Sulfate-Based Ionic Liquids As Solvents For Decomposition Of Lignocellulose Materials From Coconut Husk Fiber In Malaysia

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ABSTRACT : The aim/objectives of study is to investigates the properties of untreated and treated coconut husk fibers, focusing on the structural and chemical changes that occur during various treatment processes. Ionic liquids (ILs), unique salts composed of organic cations and inorganic or organic anions, remain in liquid form at room temperature. The research methodology of study is characterized by low vapor pressure, excellent thermal stability, and high solubility, making them highly versatile for a wide range of applications, particularly in biomass processing. Coconut husk fibers, known for their strength, durability, and natural resistance to wear, hold significant potential for applications in composites and environmental solutions. The theoretical and practical implications: To assess the effects of different treatments on the fibers' morphology, elemental, and chemical composition, this research employs methods such as Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM), and Carbon, Hydrogen, Nitrogen, Sulfur (CHNS) elemental analysis. The data analysis and research findings: The findings reveal that treatments using Triethylammonium Sulfate (TEAS) and Diethylammonium Sulfate (DEAS) yield 75.33% and 83.66%, respectively, under optimal conditions of 130°C for 5 hours. The contributions of study that these results suggest that these ILs effectively facilitate lignocellulose breakdown in coconut husk fibers, offering valuable insights into the structural changes induced by the treatments.

Keywords- *Ionic Liquids, Triethylammonium Sulfate (TEAS), Diethylammonium Sulfate (DEAS), Decomposition, Lignocellulose, Coconut Husk.*

1. INTRODUCTION

Plant biomass is a renewable source; amongst this, lignocellulose is recognized as the most abundant. It represents a complex structure composed of the polymer's cellulose and hemicellulose and lignin, in association with minorities like proteins, lipids, and inorganic substances (Arundina et al., (2021), Ojo, 2023). Currently, lignocellulose waste is being investigates as a feedstock for identifying the most efficient method of converting it into bioethanol and other applications. The utilization of lignocellulosic materials as feedstock to produce bioethanol has been highlighted as a potential solution to the challenges associated with fossil fuels (Adewuyi, 2022). Of all the lignocellulose materials, coconut husk fiber is considered particularly promising for feedstock applications due to its significant byproducts in industrial sectors.

Coconut husk fibre constitutes a biomass residue with higher lignin content compared to wood-based biomass. The chemical composition of coconut husk is influenced by its cellulose content, which varies depending on its diversity and geographical location. Studies have shown that the abundance of waste generated by coconuts and the availability of industrial technology for producing bioethanol from lignocellulosic biomass provide an opportunity to establish a trial plant for bioethanol production (Terenoi David Wafula, 2023). However, the complex composition of coconut husk fiber, characterized by high lignin content alongside cellulose and hemicellulose, presents significant challenges to enzymatic hydrolysis and fermentation processes.

Effective pretreatment, such as alkaline and acid pretreatment is essential for break down the rigid structure and expose fermentable sugars. However, these methods often require high costs and energy inputs. Furthermore, these approaches are not highly effective for fractioning coconut husk fiber (Anuchi et al., 2022). Additionally, the use of organic solvents or organosolv pretreatment, while effective, is associated with inherent dangers such as high costs and flammability, making it less favorable from a safety perspective. Various pretreatment methods have been explored for this feedstock, but ionic liquids (ILs) emerge as a promising alternative due to their cost-effectiveness and efficiency in processing coconut husk fiber (Anuchi et al., 2022). Ionic liquids are particularly effective at breaking down the tough lignocellulosic structure, facilitating the extraction of valuable components like sugars and cellulose. They are also environmentally friendly, producing fewer pollutants compared to conventional chemicals (Bhagia et al., (2022). Additionally, their reusability enhances cost efficiency and process sustainability.

Ionic liquids (ILs) are defined as liquids with a melting point below 100°C and are characterized by low vapor pressure, high thermal stability, and reduced flammability compared to common organic solvents. Consequently, ILs are relatively safe to handle, reusable, and recyclable. Among the various types of ionic liquids, sulfate-based ILs are identified as particularly effective in lignocellulose decomposition. Sulfate anions impart greater efficiency and selectivity to these ILs. According to Zahari et al. (2018), the inclusion of sulfate anions $[HSO_4]^-$ enhances product ester yield by facilitating separation from the heavy IL phase. While organic cations solubilize cellulose and hemicellulose, sulfate anions interact with lignin to achieve partial or total dissolution.

2. STATEMENT OF PROBLEM

The coconut husk fiber is an industrial waste that has often created a serious problem in terms of waste management and remains underutilized despite its wide availability. Its slow decomposition rate contributes to environmental pollution and places pressure on waste management systems. Moreover, much of the rich lignocellulosic composition of coconut husk fiber, consisting of cellulosic, hemicellulosic, and lignin, remains poorly utilized. Efficient methods of decomposition for coconut husk fiber are highly required for the transformation of this underutilized raw material into sustainable bioresources. Traditional decomposition techniques, though in common use, are usually energy-intensive, environmentally hazardous, and economically unviable Díez et al., (2020), Evaluation of Coconut (Cocos nucifera) Husk Fibre as a Potential Reinforcing Material for Bioplastic Production. (2019), Fan, X. et al., (2023). The search for innovative and ecologically friendly methods of processing coconut husk fiber is, therefore, imperative. This thesis intends to contribute to the solution of this problem by exploring new ways of decomposing coconut husk fiber and recovering its valuable lignocellulosic components. The implication of these results, while serving to lessen the challenges in the waste management of coconut husk fiber, also creates wide openings to produce biofuels.

3. OBJECTIVES OF THE STUDY

3.1 To synthesize and evaluate sulfate-based ionic liquids for decomposition of lignocellulose from coconut husk fiber.
3.2 To characterize and analyze the synthesized sulfate-based ionic liquids used for decomposition of lignocellulose from coconut husk fiber.
3.3 To determine and quantify the efficiency of the decomposition process of lignocellulose from coconut husk fiber by using sulfate-based ionic liquids and assess their characteristics.

4. LITERATURE REVIEW

In recent years, one of the most frequent and renewable organic resources on Earth is biomass made from lignocellulosic materials. It is mostly made up of three main parts: cellulose, hemicellulose, and lignin. Plants gain strength and resistance from this complex and rigid structure, which is formed by the intricate binding of these constituent elements. Lignocellulosic materials can be derived from a wide range of sources, including industrial leftovers like coconut husk fibre, forestry wastes, dedicated energy crops like switchgrass and miscanthus leaves, and agricultural residues like straw and grain stover. Table 4.1 shows the sources and selected examples of lignocellulosic materials.

Table 4.1 Sources and selected examples of lignocellulosic materials

SOURCES	EXAMPLES
Agricultural residues	Sugarcane bagasse, corn and rice straw, cotton stalk, corn cobs and leaves, wheat straw, barley straw, sweet sorghum straw, potato haulms, and cocoa pods.
Forestry residues	Spruce chips, willow, cedars, poplar, and eucalyptus.
Industrial wastes	Brewer's spent grains, chemical pulps (e.g., waste sulphate liquor from pulp), and waste papers from paper mills.
Food wastes	The kitchen remains, such as vegetable peels and fruit waste Agro wastes
Animal manure	(e.g., solid cattle, cow, and pig manure).

5.

The term "lignocellulose" is the generic denomination for the constituents of plant cell walls, among them cellulose, hemicellulose—a polysaccharide—, and lignin, a phenolic macromolecule. The mass percentages of cellulose, hemicellulose, and lignin in these polymers range from 35 to 55%, 20 to 40%, and 10% to 25%, respectively, together with other polar and non- polar substances.

Cellulose is the most abundant renewable carbon resource on earth and is regarded as the key to the mechanical strength of plants. In most plants, the vegetative biomass is mainly composed from the thicker secondary cell wall that develops inside the primary wall. Where a secondary cell wall starts at the end of a cell's growth phase, the primary cell wall is laid out in the cell division and growth stages. In a stronger and more thickened structure, the secondary wall contributes importantly to the plant's mechanical strength and biomass production (Kaur et al., 2016). Besides that, repeating units of glucose monomers make up the straight-chain polymer also known as cellulose (Chai et al., 2022). In cellulose, β (1→4) glycosidic linkages connect every glucose molecule to the next, creating complex, linear chains. The strong structure that results from these chains aligning parallel to one another strengthens the structural strength of plant cell walls. The cellulose fibres are more solid and durable due to the hydrogen bonds forming between next to chains, which increases their resistance to chemical and enzymatic breakdown.

Hemicellulose accompanied by cellulose and lignin, forms the solid structure of the biomass skeleton, which protects plant cells from outside disturbance while both mechanically and structurally supporting the plant tissues. The hemicellulose ratio in certain biomass feedstock types varies according to plant species, wood tissues, cell wall layers, growing conditions, climate, seasonal change, and crop treatment by farmers (Nurdin, M. et al., (2021), Podgorbunskikh, E. M., et al., (2020), Shukla, A. et al., (2023). It has also been mentioned that hemicellulose is a heteropolymer of pentoses and hexoses with glucuronic acid and record amounts of Lrhamnose and L-fucose. The widest distribution among hemicellulose polymers belongs to the xylans. Hemicellulose—both composition and structure—is dependent on the species of lignocellulose, chain length, and type of the main chain, as well as the distribution and type of side chains. This resource is renewable, biodegradable, and environmentally acceptable. Many physical and chemical properties individualize hemicellulose, giving it high molecular weight, non-ionic nature, and nontoxicity. However, owing to the high hydrophilicity of this polymer, its complex structure, with a huge abundance of hydroxyl groups, severely limits its usefulness (Uddin, M. et al., (2020), Yasin, S. (2022).

A complex organic polymer called lignin is present in plant cell walls, especially in bark and wood. Lignin provides the cell walls' cellulose, hemicellulose, and pectin components mechanical strength and aids in water conductivity in plant stems by occupying the spaces between them. With its unique cross-linked structure, lignin is made up of several functional groups, including methoxy, phenolic, and aliphatic hydroxyl groups. This structure affects the chemical characteristics and reactivity of lignin. Since the hydroxyl groups and aromatic structures are precursors to determining the characteristics and properties of the polymers, they are particularly significant (Hasanov et al., 2020). Because of that, Podgorbunskikh et al. (2020) has mention that the structure, and characteristics of lignin, which can make up as much as 10% – 45% of the cell wall, deserve extra attention because after pretreatment, lignin or its breakdown products will protect the surface from the reagents, resulting in low overall reactivity even in the presence of poor cellulose crystallinity and a well-developed specific surface area as stated in Figure 4.1. and 4.2 below.

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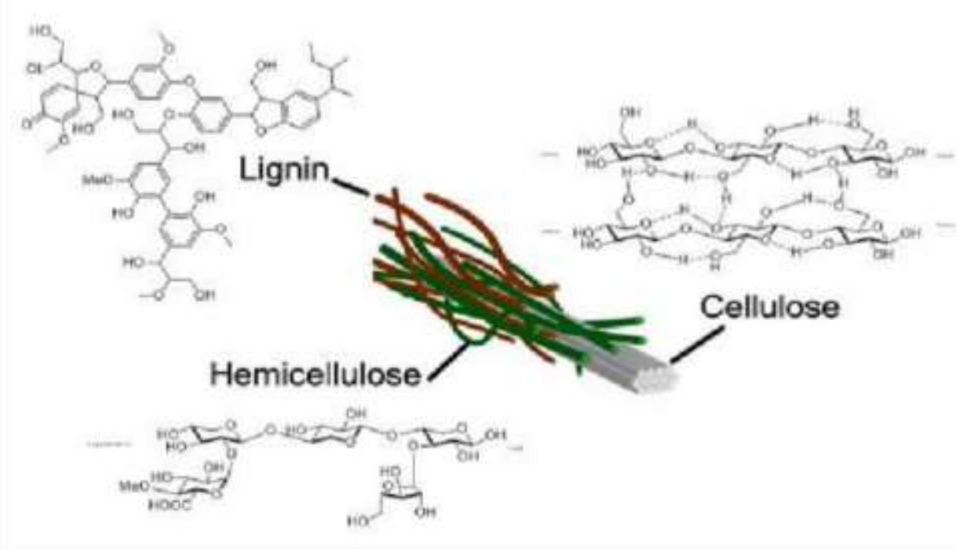


Figure 4.1 shows Cellulose, Hemicellulose, and Lignin Contained Inside Biomass (Chai et al., 2022).

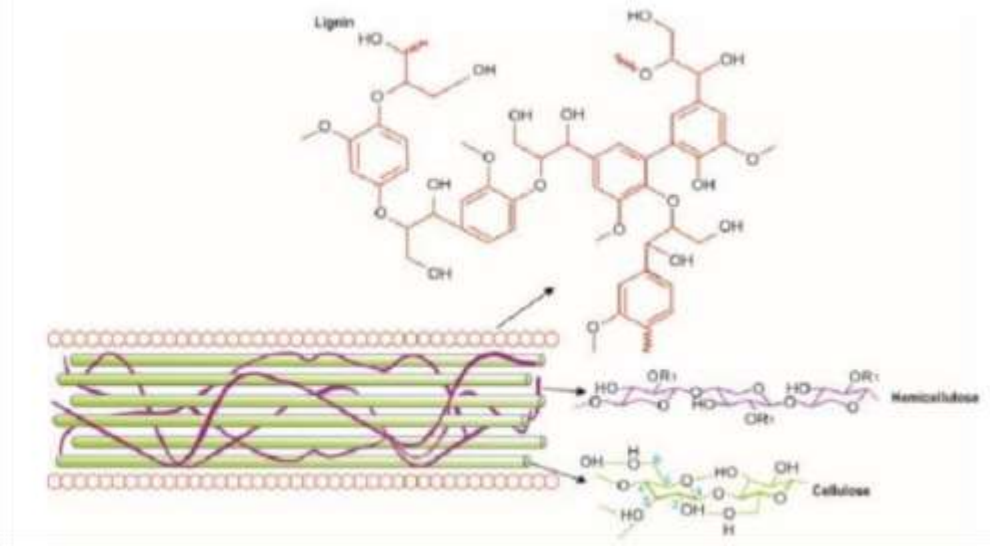


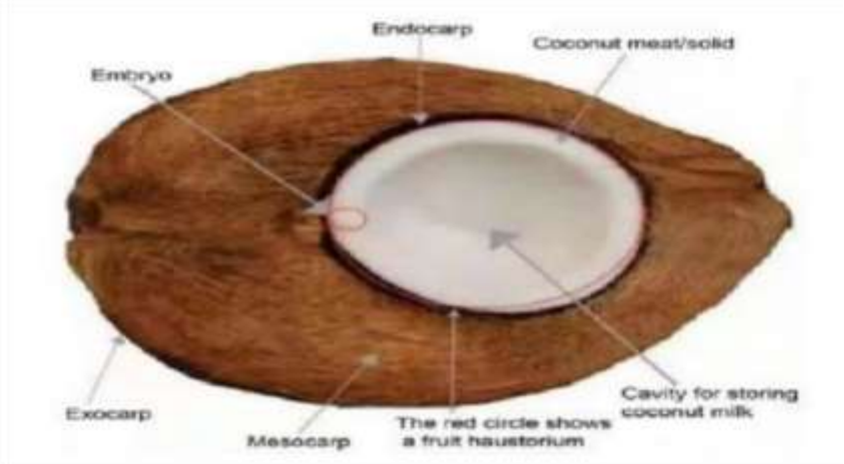
Figure 4.2 shows Lignocellulose Components and Organization (Ojo, 2023).

Around the world, coconut trees are grown year-round in more than 92 nations and planted on about 12 million hectares of land. Furthermore, coconuts are a resilient crop that can grow in a variety of climates and are resistant to disease and pest attacks (Jeetah & Jaffur, 2022). Coconut husk fibre, or Cocus nucifera, is a significant potential reinforcement material that is abundantly available in Nigeria and has a very high tensile strength. Despite this, it is primarily regarded as a waste material.

There are two broad categories of coconut fibers which is brown fiber from mature coconuts and white from young ones. Brown fibers are thicker, stronger, and more resistant to damage. At the same time, white fibers are smoother and finer but less strong. Brown coconut husk fibers also have numerous advantages, such as being resistant to fungi and rot, providing excellent insulation against cold and heat, noncombustibility, imperviousness to moisture and dampness, toughness, durability, and return to shape after constant use ("Evaluation of Coconut (Cocos Nucifera) Husk Fibre as a Potential Reinforcing Material for Bioplastic Production," 2019).

Besides that, coconut fruit are fibrous drupes, not nuts. The term drupe applies to any small, fleshy fruit that contains one seed developed from the ovary of a flower. The fruit has an outermost layer of the ovary, covered with a thin skin, and in the case of coconuts, there are thick, more fibrous middle layers of the ovary wall; the inner layer ripens into a rigid occupant of a single seed. A coconut nursery grows into a fruit by placing a coconut seed nut across. Thus, there is the fruit wall, made up of exocarp, mesocarp, and endocarp; the coconut husk; the solid endosperm, which includes the coconut flesh; liquid endosperm or coconut water; and the embryo. Figure 4.3 shows the sectional structure of coconut fruit (Zakaria, S. M., (2017), Zhang, Y. et al., (2023), Ziaei-Rad, Z. et al., (2021).

Figure 4.3 shows the Sectional Structure of Coconut Fruit (Zhang et al., 2023).



In addition, Coir fibre is fibre that is recovered from nutshells' husks. Coir fibre comes from the layers of the endocarp and exocarp in coconuts. Recovered and cleaned from coconut husks, the resultant coir fibre is usually golden or brown reddish. Coir fibre threads are usually 0.01 to 0.04 inches in diameter. Each coconut husk contains 20-30% fibre of variable lengths. Coir fibre, which comes from coconut husks, is heavy and harsh; some even have more outstanding characteristics such as strong wear ability. This forms a quality of enhanced hardness, together with high wear properties. Coir fibre shows better moisture resistance than any other plant-based natural fibre, combined with the capability of resisting the action of sea salt and other forms of heat exposure (Hasan et al., 2021). Figure 4.4 shows the photographs of the coconut palm tree, coconut fruits, coconut husk, and coir fiber morphology.

Figure 4.4 The photographs of the (a) coconut palm tree, (b) coconut fruits, (c) coconut husk, and (d) coir fiber morphology (Hasan et al., 2021).

According to Stelte et al. (2023), coconut fibre has spread throughout the littoral and interior areas of most tropical countries. Its wide distribution has been secured by its usefulness and its ability to grow in all forms of environments. The coconut is tolerant to saltwater, resistant to biodegradation, and mechanical forces that enable it to float in seawater over a long period, sometimes hundreds of miles and grow on soils on beaches when thrown onto land. Apart from that, coconuts have long been used by man for food, beverage, and oil, and for providing shelter and serving aesthetic purposes. This is attributed to the fact that coconut husk fibre is regenerative and ensures the supply of lignocellulose material without depleting limited supplies. Coconut trees are known to be very hard, producing fruit for a few years, thereby acting as an efficient and renewable supply for husks. About this, concerning proper recycling or reusing coconut husk for essential products, such activities as disposing of it for proper utilization of lignocellulose material would reduce the generation of waste.

4.2. Method of Lignocellulose Material Decomposition

As already mentioned earlier, coconut husk fibres contain lignocellulose, a complex and hard substance made up of cellulose, hemicellulose, and lignin. Decomposing lignocellulose materials is challenging due to their complicated structure. There are several methods for breaking down lignocellulose compounds. Hawrot-Paw & Stańczuk (2023) identified physical, chemical, and biological methods. Figure 4.5 shows a schematic layout of the classes and types of pretreatment processes.

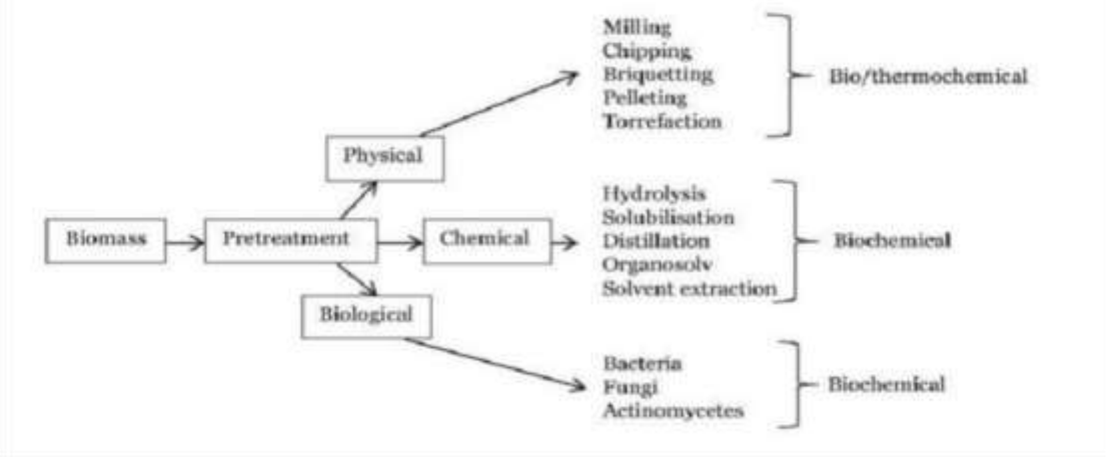


Figure 4.5 shows a layout showing different pretreatment methods for biomass and their corresponding energy conversion routes (Anukam & Berghel, n.d.).

Physical pretreatment methods such as mechanical crushing, ultrasonic, and microwave treatments improve the breakdown of lignocellulosic biomass by changing its structure. Mechanical crushing, such as ball milling, grinds biomass into fine powders by reducing cellulose crystallinity and particle size, increasing hydrolysis efficiency but using a lot of energy. Steam explosion alters the structure of biomass by fast heating and decompression, making it both cost- effective and energy intensive. Ultrasonic and microwave treatments use sound waves or microwaves to break down molecular structures, lowering crystallinity and increasing hydrolysis efficiency; nevertheless, these procedures are frequently prohibitively expensive for large-scale industrial applications. Each method involves a trade-off between efficiency, energy consumption, and cost. (Mustafa et al., 2022).

Then lignocellulose biomass is chemically pretreated by breaking down its complex structure using acids, bases, ionic liquids, or organic solvents. Alkaline pretreatment uses solutions such as calcium, potassium, sodium, or ammonium hydroxide to reduce lignin content and boost cellulose recovery, although it can also result in sugar loss and inhibitory byproducts. Acid pretreatment, which uses mineral acids such as sulfuric or phosphoric acid, changes the structure of biomass to encourage enzyme hydrolysis, however it can cause equipment corrosion and raise environmental problems. Organic solvent pretreatment successfully destroys lignin and separates cellulose and hemicellulose without causing significant structural changes, but it is expensive, difficult to recover, and may have harmful consequences on fermentation and the environment. Each strategy considers efficiency, cost, and environmental impact (Mustafa et al., 2022).

It is a fact that for biological methods reliant on the enzymatic activity of bacteria and fungi, there exist two types of exogenous enzyme systems: one responsible for polysaccharides degradation and another, the ligninolytic system (Hawrot-Paw & Stańczuk, 2023). Because of that, bacteria and fungi are being used to release enzymes that degrade lignin and cellulose, hence weakening the biomass cell wall and aiding in hydrolysis. This process converts carbohydrates into useful compounds like furfural and levulinic acid. However, in a more efficient manner, lignin is broken down by fungi than by bacteria. Due to that, it makes biological pretreatment energy-efficient, mild in its circumstances of operation, and not producing hazardous byproducts. It uses enzymes to breakdown lignin, cellulose, and hemicellulose. However, biological pretreatment is an environmentally safe and sustainable technology, despite the need for strict growth conditions, plenty of space, and a longer processing time compared to other methods (Mustafa et al., 2022). Figure 4.6 shows the effect of pretreatment to the lignocellulosic biomass.

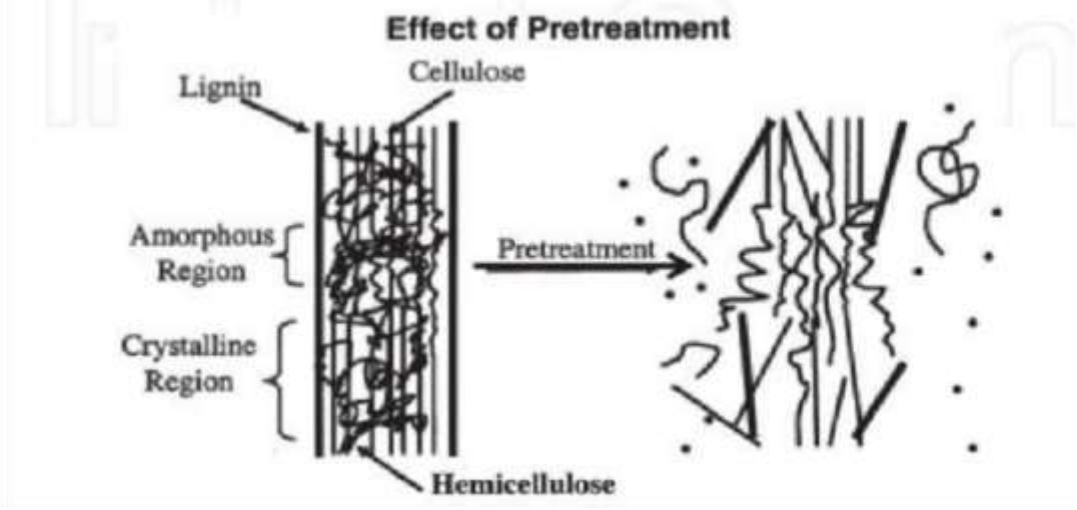


Figure 4.6 A schematic representation of the impact of pretreatment on the surface and internal structure of lignocellulosic biomass (Anukam & Berghel, n.d.).

However, due to their distinctive features that enable efficient lignocellulose biomass separation without harming the environment and being non-corrosive, ionic liquids are used for this study for lignocellulose decomposition experiments. Without compromising the structure of cellulose, they can also dissolve lignin and hemicellulose selectively Mastura Zakaria et al., (2017). Ionic liquids' attractiveness as a lignocellulose processing medium is further enhanced by the fact that they may be recycled and utilised again.

7. MATERIALS AND METHOD

7.1 Materials

Table 5.1 presents the materials that were utilized in this research.

Table 5.1 List of Materials used in this research.

MATERIALS	MOLECULAR FORMULA
Triethylamine	$C_6H_{15}N$
Diethylamine	$C_4H_{11}N$
Sulfuric acid	H_2SO_4
Ethanol	CH_3CH_2OH
Methanol	CH_3OH
Deuterated methanol	CD_3OD
Diethyl ether	$(C_2H_5)_2O$
Distilled Water	H_2O
Coconut husk fibre (raw materials)	-

7.2 Instrumentations

Table 5.2 shows an overview of the instruments that are normally used in this type of study.

Table 5.2 The instruments used in this study.

INSTRUMENTS	MODEL
Fourier Transform Infrared Spectroscopy (FTIR)	Nicolet iS50, Thermo Fisher Scientific, USA
Nuclear Magnetic Resonance Spectroscopy (NMR)	Bruker DPX 400, Germany
Thermogravimetric Analysis (TGA)	Mettler Toledo, Switzerland
Field emission scanning electron microscopy (FESEM)	Jeol IT 800 SHL, Japan
CHNS elemental analysis (CHNS)	Elementar MAcrocube

7.3 Design of Experiment

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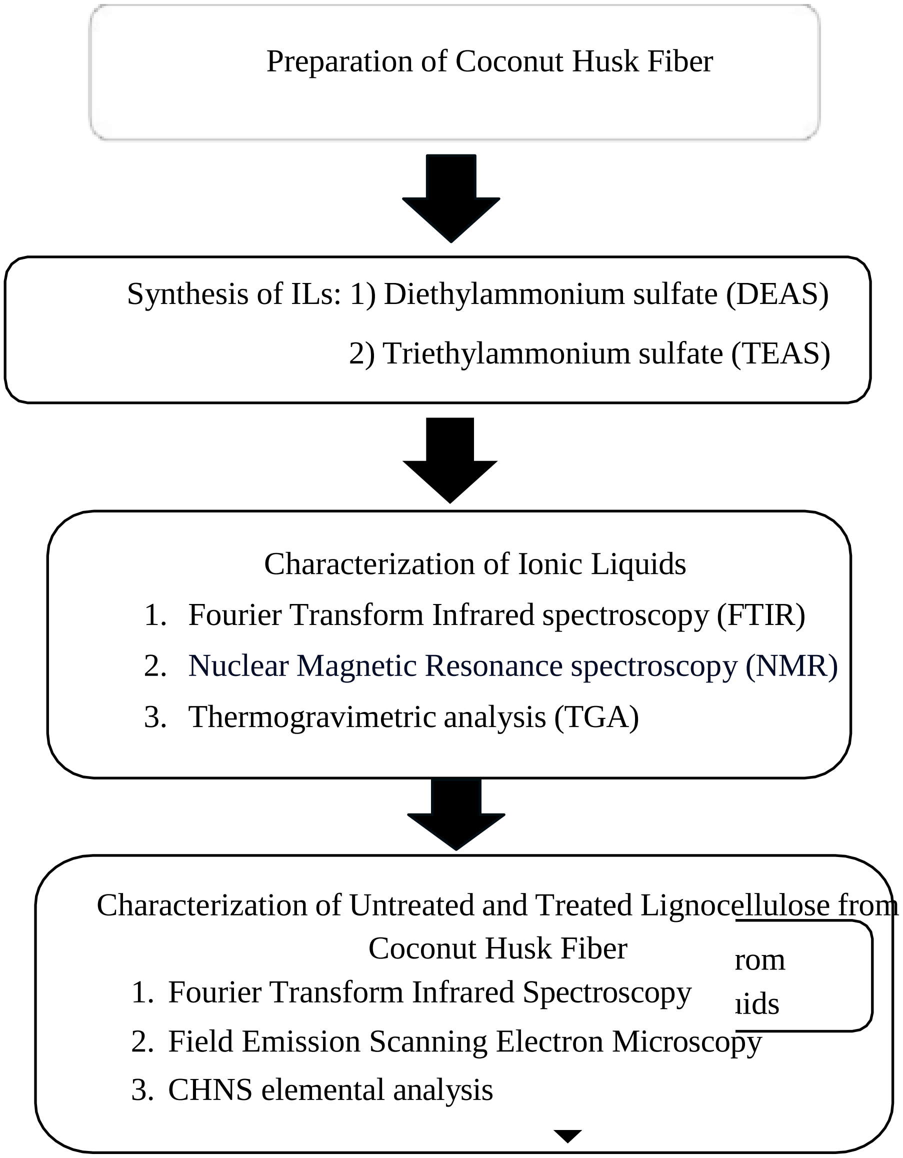

Figure 5.1 The experimental design in this research.

8. RESULT AND DISCUSSIONS

8.1 Research Objective 1: Synthesis of Ionic Liquids

8.1.1. Diethylammonium sulfate (DEAS)

Diethylammonium sulfate (DEAS) was synthesized by the reaction of diethylamine with sulfuric acid. The synthesized DEAS product was white in color, meaning that it had a purer composition with fewer impurities that absorb light. Besides, the product had a mild odor, showing lower volatility and the presence of fewer VOCs compared to TEAS. This would also reflect that the synthesis procedure efficiently removed the impurities, besides minimising VOC content, making DEAS more suitable for applications involved.

8.1.2. Triethylammonium Sulfate (TEAS)

On the other hand, TEAS, synthesized using triethylamine and sulfuric acid as reactants in its reaction, showed a yellowish liquid. Its yellow coloration may be due to residual impurities and organic compounds in its structure. The stronger smell detected for TEAS may have resulted from the release of VOCs or sulfur-containing by-products and interactions of its ammonium structure with air. Below are the comparisons for both ionic liquids of the colors in figure 6.1.

Figure 6.1 Diethylammonium Dulfate (DEAS) & Triethylammonium Sulfate (TEAS) ionic liquids

8.2. Research Objective 2 : Characterization of Ionic Liquids

8.2.1. Diethylammonium sulfate (DEAS) using FTIR

FTIR analysis of DEAS shows several characteristic absorbance bands of its functional groups, including the amine group (NH), methyl group (CH_3), carbon-nitrogen bond (C─N), sulfone group (SO_2), methylene group (CH_2), and sulfoxide group (SO).

A wide absorption at 3354 cm^{-1} corresponds to NH stretching vibrations in amine groups as a result of extensive hydrogen bonding interaction. Indeed, water and ammonium groups participate in contact ion pairing interactions with the sulfate ions. The peak observed at 1639 cm^{-1} represents NH bending vibrations, further confirming the presence of a diethylammonium cation. Absorption in the region of 1456–1189 cm^{-1} corresponds to CH_2 bending vibrations.

The peak at 1189 cm^{-1} could be assigned to S=O stretching in sulfate ions, confirming the ionic nature of the compound. Peaks within the 1050–1016 cm^{-1} range may be assigned to the C─N stretching frequency of the amine group and additional S=O stretching. Figure 6.2 below is the FTIR spectrum of the synthesized DEAS ionic liquid.

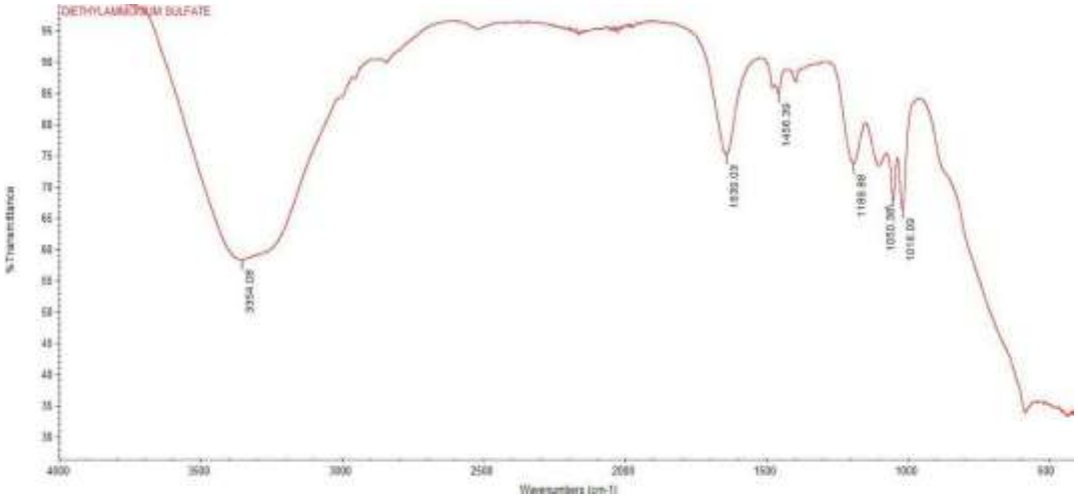

Figure 6.2 FTIR spectrum of the synthesized DEAS ionic liquid

8.2.2. Diethylammonium sulfate (DEAS) using NMR

The results of the ^1H NMR analysis of DEAS is shown subsequently. The ^1H NMR spectrum in deuterated methanol solvent reveals sharp peaks corresponding to the distinct hydrogen atoms contained in the molecule analyzed. Table 6.1 and a figure 6.3 below describe the ^1H NMR results of DEAS.

Table 6.1 Summary of ^1H NMR of DEAS.

Hydrogen Atoms (H)	Chemical Shift (ppm)	Peak Type
3H	1.32	m
2H	3.10	s
1H	8.17	s

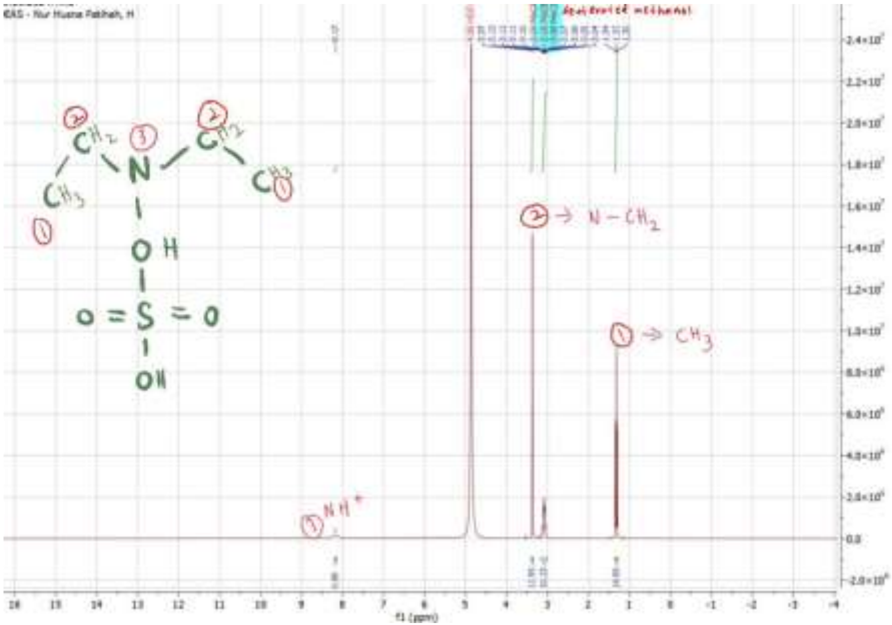

Figure 6.3 ^{1}H NMR spectra for DEAS.

Meanwhile, protons of the CH₂ group directly bonded with nitrogen (N─CH₂) present an upfield signal shift because nitrogen has induced deshielding effects. The peak also exhibited coupling patterns due to splitting caused by neighboring protons that confirm the presence of an ethyl group. Signals in the range of 1.14–1.32 ppm represent protons of the terminal methyl group (─CH₃) in the ethyl group. These usually appear as a triplet, due to splitting by the adjacent CH₂ group. The chemical shift is downfield because of proximity to the more deshielded portions of the molecule.

Figure 6.4 is the ^{13}C NMR of the DEAS. The appearance of CH₃ at 10.55 ppm is because the methyl carbons are less deshielded compared to the carbon atoms by the N─CH₂, shifting to the lower ppm region. The CH₂ carbons appear around 48.91 ppm since the carbon atoms that are attached to nitrogen are deshielded; hence shifting to a higher ppm region.

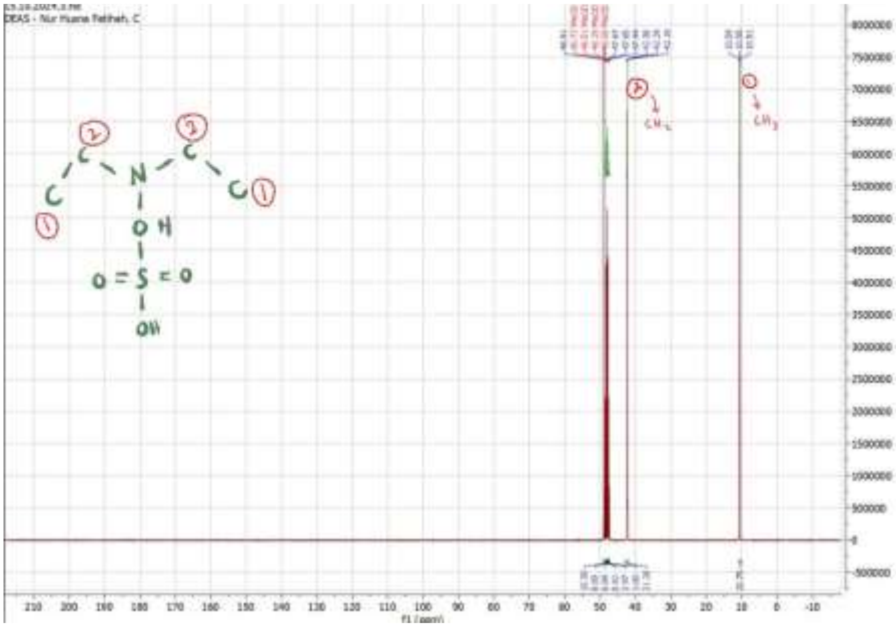

Figure 6.4 ^{13}C NMR spectra for DEAS.

8.2.3. Diethylammonium sulfate (DEAS) using TGA

Figure 6.5 shows that, at 30°C, that is, at ambient temperature, there is a slight weight loss indicative of the probable evaporation of some solvent components. At increased temperatures up to 140°C, this action furthers the removal of volatile components, including the residual solvents. The DEA ionic liquid is thermally stable within a temperature range of 150°C to 290°C, as it remains at a constant weight percentage; hence, it can be used for high-temperature decomposition. Further weight loss and decomposition occur from 320°C up to 500°C, where the breakdown of the compound into its constituent components occurs at temperatures beyond 290°C.

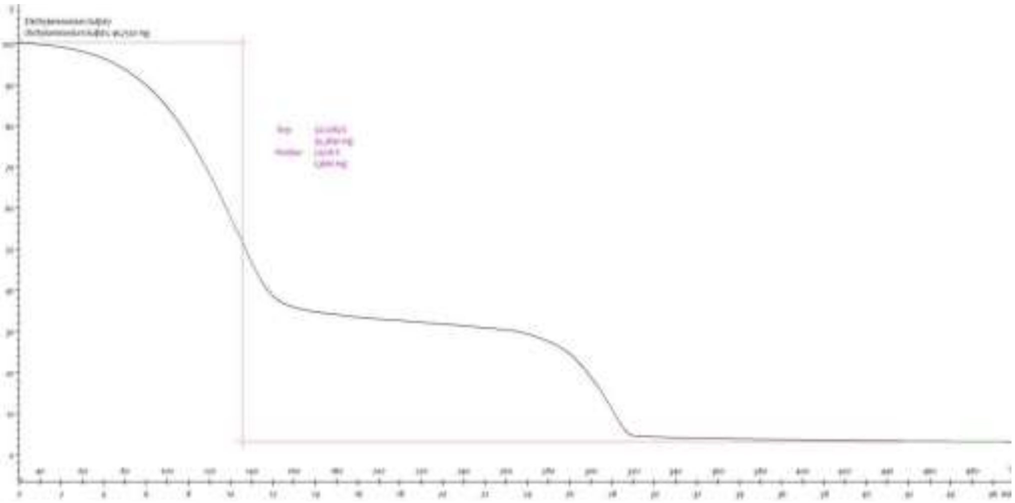

Figure 6.5 TGA decomposition of DEAS

8.2.4. Triethylammonium Sulfate (TEAS) using FTIR

Figure 6.6: The FTIR spectra of TEAS are shown displaying absorbance versus wavenumber (cm^{-1}). A number of peaks are apparent in the FTIR spectrum, reflecting many different types of chemical vibrations in this sample.

In this respect, one broad absorption band at 3356 cm^{-1} was assigned to NH stretching vibrations of the amine group, reflecting strong hydrogen bonding interactions. The absorption at 1640 cm^{-1}, ascribed to NH bending vibrations, confirmed the presence of a triethylammonium cation.

Absorption at 1477 cm^{-1} represents $-CH_2$ bending vibrations, and the peak at 1188 cm^{-1} represents S=O stretching vibrations due to sulfate ions, indicating further that the compound is ionic. Peaks between 1049-1016 cm^{-1} are assigned to C─N stretching vibrations in the amine group with additional S=O stretching vibrations.

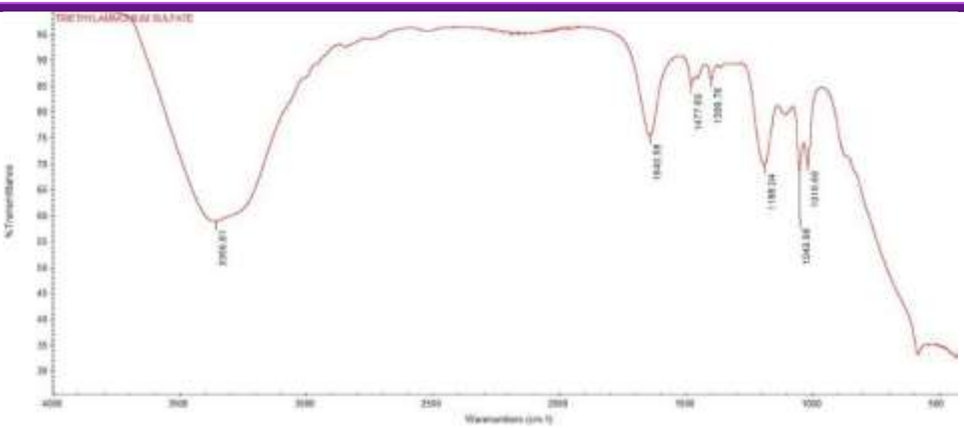

Figure 6.6 FTIR spectrum of the synthesized TEAS ionic liquid

8.2.5. Triethylammonium Sulfate (TEAS) using NMR

Figure 6.7 displays the ^{1}H-NMR spectra of [TEA][HSO_4]. The singlet at 4.87 ppm is due to residual water. The strongest peak, centered at 1.32 ppm, is from the nine protons of the CH_3 groups of [TEA]+. It appears as a triplet due to coupling with the neighboring methylene (CH_2) protons. Other prominent peak-2 at about 3.21 ppm corresponds to six methylene (CH_2) protons of the cation, and that also has the appearance of a quadruplet on account of coupling with the adjacent CH_3 protons. Then, one moderate peak centered at 3.37 ppm appears, which was not the case in the ^{1}H NMR of pure triethylamine, TEA.

Table 6.7 Summary of ^{1}H NMR of TEAS.

Hydrogen Atoms (H)	Chemical Shift (ppm)	Peak Type
3H	1.32	m
2H	3.21	s

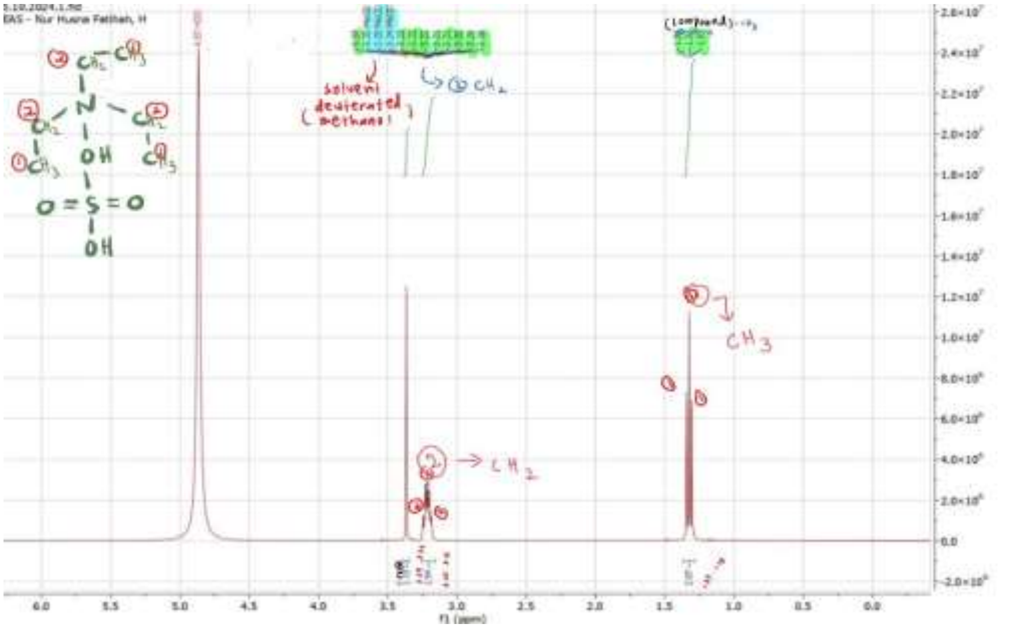

Figure 6.7 ^{1}H NMR spectra for TEAS.

Meanwhile, the 13C NMR spectra for the compound TEAS are shown in Figure 6.8. The carbon chemical shifts for the compound TEAS are observed at 8.20 ppm and 46.7 ppm.

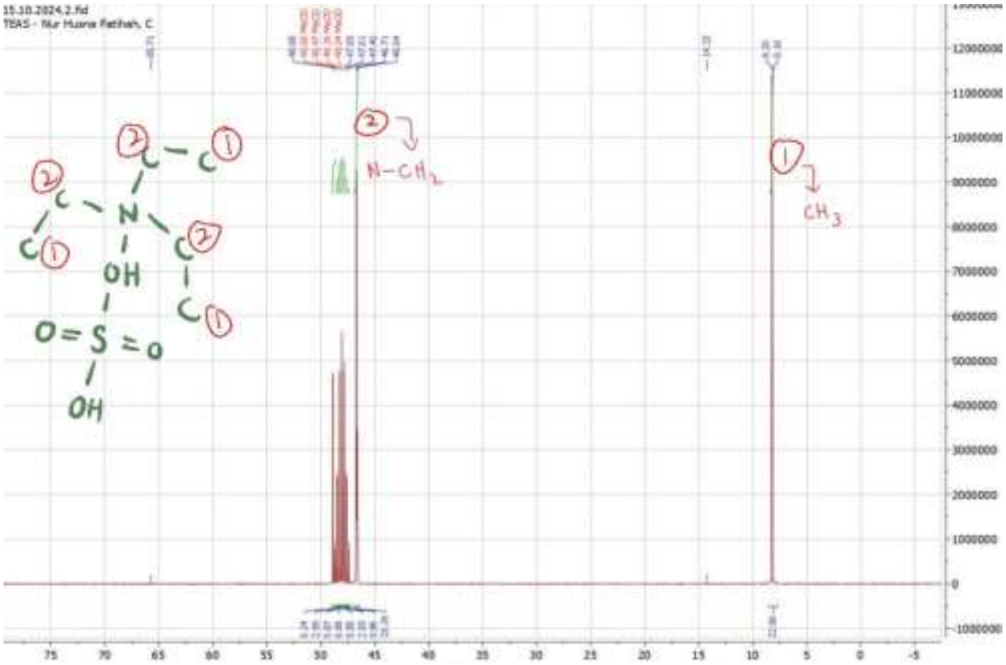

Figure 6.8 ^{13}C NMR spectra for TEAS.

8.2.6. Triethylammonium Sulfate (TEAS) using TGA

As theoretically expected, the larger the structure, the higher the thermal stability since large molecules have stronger chemical bonds and steric hindrance. Therefore, TEAS exhibits higher stability than DEAS due to the greater number of ethyl groups it contains. Figure 6.9 shows the TGA results of IL [TEA][HSO_4]. The weight percentage reduction within the temperature range of 40-140°C confirms the evaporation of some solvent components, such as ethanol and water. One of the properties of the IL, [TEA][HSO_4], is its stability at high temperatures; this infers that the conjugate's properties between 150 and 260°C can be used as variables for the decomposition process. At 310°C and above, complete decomposition of the compound into its constituent elements is observed

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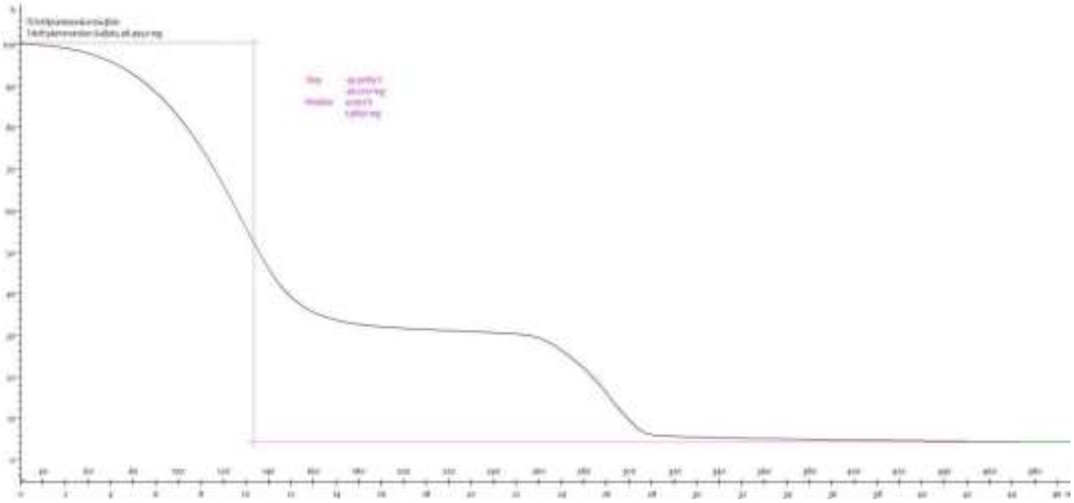


Figure 6.9 TGA decomposition of TEAS.

8.3. Research Objective 3 : Decomposition of Lignocellulose from Coconut Husk Fiber

8.3.1. Diethylammonium Sulfate (DEAS)

The parameters used in this analysis are 30°C, 80°C, and 130°C for lengths of time of 2 and 5 hours. And it is depicted that the colour changes from colourless into light brown, showing or proving that there is an existence of a chemical change between the ionic liquid and coconut husk, and also the ionic liquid turned black as the parameter temperature and time span change.

At 30°, the product turned into powder. At 80° and 130° C, the appearance would be oily and dark colored. This may relate to the chemical structure and physical state of DEAS, usually imparting an oily or greasy characteristic. Also, the sample of DEAS is in a paste form, which may be described due to its semi-solid phase at room temperature. This can be attributed to the molecular structure of DEAS, where the presence of long alkyl chains in the diethylammonium cation, such as ethyl groups —C_2H_5, leads to a more viscous and less fluid form. The paste-like consistency is typical for certain organic salts, where ionic interactions between the diethylammonium cation and sulfate anion create a structure that doesn't flow easily, especially when concentrated. Figure 6.10 presents the observations of the samples for each parameter.

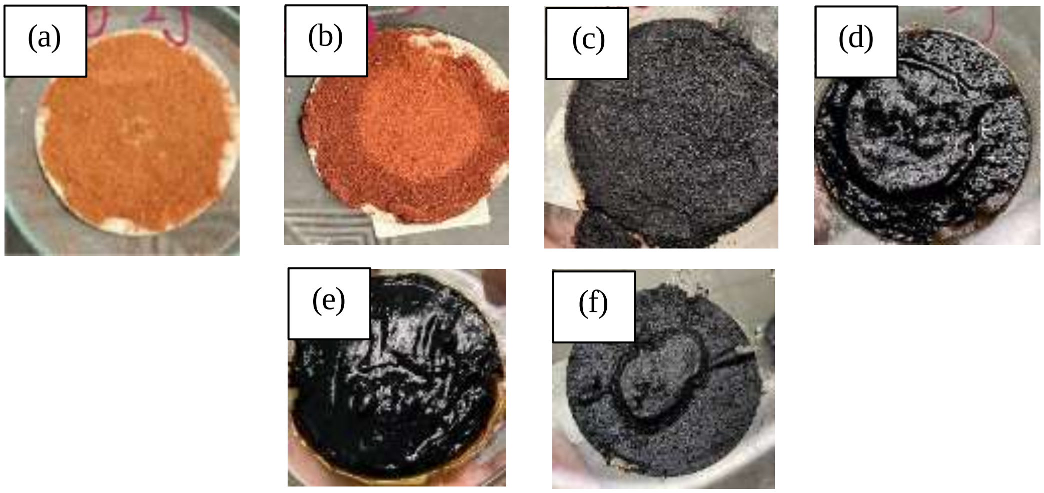


Figure 6.10 Observations of the DEAS during coconut husk decomposition: (a) 30 °C for 2 hours, (b) 30 °C for 5 hours, (c) 80 °C for 2 hours, (d) 80 °C for 5 hours, (e) 130 °C for 2 hours, and (f) 130 °C for 5 hours.

The various percentages of decomposition of coconut husk induced by the DEAS ionic liquid were calculated using an equation from section 3.1. Surprisingly, the highest percentage of decomposition, at 83.66%, was obtained at 130°C for 5 hours, proving that this temperature and time combination is effective. Table 6.3 shows the various calculated percentages of decomposition for each treated sample. However, the general percentage decomposition remains relatively low and indicates that further investigation in the search for alternative ionic liquids and optimization of decomposition parameters is required to enhance the efficiency in lignin removal from coconut husk.

Table 6.3 Percentage decomposition of the treated sample with DEAS.

Samples	**Initial weight (g)**	**Final weight (g)**	**Percentage decomposition (%)**
30 °C for 2 hours	1.0027	0.4142	58.69
30 °C for 5 hours	1.0018	0.5603	44.07
80 °C for 2 hours	1.0061	0.9213	8.43
80 °C for 5 hours	1.0014	0.4306	57.00
130 °C for 2 hours	1.0098	0.2252	77.70
130 °C for 5 hours	1.0034	0.1640	83.66

8.3.2. Triethylammonium Sulfate (TEAS)

In this work, the conditions used were: 30, 80 and 130°C for 2h and 5h. As can be seen the yellow color turns into dark red and finally black upon heating at higher temperatures for a longer time. The color of TEAS seems to be oily and dark that could be due to the chemical nature and interference of it with other components. Being a quaternary ammonium salt, it includes cations of triethylamine and sulfate anions. This could explain the greasy, oil-like texture when in a liquid or concentrated form. The dark coloring could be due to the particular formulation or impurities present within the sample analyzed or to the sulfate group itself reacting with other compounds to form colored species. Moreover, if the TEAS sample has undergone some kind of chemical reaction or exposed to certain conditions such as heat or light exposure, the deeper color is because of by-products or degradation products that may have formed. Figure 6.11 shows the observations of the sample for each parameter.

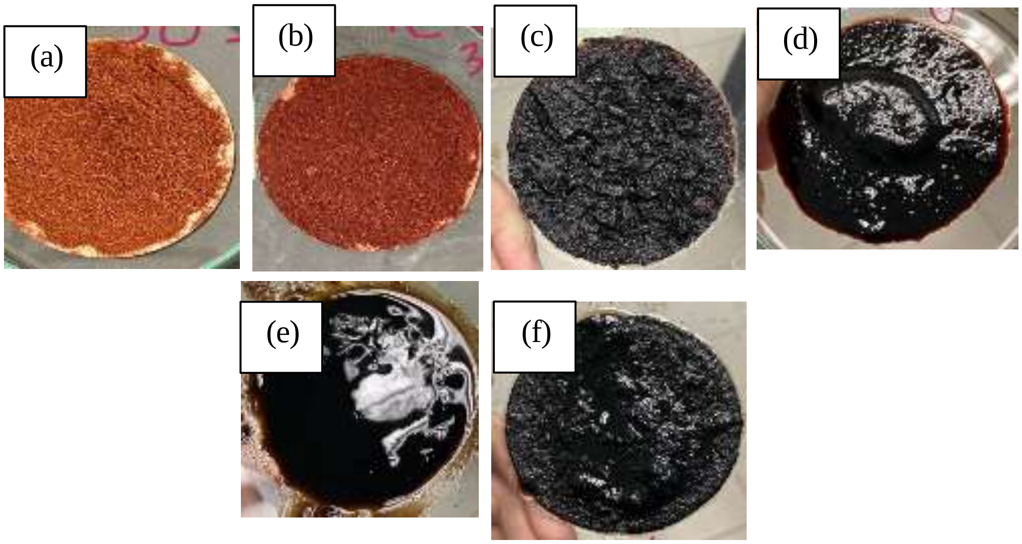


Figure 6.11 Observations of the TEAS during coconut husk decomposition: (a) 30 °C for 2 hours, (b) 30 °C for 5 hours, (c) 80 °C for 2 hours, (d) 80 °C for 5 hours, (e) 130 °C for 2 hours, and (f) 130 °C for 5 hours.

The TEAS ionic liquid has also induced the percentage of decomposition of the coconut husk, and the calculation was done by using the equation from section 3.1. From this result, it can be observed that the highest percent decomposition, 75.33%, was at 130°C for 5 hours, which could mean this is the effective temperature and time of treatment. Table 6.3 summarizes the calculated percentages of decomposition for each treated sample.

Table 6.3 Percentage decomposition of the treated sample with TEAS.

Samples	**Initial weight (g)**	**Final weight (g)**	**Percentage decomposition (%)**
30 °C for 2 hours	1.0111	0.8358	17.34
30 °C for 5 hours	1.0017	0.3892	61.15
80 °C for 2 hours	1.0161	0.5711	43.67
80 °C for 5 hours	1.0313	0.2707	73.75
130 °C for 2 hours	1.0138	0.5057	50.23
130 °C for 5 hours	1.0402	0.2566	75.33

8.4. Characterization of Untreated and Treated Lignocellulose from Coconut Husk Fiber

8.4.1. Fourier Transform Infrared Spectroscopy (FTIR)

Treated samples that were used to run FTIR spectra are DEAS 130°C, 5 hours, and TEAS 130°C, 5 hours since they have the highest percent decomposition and show the characteristic peaks corresponding to cellulose, hemicellulose, and lignin when compared to the untreated samples.

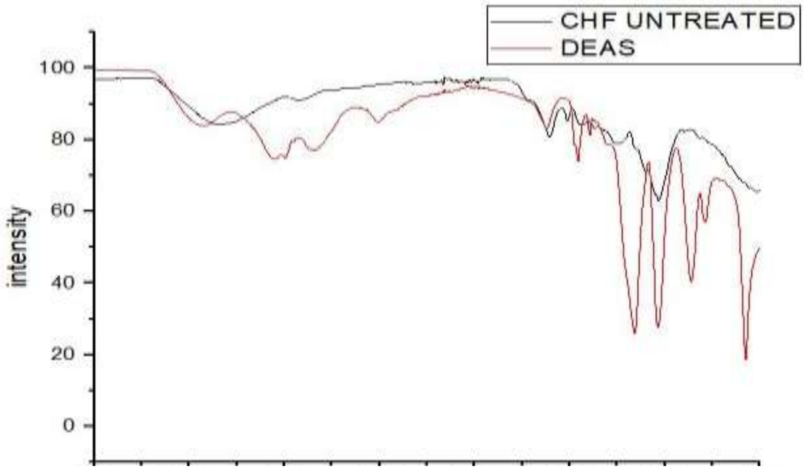
Figure 6.12 is the overall peaks of treated and untreated biomass, where a broad O-H stretching band around 3340 cm^{-1} is observed. This band corresponds to the hydroxyl groups from the polysaccharides, cellulose and hemicellulose, and the presence of water in the biomass. Besides, peaks at 2921 cm^{-1} indicate C-H stretching from aliphatic compounds in lignin and hemicellulose. The sharp peak near 1700 cm^{-1}, exactly at 1604 cm^{-1}, represents the presence of carbonyl groups in hemicellulose; the aromatic C=C stretching vibrations show a small peak at 1511 cm^{-1}, attributed to lignin. The high, sharp peak at 1031 cm^{-1} corresponds to C-O stretching in polysaccharides; finally, the β-glycosidic bond vibrations showed a very small peak close to 900–950 cm^{-1}, more precisely at 895 cm^{-1}, confirming the intact structure of polysaccharide.

Therefore, FTIR can detect changes in the FTIR spectrum that result from the solubilization process and probable structural changes in various components when dissolved in DEAS and TEAS. For example, peaks at 3400 cm^{-1} and above show slight shifts to indicate changes in the presence of amine groups in TEAS and DEAS. These groups interact with hydroxyl groups, disrupting hydrogen bonding and causing changes in the intensity of this peak.

It can be observed that the peak around 2921 cm^{-1} for the untreated biomass shows an increase in intensity or shifting due to the addition of new methyl or ethyl groups contributed from TEAS ($–CH_2CH_2OH$) or DEAS ($–CH_2CH_3$), thus showing up with new peaks in this area. Besides, the C=O stretching has dropped considerably from the actual peak of the untreated biomass, which is at 1157 cm^{-1}. This would mean that the treatments might reduce the ester functionality by forming new bonds with the biomass hence reducing carbonyl absorption in this region. The aromatic C=C stretch has disappeared, probably because treatments may cause partial depolymerization of lignin or alter its structure in such a way as to reduce the characteristic lignin- related peaks.

For C-O stretching, there is little change, this is likely due to the fact that the new interactions between biomass and the amine or sulfate groups from TEAS and DEAS, respectively, that may be formed alter the bonding of the polysaccharides. The differences are shown in Figure 6.13 (b).

Figure 6.12 FTIR spectra of the untreated and treated sample for both IL treatment.



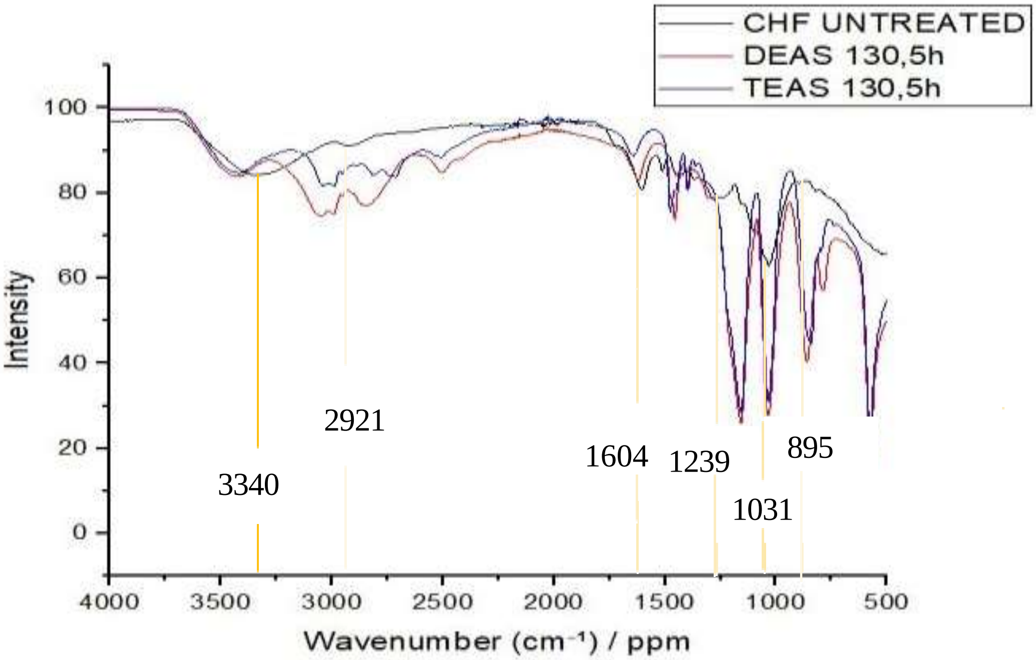


Figure 6.13 FTIR spectra of the untreated biomass and their treatments.

8.4.2. Field emission scanning electron microscopy (FESEM)

FESEM images showed striking structural differences between untreated and treated biomass. Indeed, the rough and compact, thus uneven and irregular, surface of the untreated biomass, as revealed by the micrographs, is typical of natural lignocellulosic biomass, owing to its composition of cellulose microfibrils enveloped by hemicellulose and lignin tightly bound matrix components. These create barriers, making access poor, hence resistance to biomass degradation. The heterogeneous surface is a reflection of the natural recalcitrance of biomass, which causes problems for downstream processes, such as enzymatic hydrolysis and chemical conversion.

The DEAS sample appears to be rougher and more porous than the TEAS sample. FESEM images show that DEAS presents irregularities and voids, while in TEAS, the structure is smoother and denser. These changes can be explained by the treatment of coconut husk fibers. In DEAS, the fibers would likely be untreated or slightly treated, retaining natural impurities such as waxes and oils. Such impurities prevent good bonding between the fibers and the matrix, resulting in a rough and uneven surface. On the other hand, TEAS fibers may have undergone chemical or thermal treatment, which cleans them of impurities and improves fiber-matrix adhesion; hence, the surface is more uniform and compact. The higher decomposition percentage of DEAS is directly related to the untreated fibers and porous structure. The presence of natural components in the untreated fibers, such as hemicellulose, is easily degraded by thermal stress. Moreover, the existence of voids and weak bonding in DEAS provides structural weaknesses and enhances the decomposition process. The treated fibers remove the thermally unstable components from the fibers in TEAS, strengthening the interface between the fibers and matrix and accounting for the overall improvement in thermal stability.

In the comparison of untreated and treated fibers, the untreated fibers in DEAS retain hemicellulose and other unstable components which decompose at lower temperatures. They also lack crystallinity and thermal resistance imparted by treatment processes. On the other hand, these unstable components are removed from treated fibers in TEAS, leaving behind lignin and cellulose, which have higher thermal stability. This accounts for reduced decomposition in TEAS and a smoother, more integrated structure, as obtained from the surface morphology.

Finally, this smoother surface of the treated biomass is important for the enhancement of efficiency in downstream processes- increasing surface area, reducing structural resistance, and improving the penetration of reactants. These changes in structure underline the efficiency of TEAS and DEAS regarding overcoming natural barriers of lignocellulosic biomass and its preparation for applications involving biofuel production. Figure 6.14: Surface of the sample.

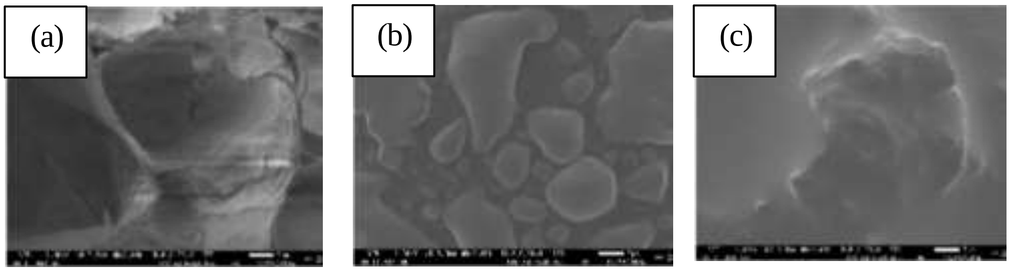


Figure 6.14 Surface of the sample. (a) untreated CHF, (b) treated CHF with DEAS, (c) treated CHF with TEAS.

8.4.3. CHNS elemental analysis

The average data obtained from CHNS analysis gives a good overview of how treatment processes change the chemical composition of coconut husk fibers concerning their decomposition. Comparison of the three-RAW CHF, DEAS, and TEAS-shows that methods of treatment considerably alter the percent values of C, H, N, and S to which the material behavior of decomposition is attributed.

RAW CHF represents the fibers that were not treated and are therefore of a high level of carbon content at 44.56%, low hydrogen of 5.288%, low nitrogen of 0.68%, and low sulfur of 0.351%. They are made up mainly of a high proportion of lignin, cellulose, and hemicellulose, with limited exposure to external chemicals. Since the material was not subjected to pretreatment, the thermal stability is lower, leading to easy and quick decomposition. The high carbon content shows the high organic matter; the low nitrogen and sulfur percentages show the limited chemical additives or contamination present. However, the impurities like oils and waxes in the untreated structure result in poor bonding with more voids in the composites which reduced the thermal stability and accelerated the decomposition under heat or stress.

However, the partially treated fibers showed considerable changes in composition in DEAS. A lower percentage of carbon content gives evidence that part of the organic components- mostly hemicellulose and portions of lignin-have been washed out of the treatment. These parts of the components are thermally unstable at low temperatures, and their removal develops in the resistance of these fibres toward decomposition. Additionally, a higher amount of nitrogen and sulfur shows that the modifications during treatment include chemical agents in nitrogen and sulphur that attach with the structural units of the fibre. Higher hydrogen content compared to the untreated fiber does reflect partial preservation of more stable cellulose at a higher temperature. However, the presence of sulfur denotes that some impurities or additives may reduce the thermal resistance of DEAS in contrast to more thoroughly treated samples such as TEAS.

It is expected that TEAS, being fibers that are extensively treated, would exhibit a composition most favorable for superior thermal stability and reduced decomposition. Compared to DEAS, TEAS has higher carbon content that only shows the elimination of the unstable organic fraction without affecting the more stable structures of cellulose and lignin. Also, hydrogen content is the highest, which could point out that the treatment is improving crystallinity and thermal resistance in the fibers. This higher hydrogen-to-carbon ratio suggests a more stable material due to its lesser tendency to decompose upon raising the temperature. The nitrogen content is close to that of DEAS, but the slightly lower sulfur would indicate a more refined treatment process with fewer sulfur-based impurities, further contributing to stability.

The treatment processes of DEAS and TEAS improve the decomposition behavior due to a change in the chemical structure of the fibers. Raw fibers like unaligned CHF, decompose very rapidly because highly thermally unstable hemicellulose and poor strong bonding of fibers with a matrix in the composite are major factors. The partial elimination of these thermally unstable components due to the DEAS treatment decreases decomposition rates, hence resulting in enhanced thermal stability for the fibers. TEAS treatment furthers this step by optimizing chemical composition through higher amounts of impurities being taken away, while the cellulose and lignin stable to high temperatures remain. It enhances the interfacial adhesion between the fibers and the composites, improving their decomposition resistance in Table 4.4. below.

Table 4.4 Summary of average data for untreated and treated sample

SAMPLE	C (%)	N (%)	H (%)	S (%)
RAW CHF	44.56	0.68	5.288	0.351
DEAS	27.49	6.88	7.824	15.185
TEAS	34.14	6.39	9.947	13.51

In general, both treatments in DEAS and TEAS are good for retarding decomposition, but more effectively, TEAS did better. Refining the chemical composition of these treatments, thermal stability is improved and hence suitable for applications involving long-term durability and environmental stress resistance.

9. CONCLUSION AND RECOMMENDATIONS

9.0. The research objectives (RO) of this study are:

i) To synthesize and evaluate sulfate-based ionic liquids for decomposition of lignocellulose from coconut husk fiber.
ii) To characterize and analyze the synthesized sulfate-based ionic liquids used for decomposition of lignocellulose from coconut husk fiber.
iii) To determine and quantify the efficiency of the decomposition process of lignocellulose from coconut husk fiber by using sulfate-based ionic liquids and assess their characteristics.

9.1. Research Objectives Analysis

Research Objective (RO)	Explanations	Remarks
RO 1	To synthesize and evaluate sulfate-based ionic liquids for decomposition of lignocellulose from coconut husk fiber.	**Supported**
RO 2	To characterize and analyze the synthesized sulfate-based ionic liquids used for decomposition of lignocellulose from coconut husk fiber.	**Supported**
RO 3	To determine and quantify the efficiency of the decomposition process of lignocellulose from coconut husk fiber by using sulfate- based ionic liquids and assess their characteristics.	**Supported**

9.2.Conclusion

Based on the overall research, TEAS was the best ionic liquid that could enhance decomposition resistance and thermal stability in coconut husk fibers. The treatment with TEAS showed better results in enhancing thermal stability, where the fibers showed higher resistance to decomposition at high temperatures. The surface topography of the fibers after TEAS treatment also smoother and compact, which reflected the cleanliness of the fibers and enhanced adhesion between the fibers and the matrix. This treatment also conserved a higher amount of carbon residue, indicating that heat-resistant components such as cellulose and lignin were preserved. Consequently, thermal stability and structural integrity of coconut husk fibers were higher for TEAS treatments, hence making them ideal for various applications requiring durability and withstanding environmental attacks, such as biofuels and biocomposites. Therefore, TEAS has emerged as an optimum selection to improve the properties of coconut husk fibers in the said applications.

9.3.Recommendations

The obtained positive tendencies have to be optimized for a certain maximum advantage of these treatments regarding the parameters of treatment such as temperature, duration, and concentration of ionic liquids. Besides, further research into different ionic liquids with varied cations and anions may result in even better decomposition efficiency and stability of the fibers. Further research is also necessary in the context of the environmental sustainability of such treatments with ionic liquids, considering the recyclability of ionic liquids themselves. Besides, checking long-term durability under realistic conditions would become mandatory for confirmation of their suitability for sustainable applications.

10.0. ACKNOWLEDGEMENT

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REFERENCES

[1] Adewuyi, A. (2022). Underutilized Lignocellulosic Waste as Sources of Feedstock for Biofuel Production in Developing Countries. In *Frontiers in Energy Research* (Vol. 10). https://doi.org/10.3389/fenrg.2022.741570

[2]Anuchi, S. O., Campbell, K. L. S., & Hallett, J. P. (2022). Effective pretreatment of lignin-rich coconut wastes using a low-cost ionic liquid. *Scientific Reports*, *12*(1). https://doi.org/10.1038/s41598-022-09629-4

[3] Anukam, A., & Berghel, J. (n.d.). *Characterization: A Review*. www.intechopen.com

[4] Arundina, R. Y., Permana, I., Togatorop, E. R. S., Ismadi, I., Kusumah, S. S., Budiman, I., Subyakto, S., & Marlina, R. (2021). Synthesis and Characterization of Activated Carbon from Lignocellulosic Biomass: Oil Palm Empty Fruit Bunches and Mahogany Sawdust. *Jurnal Bahan Alam Terbarukan*, *10*(2). https://doi.org/10.15294/jbat.v10i2.33488

[5] Bhagia, S., Ďurkovič, J., Lagaňa, R., Kardošová, M., Kačík, F., Cernescu, A., Schäfer, P., Yoo, C. G., & Ragauskas, A. J. (2022). Nanoscale FTIR and Mechanical Mapping of Plant Cell Walls for Understanding Biomass Deconstruction. *ACS Sustainable Chemistry and Engineering*, *10*(9). https://doi.org/10.1021/acssuschemeng.1c08163

[6] Chai, Y. D., Pang, Y. L., Lim, S., Chong, W. C., Lai, C. W., & Abdullah, A. Z. (2022). Recent Progress on Tailoring the Biomass-Derived Cellulose Hybrid Composite Photocatalysts. In *Polymers* (Vol. 14, Issue 23). https://doi.org/10.3390/polym14235244

[7] Díez, D., Urueña, A., Piñero, R., Barrio, A., & Tamminen, T. (2020). Determination of hemicellulose, cellulose, and lignin content in different types of biomasses by thermogravimetric analysis and pseudocomponent kinetic model (TGA-PKM Method). *Processes*, *8*(9). https://doi.org/10.3390/pr8091048

[8] Evaluation of Coconut (Cocos nucifera) Husk Fibre as a Potential Reinforcing Material for Bioplastic Production. (2019). *By-Products of Palm Trees and Their Applications*, *11*. https://doi.org/10.21741/9781644900178-14

[9] Fan, X., Liu, S., Jia, Z., Koh, J. J., Yeo, J. C. C., Wang, C. G., Surat'man, N. E., Loh, X. J., Le Bideau, J., He, C., Li, Z., & Loh, T. P. (2023). Ionogels: recent advances in design, material properties and emerging biomedical applications. In *Chemical Society Reviews* (Vol. 52, Issue 7). https://doi.org/10.1039/d2cs00652a

[10] Harahap, B. M. (2020). Degradation Techniques of Hemicellulose Fraction from Biomass Feedstock for Optimum Xylose Production: A Review. *Jurnal Keteknikan Pertanian Tropis Dan Biosistem*, *8*(2), 107–124. https://doi.org/10.21776/ub.jkptb.2020.008.02.01

[11] Hasan, K. M. F., Horváth, P. G., Bak, M., & Alpár, T. (2021). A state-of-the-art review on coir fiber- reinforced biocomposites. In *RSC Advances* (Vol. 11, Issue 18, pp. 10548–10571). Royal Society of Chemistry. https://doi.org/10.1039/d1ra00231g

[12] Hasanov, I., Raud, M., & Kikas, T. (2020). The role of ionic liquids in the lignin separation from lignocellulosic biomass. In *Energies* (Vol. 13, Issue 18). https://doi.org/10.3390/en13184864

[13] Hawrot-Paw, M., & Stańczuk, A. (2023). From Waste Biomass to Cellulosic Ethanol by Separate Hydrolysis and Fermentation (SHF) with Trichoderma viride. *Sustainability (Switzerland)*, *15*(1). https://doi.org/10.3390/su15010168

[14] Jeetah, P., & Jaffur, N. (2022). Coconut Husk, a Lignocellulosic Biomass, as a Promising Engineering Material for Non-wood Paper Production. *Journal of Natural Fibers*, *19*(13), 5622–5636. https://doi.org/10.1080/15440478.2021.1889428

[15] Lu, Y., He, Q., Fan, G., Cheng, Q., & Song, G. (2021). Extraction and modification of hemicellulose from lignocellulosic biomass: A review. In *Green Processing and Synthesis* (Vol. 10, Issue 1). https://doi.org/10.1515/gps-2021-0065

[16] Mastura Zakaria, S., Idris, A., & Alias, Y. (2017). Lignin in ionic liquids. In *BioResources* (Vol. 12, Issue 3).

[17] Mustafa, A. H., Rashid, S. S., Rahim, M. H. A., Roslan, R., Musa, W. A. M., Sikder, B. H., & Sasi, A. (2022). Enzymatic Pretreatment of Lignocellulosic Biomass: An Overview. *Journal of Chemical Engineering and Industrial Biotechnology*, *8*(1), 1–7. https://doi.org/10.15282/jceib.v8i1.7030

[18] Nurdin, M., Abimanyu, H., Putriani, H., Setiawan, L. O. M. I., Maulidiyah, M., Wibowo, D., Ansharullah, A., Natsir, M., Salim, L. O. A., Arham, Z., & Mustapa, F. (2021). Optimization of OPEFB lignocellulose transformation process through ionic liquid [TEA][HSO4] based pretreatment. *Scientific Reports*, *11*(1). https://doi.org/10.1038/s41598-021-90891-3

[19] Podgorbunskikh, E. M., Bychkov, A. L., Ryabchikova, E. I., & Lomovsky, O. I. (2020). The effect of thermomechanical pretreatment on the structure and properties of lignin-rich plant biomass. *Molecules*, *25*(4). https://doi.org/10.3390/molecules25040995

[20] Shukla, A., Kumar, D., Girdhar, M., Kumar, A., Goyal, A., Malik, T., & Mohan, A. (2023). Strategies of pretreatment of feedstocks for optimized bioethanol production: distinct and integrated approaches. In *Biotechnology for Biofuels and Bioproducts* (Vol. 16, Issue 1). BioMed Central Ltd. https://doi.org/10.1186/s13068-023-02295-2

[21] Stelte, W., Reddy, N., Barsberg, S., & Sanadi, A. R. (2023). Coir from coconut processing waste as a raw material for applications beyond traditional uses. *BioResources*, *18*(1). https://doi.org/10.15376/biores.18.1.Stelte

[22] Uddin, M., Basak, D., Hopefl, R., & Minofar, B. (2020). Potential application of ionic liquids in pharmaceutical dosage forms for small molecule drug and vaccine delivery system. *Journal of Pharmacy and Pharmaceutical Sciences*, *23*(1). https://doi.org/10.18433/jpps30965

[23] Yasin, S. (2022). Ionic Liquids Nitrogen-Based, Preparation, Characterization, and Application. *Pharmaceutics and Pharmacology Research*, *5*(6), 01–05. https://doi.org/10.31579/2693- 7247/083

[24] Zahari, S. M. S. N. S., Azman, H., & Karim, L. (2018). Triethylammonium hydrogen sulfate ionic liquid as a low-cost solvent: A short review of synthesis, analysis and applications. *MATEC Web of Conferences*, *204*. https://doi.org/10.1051/matecconf/201820400006

[25] Zakaria, S. M., Idris, A., & Alias, Y. (2017). Lignin extraction from coconut shell using aprotic ionic liquids. *BioResources*, *12*(3). https://doi.org/10.15376/biores.12.3.5749-5774

[26] Zhang, Y., Liu, Q., Chen, J., Sun, C., Lin, S., Cao, H., Xiao, Z., & Huang, M. (2023). Developing non- invasive 3D quantificational imaging for intelligent coconut analysis system with X-ray. *Plant Methods*, *19*(1). https://doi.org/10.1186/s13007-023-01002-4

[27] Ziaei-Rad, Z., Fooladi, J., Pazouki, M., & Gummadi, S. N. (2021). Lignocellulosic biomass pre- treatment using low-cost ionic liquid for bioethanol production: An economically viable method for wheat straw fractionation. *Biomass and Bioenergy*, *151*. https://doi.org/10.1016/j.biombioe.2021.106140