liquid needed to be collected by using syringe, and weight to get the initial weight. After dropping the droplet into the equipment, the weight of the syringe is once again weighted to get the amount of ionic liquid inserted. Then, the value are required to be key in into the data panel of the equipment. After a few minutes, the water content data is shown.

Bromide content measurements will be conducted by ion chromatography (Metrohm model 761 Compact IC) with (150 x 4.0)mm analytical column (Metrosep A Supp 5-150) and (5.0 X 4.0)mm guard column (Metrosep A Supp 4/5). The measurement will be analyzed using Metrodata IC Net 2.3 software.

iii. Thermogravity Measurements

The start and onset temperatures of the present synthesized ionic liquids will be determined by using Perkin-Elmer, Pyris V-3.81. The samples will be placed in aluminum pans under nitrogen atmosphere at a heating rate of 10°C˙min-1.

iv. Densities and Viscosities Measurements

The density and viscosity of all ionic liquids will be measured in a temperature range (293.15 – 353.15) K at atmospheric pressure using a Stabinger viscometer (Anton-Paar model SVM3000). The temperature is controlled to within ± 0.01°C. The repeatability of measurements are (5.3 10^{-4} g˙cm^{-3} and 0.75 % for density and viscosity, respectively. The standard calibration fluid provided by the supplier will be used for the calibration of the viscometer followed by the validation of the measurements using ionic liquids with known densities and viscosities.

3.2.5. Biomass Dissolution Testing

After finish synthesizing and characterizing the ionic liquids that will be used, dissolution of the particular sago waste will be done. Several step need to be fulfilled before the dissolution. The simplified steps are shown in the figure below:

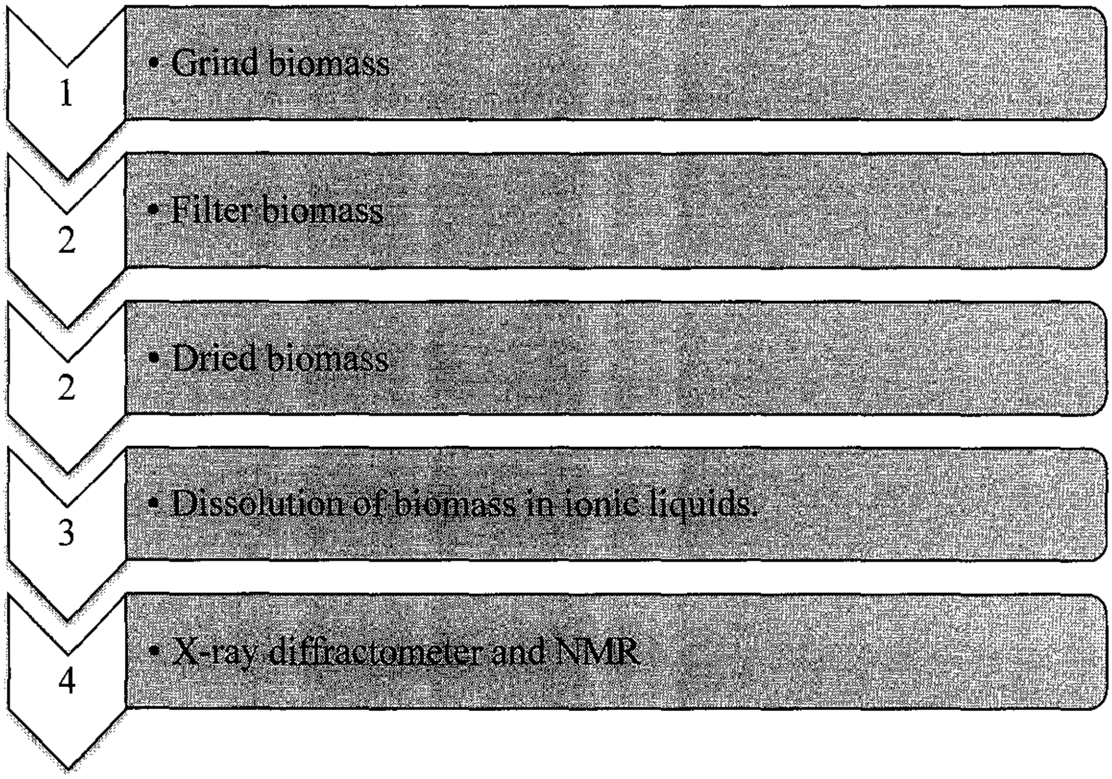


Figure 16: Simplified Steps of Dissolution Testing

Dissolution of biomass in ionic liquids

The procedures for dissolution of biomass are based on the methodology by *Jurgen Vits et. al.* (2009) in his journal, "**Extended Dissolution Studies of Cellulose in Imidazolium Based Ionic Liquids**". The method is as follow:

1. A small flask is filled with 1g of [C_2CNMim] [DOSS], weighted on a macro balance.
2. The ionic liquid is heated for 30 min at 120°C in oil bath to remove the water content.
3. Sago waste is added (5 wt%) and then the mixture is mixed with magnetic stirrer at 100°C for a 20 hours.
4. After finish dissolving the sago, the material needed to be washed and separated between dissolved and undissolved sago.
5. The sample is dissolved with 10ml of Dimethyl Sulfoxide (DMSO), stirred at 400 rpm for 30 mins.
6. Empty centrifuge tube is weighted. The sample is filled in the tube.
7. The sample is the centrifuged with 1500 rpm for 15 mins.
8. The resulting sample is in two phase. The sample is separated between the two phases and the liquid phase is kept for future analysis.
9. Step 5 to 8 is repeated once with DMSO and another time with distilled water.
10. The centrifuge tube with the undissolved sample is kept in oven for 2 days at 80°C.
11. The mass of the tube with undissolved dried sample is weighted.
12. Weight percent is calculated
13. The dissolved sample is the vacuum filtered to separate the sago.
14. FTIR Analysis is done to confirm the content of the sample.

CHAPTER 4

4. RESULTS AND DISCUSSION

4.1. IONIC LIQUID SYNTHESIS

Throughout the project, total of three different type of ionic liquids have been synthesized by procedure mentioned in previous chapter. 1-methyl-3-propionitrile imidazolium chloride was prepared by using quartenization whereas 1-methyl-3-propionitrile imidazolium dioctylsulfosuccinate and 1-methyl-3-propionitrile imidazolium dihexylsulfosuccinate was synthesized by metathesis. The ionic liquids and their respective characteristics are as follows:

No	Image	Sample	Colour	Physical State
1		1-methyl-3-propionitrile imidazolium chloride	Yellowish	Viscous liquid
2		1-methyl-3-propionitrile imidazolium dioctylsulfosuccinate	Yellowish	Very viscous liquid
3		1-methyl-3-propionitrile imidazolium dihexylsulfosuccinate	Yellowish	Very viscous liquid

4.1.1. Quartenization

4.1.1.1. Synthesis of 1-methyl-3-propionitrile imidazolium chloride

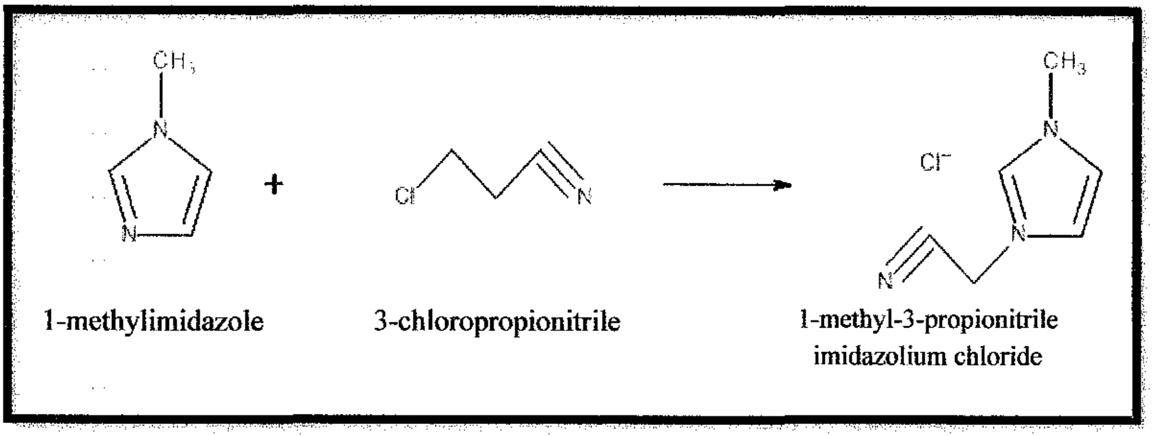


Figure 17 : Reaction Scheme of Quartenization

4.1.1.2. Findings

1-methylimidazole is yellowish in colour while 3-chloropropionitrile is colourless. This gives the solution slight yellow in colour after reaction of both reactants. The liquid also categorized as viscous liquid. The product is used for metathesis.

4.1.1.3. Discussion

The quartenization is complete and success. However, because of lack of chemical, limited amount of ionic liquid can be synthesized. In the future, the availability of the chemical plays important roles in planning an experiment and need to be taken into consideration by double checking it.

The ordered chemical should be done efficiently as with limited time, process such as ionic liquid synthesize which required a long time to finish is required to be done early.

4.1.2. Metathesis

4.1.2.1. Synthesis of 1-methyl-3-propionitrile imidazolium DOSS

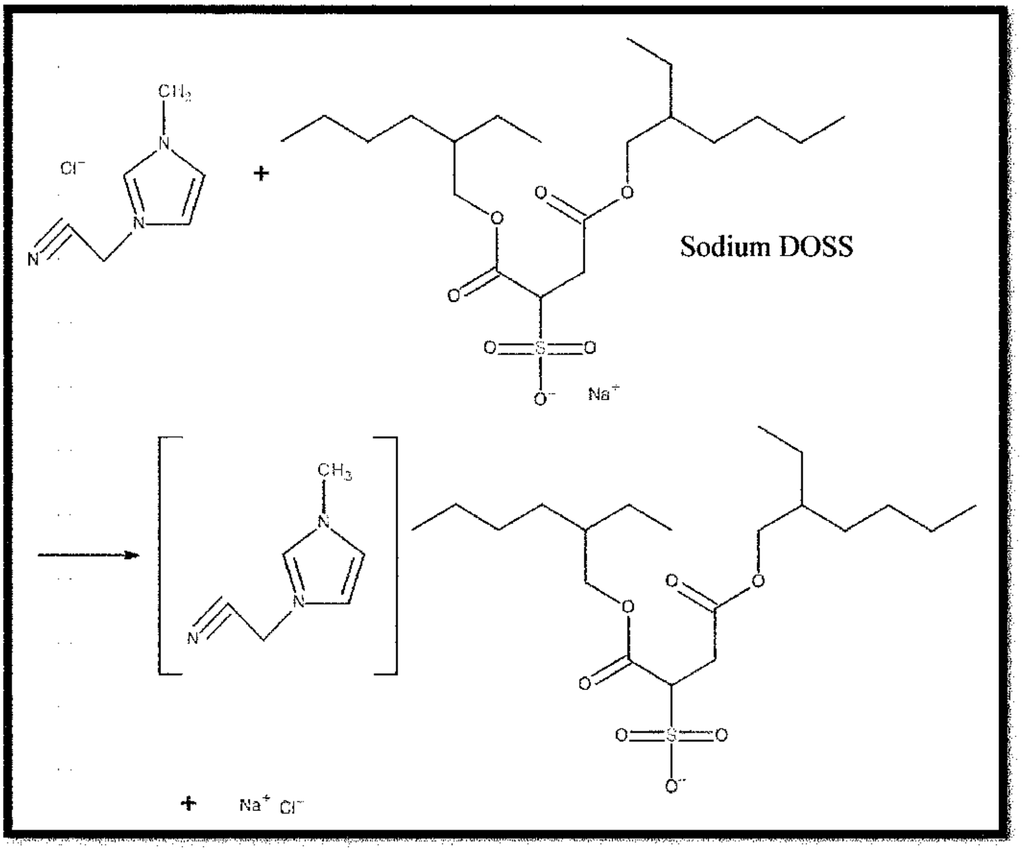


Figure 18 : Reaction Scheme Metathesis 1

Sodium dioctylsulfosuccinate is in solid form in which needed to be dissolved in acetone first before starting the metathesis. 1-methyl-3-propionitrile imidazolium chloride is yellowish in colour. Thus, the product which is 1-methyl-3-propionitrile imidazolium DOSS is yellowish in colour and the structure is very viscous. The reaction also produces white precipitate that needed to be filtered

4.1.2. Metathesis

4.1.2.1. Synthesis of 1-methyl-3-propionitrile imidazolium DOSS

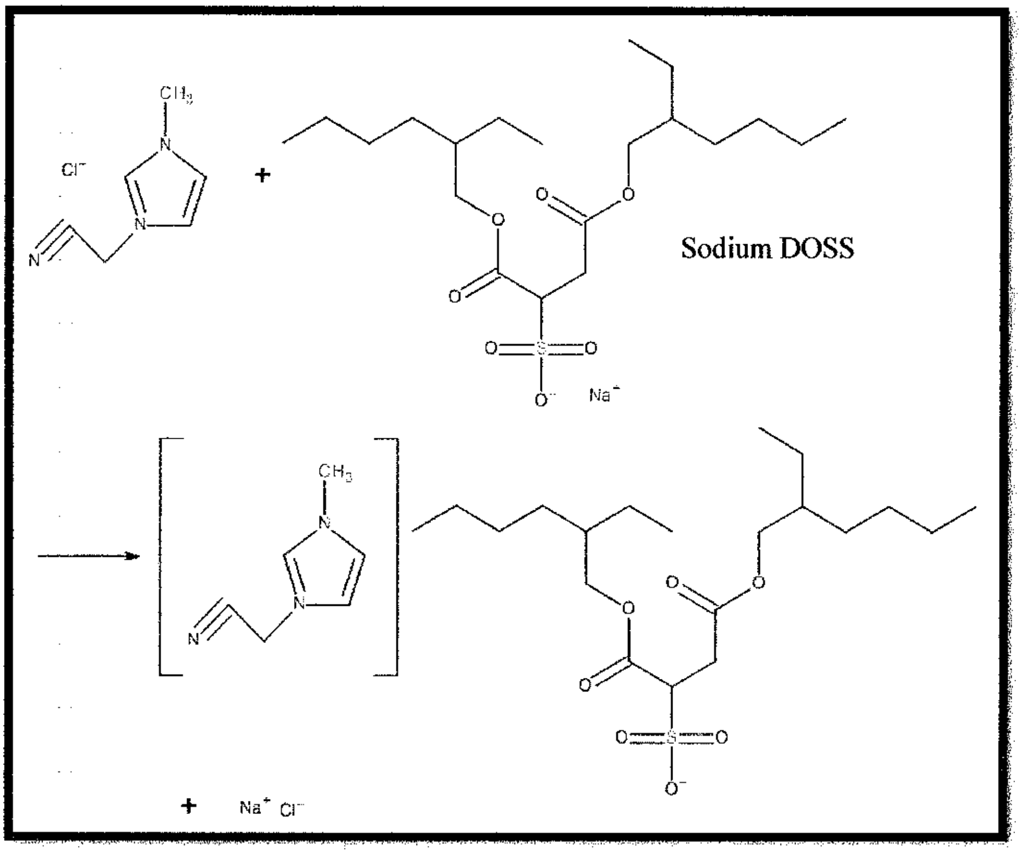


Figure 18 : Reaction Scheme Metathesis 1

Sodium dioctylsulfosuccinate is in solid form in which needed to be dissolved in acetone first before starting the metathesis. 1-methyl-3-propionitrile imidazolium chloride is yellowish in colour. Thus, the product which is 1-methyl-3-propionitrile imidazolium DOSS is yellowish in colour and the structure is very viscous. The reaction also produces white precipitate that needed to be filtered

4.1.2.2. Synthesis of 1-methyl-3-propionitrile imidazolium dihexylsulfosuccinate

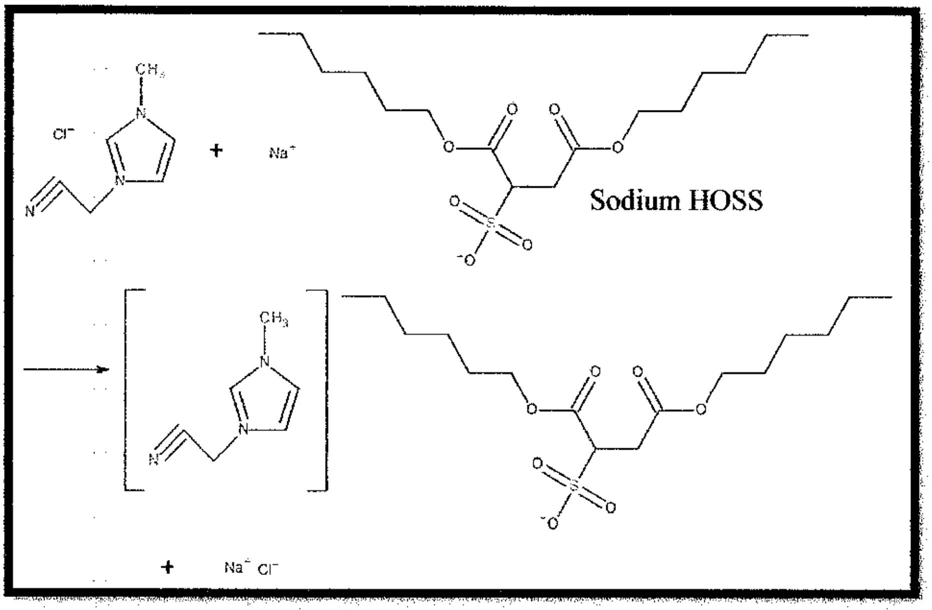


Figure 19 : Reaction Scheme Metathesis 2

Sodium HOSS is in liquid form, but still to ensure the perfect reaction, the reactant is mixed with the solvent. 1-methyl-3-propionitrile imidazolium chloride is yellowish in colour. Thus, the product which is 1-methyl-3-propionitrile imidazolium HOSS is yellowish in colour and the structure is very viscous. The reaction also produces white precipitate that needed to be filtered.

4.1.2.3. Discussion

The product of the first metathesis can be considered a success without much problem and difficulty. Because the product seems to be very viscous, the metathesis is success. The expected product of the metathesis is 1-methyl-3-propionitrile imidazolium DOSS and 1-methyl-3-propionitrile imidazolium HOSS with sodium chloride (NaCl). The NaCl was represented by the white precipitate that being filtered.

4.2. CHARACTERIZATION

4.2.1. Water Content Measurement

The first characterization that been done is water content measurement. By using Karl Fischer equipment to measure the water content, the result is as followed.

Table 4: Water Content

No	**Sample**	**Test No**	**Amount (g)**	**Water Content**	
				PPM	**%**
1	1-methyl-3-propionitrile imidazolium DOSS	1	0.0276	359.46	0.04
		2	0.0239	329.85	0.03
		3	0.0241	526.33	0.03
AVERAGE				**405.20**	**0.04**
No	**Sample**	**Test No**	**Amount (g)**	**Water Content**	
				PPM	**%**
1	1-methyl-3-propionitrile imidazolium HOSS	1	0.0313	567.31	0.06
		2	0.0325	513.20	0.05
		3	0.0224	621.31	0.06
AVERAGE				**567.27**	**0.06**

The acceptable value for water content for ionic liquid is below 0.05% and 500 PPM. From the table, the value for the water content in the [C_2CNMim][HOSS] is higher than the acceptable value. This may cause from several occasion that will be discuss further in the next section.

4.2.1.1. Discussion

The value for the water content is larger than the acceptable value for ionic liquids. This may cause by several reasons:

i. After coming out from the vacuum oven, some of water from the atmosphere may be absorbed by the ionic liquid as the liquid is still hot, thus increasing the hygroscopic effect of the ionic liquid.
ii. While waiting for the ionic liquid to be cooled to room temperature, the vessel is seal with the cover and also parafilm only. The protection might be not good enough to prevent some water from the atmosphere to be absorbed into the ionic liquid.
iii. During the testing, the ionic liquid had to be exposed to take the sample. Thus allowing water to be absorbed into the ionic liquid/

The result can be better improved with a certain improvement of the methodology. For example, after coming out from the vacuum oven, the samples are required to be taken as soon as possible into the drykeeper where the humidity is very low. This can allowed the ionic liquid to be cool to room temperature without allowing contact to atmospheric moisture.

4.2.2. Chloride Content

Chloride content measurement is done by using the Ion Chromatography (IC) equipment. The purpose is to determine the content of leftover chloride anion inside the ionic liquid. The result for each ionic liquid is as follow

[C_2CNMim] DOSS

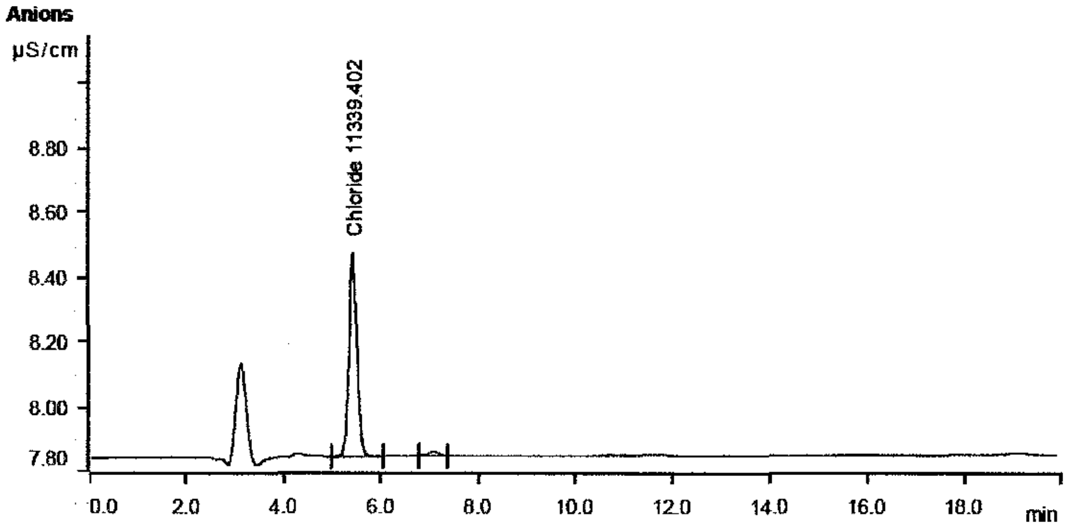


Figure 20 : Graph for Chloride Content of [C_2CNMim][DOSS]

Table 5 : Result of IC [C_2CNMim][DOSS]

Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration ppm	Component name
1	5.420	0.1163	0.630	11339.402	Chloride
2	7.073	0.0027	0.013	invalid	

The result for [C_2CNMim] [DOSS] shows a slightly higher chloride content with 11339.402 ppm.

[C_2CNMim] HOSS

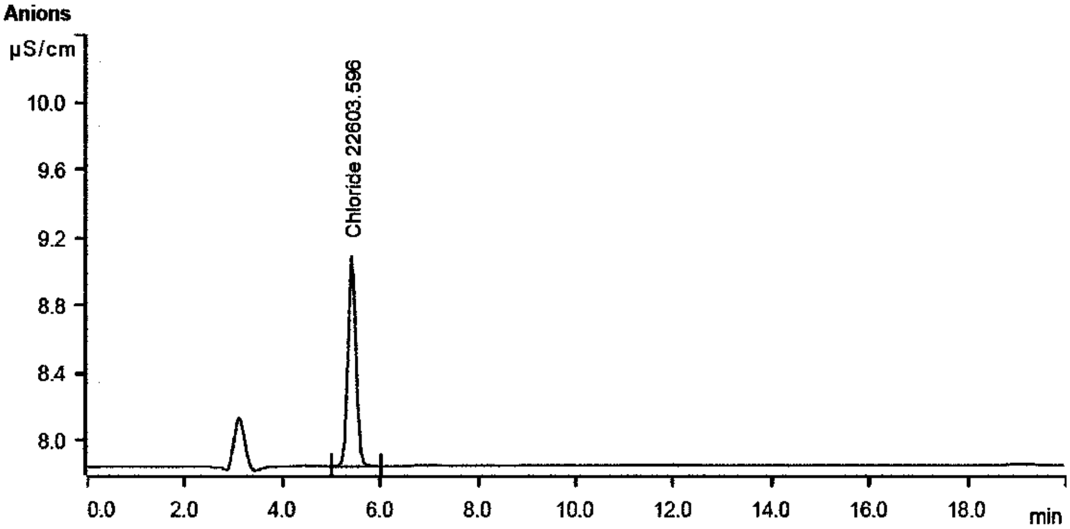


Figure 21 : Graph of Chloride Content for [C_2CNMim][HOSS]

Table 6 : Result of IC [C_2CNMim][HOSS]

Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration ppm	Component name
1	5.413	0.2319	1.244	22603.596	Chloride

The result for [C_2CNMim] [DOSS] shows a slightly higher chloride content with 22603.596 ppm.

4.2.2.1. Discussion

By using Ion Chromatography (IC), the chloride content for both ionic liquid can be known. From the result of IC, the value of chloride content is quite high. It is because of the unreacted chloride anion during metathesis reaction. This chloride can then be future removed by washing it with ethyl acetate that can dissolve the chloride anion thus removing it.

4.2.3. TGA Analysis

TGA Analysis is to determine the decomposition temperature of the ionic liquid. This is essential to determine the maximum temperature the ionic liquid can be used before it started to decompose. The parameter that being used for both testing are temperature from 50°C to 500°C, with increase of 10°C per min and Nitrogen as inert. The result for TGA analysis is as follow:

[C$_2$CNMim][DOSS]

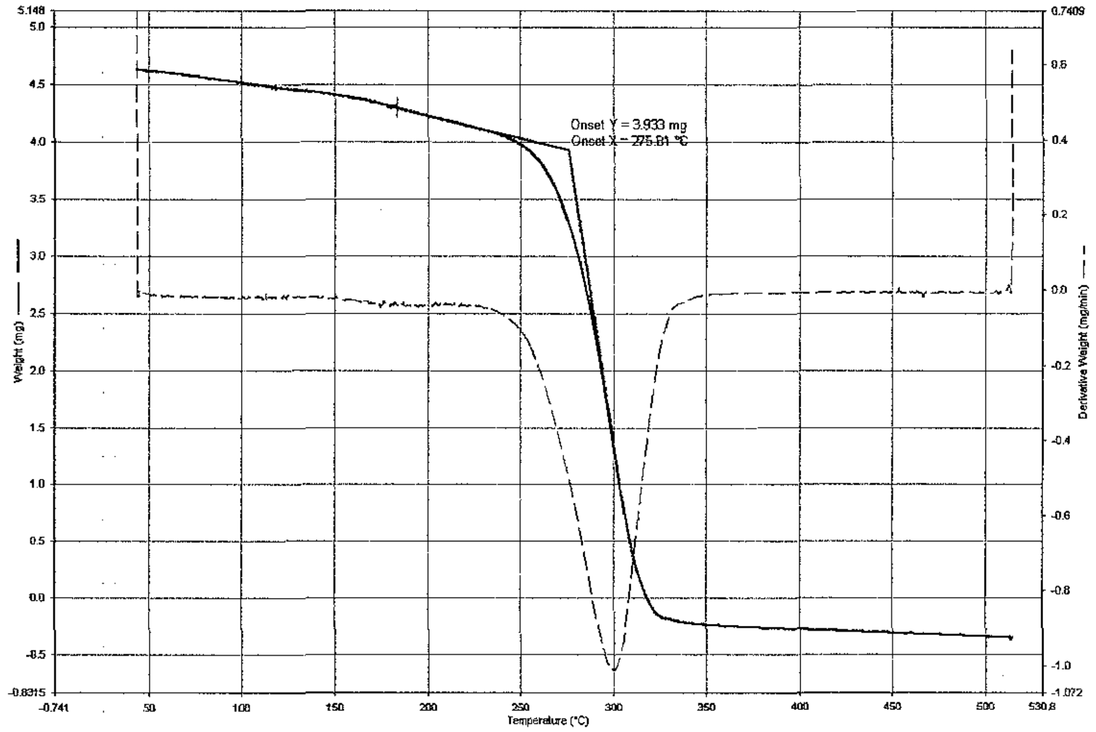


Figure 22 : TGA Analysis for [C$_2$CNMim] [DOSS]

Decompose Temperature = 275.81°C

[C_2CNMim][HOSS]

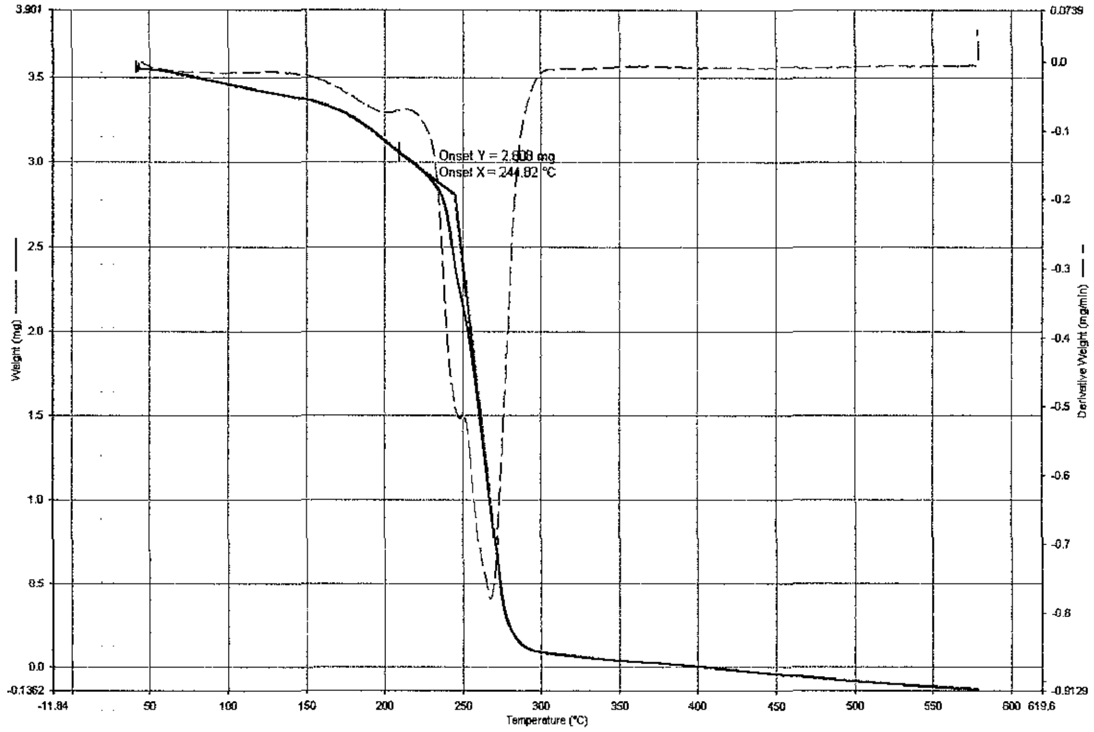


Figure 23 : TGA Analysis for [C_2CNMim] [HOSS]

Decompose Temperature = 244.82°C

4.2.3.1. Discussion

By using thermogravimetric analysis (TGA), we can get the temperature when the ionic liquids started to decompose. It shows changes in weight in relation to change in temperature. The graph shows a declining trend as soon as the analysis starts. This is because of the water content inside the ionic liquid is decomposed as the temperature increased. Then, for ionic liquid, it started to decompose when the dotted line graph start to decrease. It shows the anion that decomposed during the process. Then, by taking tangent for the graph, the value for decomposition temperature can be measured.

4.2.4. Viscosity Analysis

Because of the unavailability of Stabinger viscometer, an alternative viscometer is being used. Brookfield CAP+2000 Viscometer is used. The concept behind the equipment is using shear rate to calculate the viscosity. By testing with different type of spindle, the best data with the highest relevancy is chosen. The result for viscosity analysis is as followed:

Table 7 : Viscosity Analysis

Ionic liquid	Viscosity (cp)
[C_2CNMim] [DOSS]	2572.4
[C_2CNMim] [HOSS]	3196.2

The resulting ionic liquid is supposed to have higher viscosity compared to the achieved value. But because of increasing water content in the ionic liquid, the ionic liquid become less viscous, thus effecting the result.

4.2.5. RAMAN Analysis

4.2.5.1. Metathesis with Na DOSS

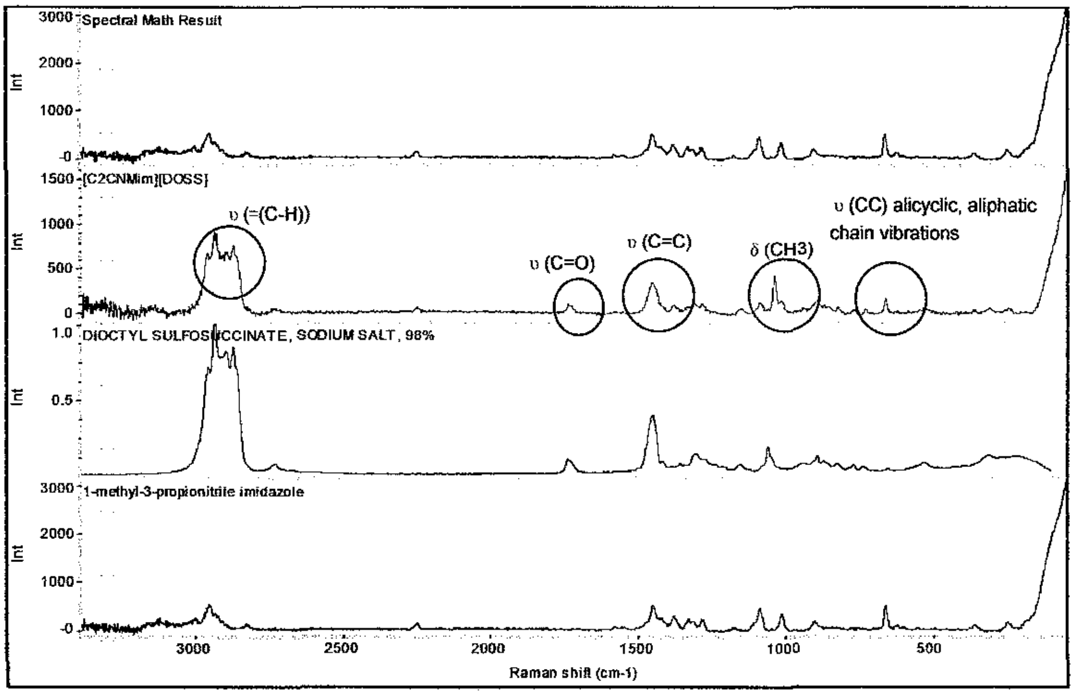


Figure 24 : Raman Analysis for [C_2CNMim] [DOSS]

The above result shows the Raman analysis for [C_2CNMim] [DOSS] and its reactant. The top graph shows the synthetic spectral math result from using 1-methyl-3-propionitrile imidazole taken from previous quartenization, and Na DOSS from the library provided in the software. The synthetic result is the estimated result predicted by using the software. The resulting ionic liquid synthesized is appromixately similar with the synthetic ionic liquid generated by Raman.

The first peak shows functional group of υ(=(C-H)), which proves the existent of the double bond in the ionic liquid. Then, the second part, shows the existence of υ(C=O) functional group, which proven the existence of DOSS anion in the ionic liquid. The third shows existence of υ(C=C) as from the theoretical structure, contains number of (C=C). The fourth peak shows the existence of δ(CH3) in the ionic liquid. The last peak shows the existence of υ(CC) alicyclic, aliphatic chain vibrations proving that imidazolium existed in the ionic liquid. From here, it is proven that the result of the experiment went as expected and producing [CH2CNMim] [DOSS] ionic liquid.

4.2.5.2. Metathesis with Na HOSS

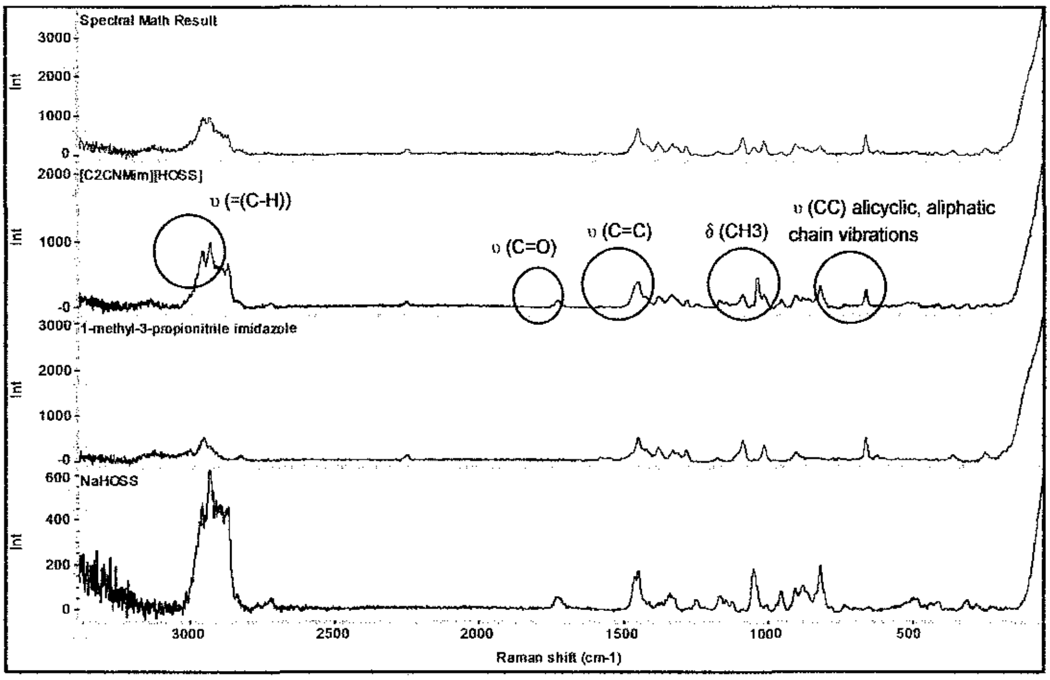


Figure 25 : Raman Analysis for [C_2CNMim] [HOSS]

The above result shows the Raman analysis for [C_2CNMim] [HOSS] and its reactant. The top graph shows the synthetic spectral math result from using 1-methyl-3-propionitrile imidazole taken from previous quartenization, and Na HOSS from the library provided in the software. The synthetic result is the estimated result predicted by using the software. The resulting ionic liquid synthesized is appromixately similar with the synthetic ionic liquid generated by Raman.

Basically, the structure of both DOSS and HOSS will be almost similar in term of bonding and functional group. The different of both anion is the formula. For DOSS, the formula is $C_{20}H_{37}NaO_7S$, whereas HOSS, $C_{16}H_{29}NaO_7S$.The first peak shows functional group of υ(=(C-H)), which proves the existent of the double bond in the ionic liquid. Then, the second part, shows the existence of υ(C=O) functional group, which proven the existence of DOSS anion in the ionic liquid. The third shows existence of υ(C=C) as from the theoretical structure, contains number of (C=C). Lastly, the peak shows the existence of δ(CH3) in the ionic liquid. The last peak shows the existence of υ(CC) alicyclic, aliphatic chain vibrations proving that imidazolium existed in the ionic liquid. From here, it is proven that the result of the experiment went as expected and producing [CH2CNMim] [HOSS] ionic liquid.

4.3. SAGO WASTE DISSOLUTION TESTING

4.3.1. Undissolved Sample Testing

By varying the temperature and concentration of the sago waste, the following result is achieved:

[C_2CNMim][DOSS]

Table 8 : [C_2CNMim] [DOSS] -Varies Temperature

Bottle No.	Temp. (°C)	Conc. (%)	Weight (g)				Percent undissolved	Percent dissolved
			Initial sago	Tube	Tube after drying	Undissolved sago		
1	100	5%	0.051	6.39	6.41	0.020	39.22	60.78
2	105	5%	0.051	5.58	5.59	0.010	19.61	80.39
3	120	5%	0.050	6.34	6.35	0.008	16.00	84.00
4	130	5%	0.051	6.34	6.35	0.007	14.12	85.88

Table 9 : [C_2CNMim] [DOSS] - Varies Sago Concentration

Bottle No.	Temp. (°C)	Conc. (%)	Weight (g)				Percent undissolved	Percent dissolved
			Initial sago	Tube	Tube after drying	Undissolved sago		
5	130	7%	0.070	5.56	5.58	0.025	35.00	65.54
6	130	9%	0.092	6.03	6.06	0.032	34.46	65.00
7	130	10%	0.102	5.56	5.61	0.055	53.82	46.18

[C_2CNMim][HOSS]

Table 10 : [C_2CNMim] [HOSS]

Bottle No.	Temp. (°C)	Conc. (%)	Weight (g)				Percent undissolved	Percent dissolved
			Initial sago	Tube	Tube after drying	Undissolved sago		
8	130	5%	0.05	6.46	6.474	0.014	28.00	72.00

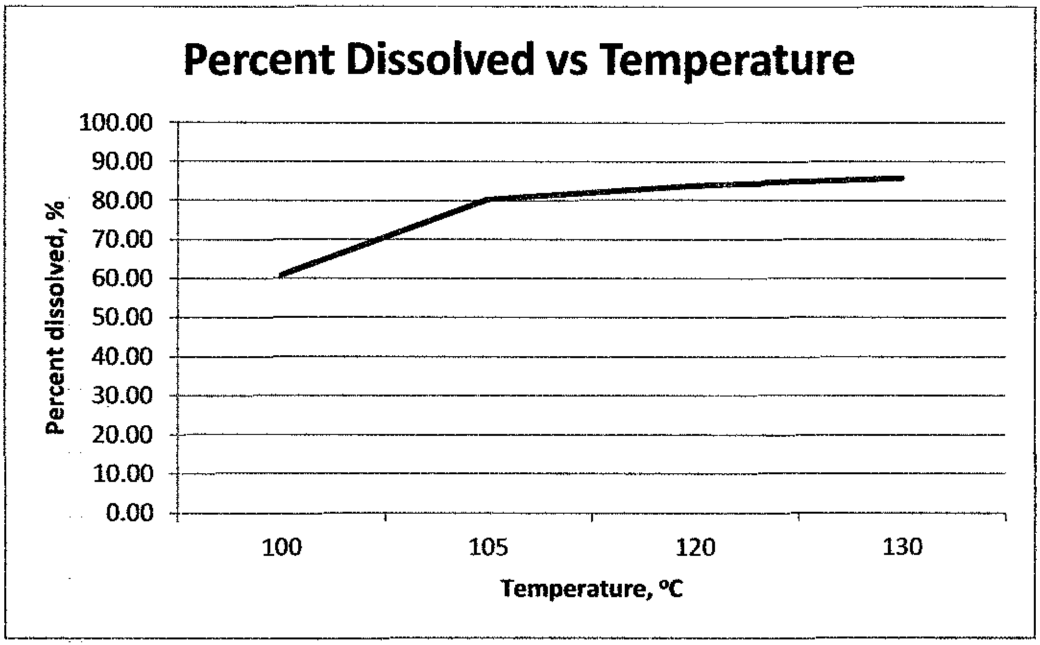


Figure 26 : [C_2CNMim] [DOSS] - Percent Dissolved vs. Temperature

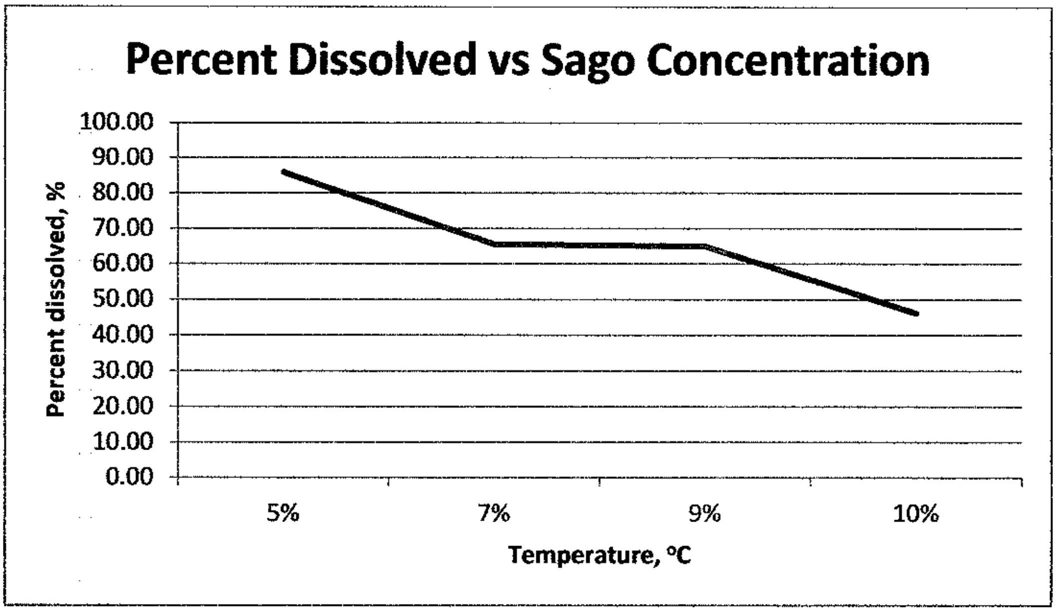


Figure 27 : [C_2CNMim] [DOSS] - Percent Dissolved vs. Sago Concentration

4.3.1.1. Discussion

From the result obtained above, both ionic liquids have the capability to dissolve the sago waste. The manipulated variables that are used for the testing is:

Temperature : 100°c, 105°C, 120°C, 130°C

Sago concentration : 5%, 7%, 9%, 10%

The reason these values are chosen because of the experiment is to have preliminary study to dissolution of sago biomass towards ionic liquid. Moreover, there are other studies on going where sago biomass is being tested with other conventional ionic liquids. The value for the variables is chosen based on the experiment done by them where they are still waiting for their thesis to be published.

From the result of the experiment, it shows that by increasing temperature, we can also increase the dissolution of the sago waste. For a solid to dissolves in a liquid, a change in the physical state of the solid analogous to melting took places. Heat is required to break the bonds holding the molecules in the solid together. By adding more heat, it will help facilitates the dissolving reaction by providing energy to break bonds in the solid phase of the sago waste.

For the relation between sago concentration and percent dissolve, it shows that by increasing the concentration of sago, it will reduce the dissolution of sago waste. this occurred because of the equilibrium state between dissolved and undissolved solute. As dissolution occurred, it reached a saturation point where no solute will dissolve. So it reduces the amount of sago dissolved in the ionic liquid.

For the second ionic liquid, which is [C_2CNMim] [HOSS], because of insufficient chemical, only one experiment is managed to be done. By taking the temperature of 130°C and sago concentration of 5%, we can observed that the dissolution of biomass is slightly lesser compared to the [C_2CNMim] [DOSS]. Theoretically, longer side chain chemical will produce lesser dissolution. However, these may be the result of the higher water content and also chloride content, which affected the dissolution.

From all the result that managed to be gathered, we can conclude that for both [C_2CNMim] [DOSS] and [C_2CNMim] [HOSS] are capable to dissolve biomass. With further detailed study and experiment, these ionic liquids can be futher improved in term of the efficiency and cost saving.

4.3.2. Dissolved Sample Testing

The dissolved sample of the experiment needed to be analyzed to confirm the present of the cellulose inside the ionic liquid. This can further prove the effectiveness of the ionic liquid. According to the earlier plan for the analysis, FTIR are supposed to be used. However, because of the unavailability of the equipment, only RAMAN analysis was managed to be done. However, for the dissolved sample, after testing it several times, the result is unacceptable and cannot be used as the data to be analyzed. This is because of the fluorescent effect of the chemical, it emit photons at longer wavelength when hit by visible light. Even by using photobleaching, which is a process where the excitation laser is focused on the sample and burns off impurities to decrease the fluorescent, however, the fluorescent effect is still affecting the results. Figure 28 below shows the fluorescent effect on the RAMAN Analysis for the dissolved sample.

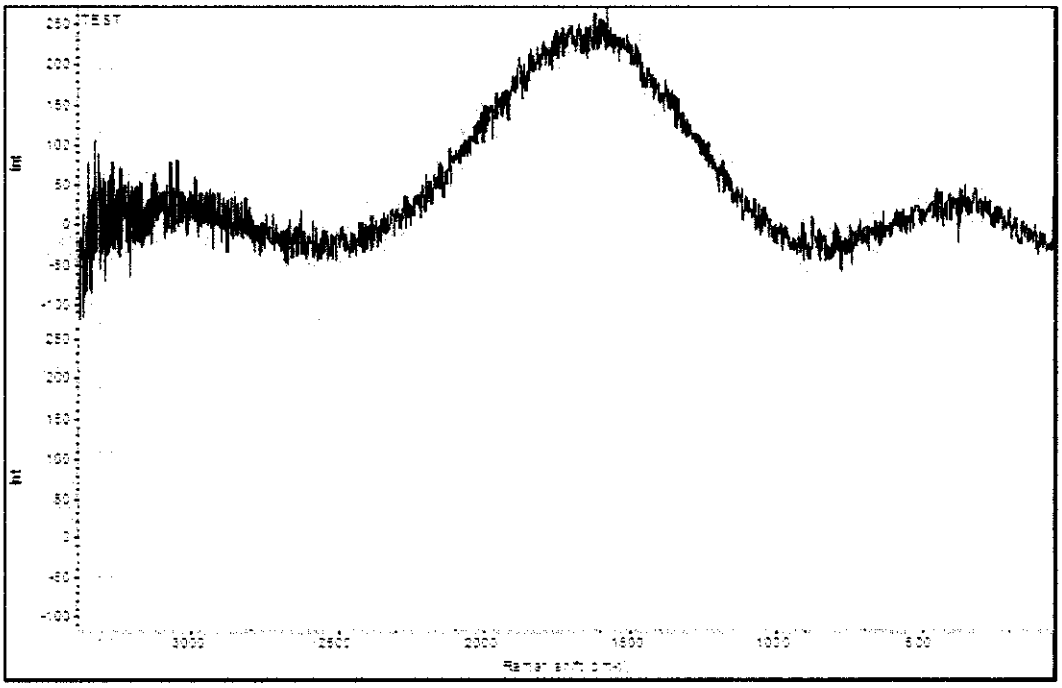


Figure 28 : RAMAN Analysis on Dissolved Sample

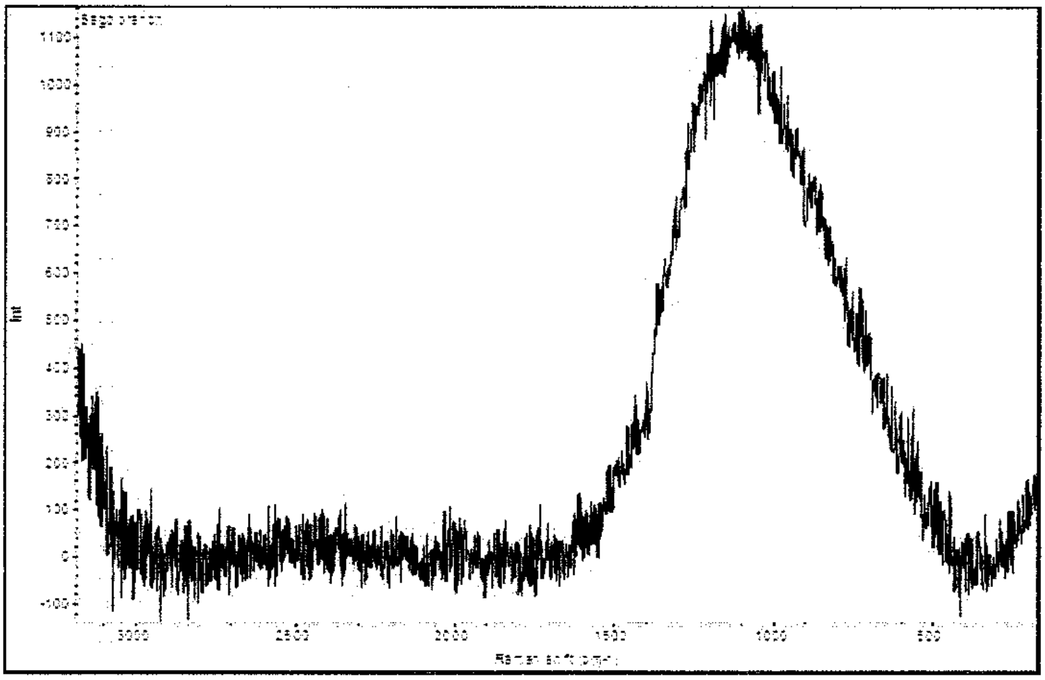


Figure 29 : RAMAN Analysis on Sago Waste Sample

The above figure shows the analysis on the sago waste sample. It also shows that the fluorescent effect also appeared on the sago waste sample. In order to further increase the reliability of the result of this experiment, analysis from FTIR is very essential, and can be considered as one of the recommendation for this project.

4.4. GANTT CHART AND KEY MILESTONE

Table 11: Gantt Chart for Experiment

No	Activities	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1.	Lab Preparation	▨	▨						Mid Semester Break								
2.	Ionic Liquid Synthesis			▨	▨	▨	▨	▨									
3.	Characterization									▨	▨						
4.	Dissolution Test									▨	▨	▨					
5	Data analysis										▨	▨					

Table 12: Key Milestone

No	Activities	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1.	Submission of Progress Report								Mid Semester Break	●							
2.	Pre-EDX												●				
3.	Submission of Draft Report													●			
4.	Submission of Dissertation (soft bound)														●		
6	Submission of Technical Paper														●		
7	Oral Presentation															●	
8	Submission of Project Dissertation (Hard Bound)																●

5. CONCLUSION AND RECOMMENDATION

In conclusion, it has been observed that both 1-methyl-3-propionitrile imidazolium dioctylsulfosuccinate and 1-methyl-3-propionitrile imidazolium dihexylsulfosucinnate has the potential in dissolving biomass and in this case, sago waste. from the Raman analysis, it can be concluded that the synthesis part of the ionic liquid is success. The fundamental knowledge regarding ionic liquids synthesizes is well mastered and explained. The ionic liquids that had been synthesized met the characteristics of an ionic liquid. All in all, the synthesis part is a success.

From the biomass testing, it is confirmed that both ionic liquid is capable of dissolving sago biomass, however the testing section is not been able to be provided perfectly as the equipment is currently out of service. There are some recommendations that I would like to suggest which are:

i. Having more characterization method, to futher understanding the properties of the ionic liquid.
ii. Do FTIR analysis on both the dissolved sample and also the regenerated sample.
iii. Doing qualitative and also quantitative analysis on the ionic liquid synthesis and biomass dissolution.

In conclusion, ionic liquids have the characteristics of 'Green Solvent', and it is very easy to be synthesis. With cheaper cost of material, ionic liquids is by far the most ideal solvent available nowadays.

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