

Synthesis, pretreatment, and recovery of [TEA][HSO₄] ionic liquid for OPEFB lignocellulosic transformation

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Abstract

In recent years, various studies have been utilized lignocellulosic biomass from oil palm empty fruit bunches (OPEFB) to be converted into bioethanol fuels. In this study, we present the techno-economical preparation for biomass pretreatment based on triethylamine hydrogen sulfate ([TEA][HSO₄]) ionic liquid. Synthesis, pretreatment, and recovery of [TEA][HSO₄] ionic liquid have been carried out via the one-pot method. Based on these results, the synthesized [TEA][HSO₄] has been characterized using IR spectroscopy showing the appearance chemical groups such as H, CH₃, CN, and SO₂. In addition, H-NMR spectroscopy was presented the CH₃CH₂- structure towards low ppm. Thermal stability has also demonstrated unique physical properties of ionic liquid (IL) with a melting point of 49°C and a decomposition temperature of 274.3°C. The effectiveness to produce the chemical components shows that the useful use of [TEA][HSO₄] was successfully synthesized with an optimum composition of 83% resulting in chemical levels of 45.84% (cellulose), 5.00% (hemicellulose), and 34.40% (lignin). The recovered [TEA][HSO₄] with a composition of 90.90% was effective in reducing the lignin content about 80%. These results also depend heavily on the temperature and separation techniques applied during the pretreatment process.

1. Introduction

Nowadays, the pretreatment technology (PT) has been promoted as one of the promising methods in treating lignocellulosic biomass (Kim et al., 2016; Sindhu et al., 2016; Fithri et al., 2020). It is utilized as renewable energy sources for producing bioethanol, biopesticides, sugars, and biofuels. In addition, the PT is crucially the first stage which plays an important role in lignocellulosic biomass transformation and to overcome the abundance of lignocellulosic waste (Naik et al., 2010; Singh et al., 2010; Arbaain et al., 2019). Based on this brief background, the PT was improved to overcome the abundance of lignocellulosic biomass waste (Natsir et al., 2018b; Arutanti et al., 2020). Unfortunately, the effectiveness of lignocellulose pretreatment has not shown optimal results because it is influenced by differences in the raw material source (Maulidiyah et al., 2017; Natsir et al., 2018a; Maulidiyah et al., 2019). According to Kassaye et al. (Kassaye et al., 2017) reported that the chemical composition in lignocellulose biomass is certainly influenced by differences in raw materials used, for example the lignocellulose in bamboo has a varied chemical composition with differences in sugar polymer content (cellulose and hemicellulose) in the range of 38-50% or 23-32% and lignin on 15-25%.

Especially in OPEFB waste is a potential source of cellulose which can serve as a promising raw material for the production of bioethanol (Rosli et al., 2017; Hassan et al., 2020). Approximately 70% of OPEFB is produced from palm oil production, and the remaining 25-30% produces palm oil (Fithri et al., 2020). Based on these problems, it encourages us to develop effective, cheap, and environmentally friendly pretreatment technologies. Several pretreatment methods have been reported to be applicable in obtaining cellulose from lignocellulosic biomass, such as the use of alkaline (Nargotra et al., 2018; Song et al., 2019; Yang et al., 2019), acidic (Nargotra et al., 2018), hydrothermal (Simanungkalit et al., 2017), steam (Amin et al., 2017; Kim et al., 2018), organosolv (Borand & Karaosmanoğlu, 2018), ionic liquids

(Mahmood et al., 2016; Halder et al., 2019), and alkaline-ionic liquid combinations (Meek et al., 2016; Nykaza et al., 2016; Kassaye et al., 2017). Generally, these methods have also an impact on the high use of hazardous chemical solvents during the pretreatment process which can cause new environmental problems (Fithri et al., 2020).

In order to overcome this problem, IL pretreatment is a promising method as a new technology that offers a deconstruction of lignocellulose biomass with a low melting point (Alayoubi et al., 2020; Nasirpour et al., 2020). The IL has special properties such as wider fluid temperatures, high thermal stability, and negligible vapor pressure (Yuan et al., 2017). Certainly, these essential properties are needed in the lignocellulose biomass transformation. In addition, the advantages of this method are environmentally friendly, high-recovery process, better delignification, effectively reduce the crystallinity of cellulose and do not damage the sugar content during the fermentation process (Li et al., 2010a).

Many studies have successfully synthesized and applied ILs in lignocellulosic biomass pretreatment such as using 1-ethyl-3-methylimidazolium-diethyl phosphate (Zaitsau & Verevkin, 2020), 1-Butyl-3-methylimidazolium chloride (Xie et al., 2020), 1-Ethyl-3-methylimidazolium acetate (Liang & Liu, 2020), 1-allyl-3-methylimidazolium chloride (Hmad & Gargouri, 2020; Ikeguchi et al., 2020), and 1-Butyl-3-methylimidazolium bis (trifluoromethyl sulfonyl) (Busato et al., 2020). Although it also shows the high-effectiveness under the pretreatment process, the use of ILs continues to be developed and modified in order to reduce production costs and also to improve the stability of ILs (Zhang et al., 2017; Hallett et al., 2019). So in this study, we observe the utilization of [TEA][HSO₄] in OPEFB biomass pretreatment by studying several treatments like synthesis, OPEFB biomass pretreatment, and recovered [TEA][HSO₄] ionic liquid. The pretreatment of the OPEFB biomass was examined with the goal that we should explain the ability to reuse [TEA][HSO₄] in reducing lignocellulosic biomass. Then to assess this, we also present the effectiveness and optimization of recovery [TEA][HSO₄] into the pretreatment process.

Referring to the various problems above, this research aims to synthesize IL based on [TEA][HSO₄] through a one-pot method with a combination of triethylamine and sulfuric acid which applied for OPEFB lignocellulosic pretreatment and studied the reuse of [TEA][HSO₄] ionic liquid. Certainly, we demonstrated the physical-chemical properties characterized by using IR, H-NMR, and TGA to confirm the result of IL synthesized. We also determine mass variation and temperature effect during lignocellulosic pretreatment.

2. Experimental Methods

2.1 Apparatus and Materials

Starting materials for synthesizing [TEA][HSO₄] were purchased from Sigma Aldrich and the apparatus used from Iwaki Pyrex. The characterization was measured by Dr. Haznan Abimanyu in Research Center for Chemistry, Indonesian Institute of Sciences by using FTIR (Nicolet FT-IR iS10, USA). The ¹H-NMR was recorded on a Bruker 500 MHz spectrometer. Chemical shifts (δ) are reported in ppm with the D₂O peak at

8.0 ppm and TGA (SDT-2960, USA) was analyzed to observe temperature rate towards % weight loss of [TEA][HSO₄].

2.2 Synthesis of [TEA][HSO₄] ionic liquid

Synthesis of [TEA][HSO₄] has been conducted by referring to the method reported by Gschwend et al. (Gschwend *et al.*, 2018). In summary, 75.9 g (750 mmol) of triethylamine was inserted into a three-neck flask and stirred by using a magnetic stirrer under cold conditions. Under stirring, it slowly added 5M H₂SO₄ 97% and ethanol solution (1:5 w/w) for 24 hours. After that, the ethanol solution was removed using a vacuum evaporator for 2 hours and dried in a vacuum oven at 40°C for 8 hours. Finally, the [TEA][HSO₄] was analyzed using FTIR, ¹H-NMR, and TGA.

2.3 Composition and temperature effect under the pretreatment process

The study of lignocellulose pretreatment on OPEFB was carried out by varying the composition of [TEA][HSO₄] with a variation concentration of 80%, 83%, and 90.9% which contains of 8.0 g, 8.30 g and 9.90, respectively. Where the [TEA][HSO₄] was inserted into Schott bottle containing distilled water and 2.0 g of OPEFB sample, then it stirred for 17 hours at 80°C and separated the filtrate with residue using a vacuum pump followed by adding ethanol solvent to increase the evaporation process under 50°C. The residue obtained was analyzed referring to the method determined by the National Energy Renewable Energy Laboratory (NREL). Based on this process, we observe the effectiveness of [TEA][HSO₄] based on the optimal weight percentage under lignocellulose pretreatment process to produce chemical content such as cellulose, hemicellulose, and lignin. Furthermore, we tested it under temperature variations at 30°C; 50°C; 80°C; 100°C; 120°C, and 150°C.

[2.4 TEA][HSO₄] ionic liquid recovery

The [TEA][HSO₄] recovered from the previous pretreatment was filtered using a vacuum filter with adding methanol solution. Then, methanol and [TEA][HSO₄] were separated again using a rotary evaporator with heating temperatures below 80°C. Then, [TEA][HSO₄] was washed using distilled water 2-3 times and centrifuged with a rotation speed of 10,000 rpm for 15 minutes at 4°C. [TEA][HSO₄] which is still mixed with water is separated again using a rotary evaporator with a heating temperature of 100°C so that [TEA][HSO₄] and distilled water are separated completely.

3. Results And Discussion

3.1 Characterization of [TEA][HSO₄] ionic liquid

The synthesized [TEA][HSO₄] was confirmed using FTIR, H-NMR, and TGA which aims to represent the determination of chemical structure and temperature profile. The FTIR data is to describe organic chemical groups and several inorganic materials. In this case, In this case, IR data (Figure 2) has shown

new wavenumbers absorption spectra at 2814.97 cm^{-1} , 1401.07 cm^{-1} , 1233.30 cm^{-1} , and 847.92 cm^{-1} showing the absorption of chemical groups such as NH, CH₃, CN, and SO₂. Some absorption of chemical peaks from H₂O, H₂SO₄ and TEA have been summarized in [TEA][HSO₄] peak but there was a shift in wavenumbers absorption because it has occurred the chemical reaction between H₂SO₄ and TEA. The [TEA][HSO₄] synthesized was successfully confirmed at the IR absorption peak on 1438.30 cm^{-1} to 1474.93 cm^{-1} shows the specific absorption of the CH₂ group, and also 1048.18 cm^{-1} to 1063.00 cm^{-1} indicated of the SO group.

To support FTIR data, we also characterize using H-NMR spectroscopy to describe the CH₃CH₂- structure in [TEA][HSO₄]. Based on the data (Figure 3A), we discover two high specific peaks that predicted from CH₃- at 1.106 ppm and CH₂-N at 3.005 ppm. Based on the chemical structure proposed in Figure 1 has shown the CH₃CH₂- a structure formed so that the direction of the chemical shift lead to low ppm. In addition, physical properties have been identified based on thermal analysis using the TGA instrument is important to analyze the performance of IL which will be applied to the lignocellulose pretreatment process. In the first step (Figure 3B), we start the thermal analysis under ambient temperature at 37°C. Then, there was a decrease in weight percentage from 37°C to 100°C exhibits that the solvent components have evaporated such as H₂O and ethanol. From 100°C to 210°C illustrates the role of [TEA][HSO₄] stabilized at high temperature, this condition can be used as a variable pretreatment process. However, IL has decomposed at temperatures of 274.3°C to 500°C.

3.2 Pretreatment process using [TEA][HSO₄] ionic liquid

For studying the effectiveness pretreatment process, we vary IL concentrations and temperatures to obtain the high cellulose content which is can be used for bioethanol production. The synthesized [TEA][HSO₄] has been tested towards OPEFB lignocellulose by varying concentration of 80%, 83%, and 90.9% under a temperature of 120°C. Based on Figure 4 shows that the effectiveness of [TEA][HSO₄] ionic liquid for OPEFB lignocellulose pretreatment can increase the cellulose content in 45.84% with the achievement of 83% [TEA][HSO₄] concentration. In addition, the increasing concentration in the usage of IL was also effective to decrease lignin content which successively drops from 53.56 (80%), 32.8 (83%), and 30.11 (90.9%). According to Gschwend et al. (2018) that the usage of [TEA][HSO₄] is intended only to observe high cellulose content so that the optimal concentration used is 83%.

Referring to the 83% [TEA][HSO₄] concentration in the pretreatment process, we also tested temperature variations for the lignocellulose pretreatment process. It has been carried out with variations of 50, 80, 100, 120, and 150°C which is intended to observe IL that can be applied in low-temperature. Figure 5 shows that good performance for producing chemical content especially in cellulose compound is shown at the temperature of 80, 100, and 120°C. This is clearly an increase in cellulose content during pretreatment using the [TEA][HSO₄] ionic liquid. However, at 150°C the cellulose content decreases due to damage to cellulose compounds and also the IL slowly decomposes. In addition, amorphous cellulose is

easily hydrolyzed because water molecules and protons easily enter the amorphous cellulose region and damage the β -1,4-glycosidic bond (Gschwend et al., 2018). Based on this variation, it is known that the optimum cellulose from the pretreatment process using [TEA][HSO₄] occurs at 120°C.

3.3 [TEA][HSO₄] ionic liquid recovery

The potential reuse of [TEA][HSO₄] for lignocellulose repretreatment is a techno-economical way to obtain optimal pretreatment processes. At this stage, the separation of IL should be carefully because the volume obtained is small and does not apply to high-scale pretreatment. In addition, the IL recovery is needed quite time-consuming so that new innovations should be improved to streamline research time. Actually, the optimization of IL recovery is a key step in biomass pretreatment because it is cheaper and reusable (Li et al., 2010b). So in this work, the recovery IL process was conducted by using simple glass tool model to separate the OPEFB biomass with [TEA][SO₄] through several stages like separation and initial & final leaching processes. Separation process was applied by eliminating lignocellulosic bonds under a methanol solution and purified with a washing process at 100°C. The successfully for recovery phase was demonstrated with the increase in viscosity properties accompanied by discolouration of brown. Based on Figure 6 demonstrates that the recovered [TEA][SO₄] has produced a dark brown colour which is indicated the discolouration of [TEA][HSO₄] recovery in the pretreatment process.

The effectiveness of IL recovery was evaluated by comparing [TEA][HSO₄] to recovery [TEA] [HSO₄] based on the chemical elements contained in the lignocellulosic biomass. This is intended to observe [TEA] [HSO₄] recovery can be reused and to reduce high-costs. Referring to the purification method above, measurements were carried out three times repeatedly to optimize the pretreatment process to produce chemical compounds, namely lignin, cellulose, and hemicellulose, as the average results are shown in Table 1.

It can be seen the comparison of [TEA] [HSO₄] to recovery [TEA][HSO₄] has a significant difference in chemical constituents. The high chemical constituents using 83% [TEA][HSO₄] fresh has indicated the high cellulose content in 45.84%. Meanwhile, the [TEA][HSO₄] recovered has dramatically decreased along with increasing concentrations. It is due to higher composition IL can prevent lignin formation from the hemicellulose monomer hydration process so that the lignin content in the high composition will decrease (Kumar et al., 2009). In addition, there is reaction stagnation caused by the terminating of β -1,4 glycosidic bonds during the addition of 72% H₂SO₄. Nonetheless, the decrease of lignocellulose contents is much smaller than before the pretreatment process.

Table 1. Comparison of chemical constituents before and after recovery [TEA][HSO₄]

Chemical constituents	% [TEA][HSO ₄] Before Recovery			% [TEA][HSO ₄] After Recovery		
	80.00%	83.00%	90.90%	80.00%	83.00%	90.90%
Cellulose	35.50	45.84	40.13	29.13	26.96	24.19
Hemicellulose	3.70	5.87	2.33	2.55	1.90	2.18
Lignin	53.56	32.8	30.11	32.57	19.85	17.09

4. Conclusion

The synthesis of [TEA][HSO₄] and its application for the lignocellulose pretreatment process based on OPEFB waste has been studied to obtain the potential reuse of IL for lignocellulose pretreatment. The one-pot method is effective for synthesizing [TEA][HSO₄] ionic liquid as evidenced by specific IR absorption which indicates the presence of chemical groups such as NH, CH₃, CN, and SO₂. The ¹H-NMR spectroscopy showing that there was formed the CH₃CH₂- structure with a chemical shift leading to low ppm. Thermal stability has also demonstrated unique physical properties of IL with a melting point of 49°C and a decomposition temperature of 274.3°C. The effectiveness to produce the chemical components shows that the useful use of [TEA][HSO₄] was successfully synthesized with an optimum composition of 83% resulting in chemical levels of 45.84% (cellulose), 5.00% (hemicellulose), and 34.40% (lignin).

Declarations

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Conflict of Interest Statement

All authors declare that this article has no conflict of interest.

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Figures

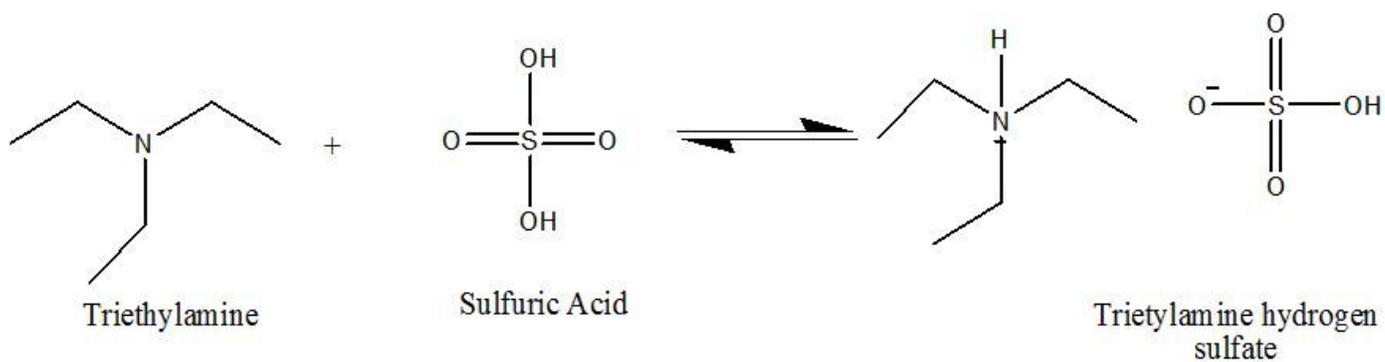


Figure 1

The proposed reaction mechanism to form of [TEA][HSO₄] ionic liquid

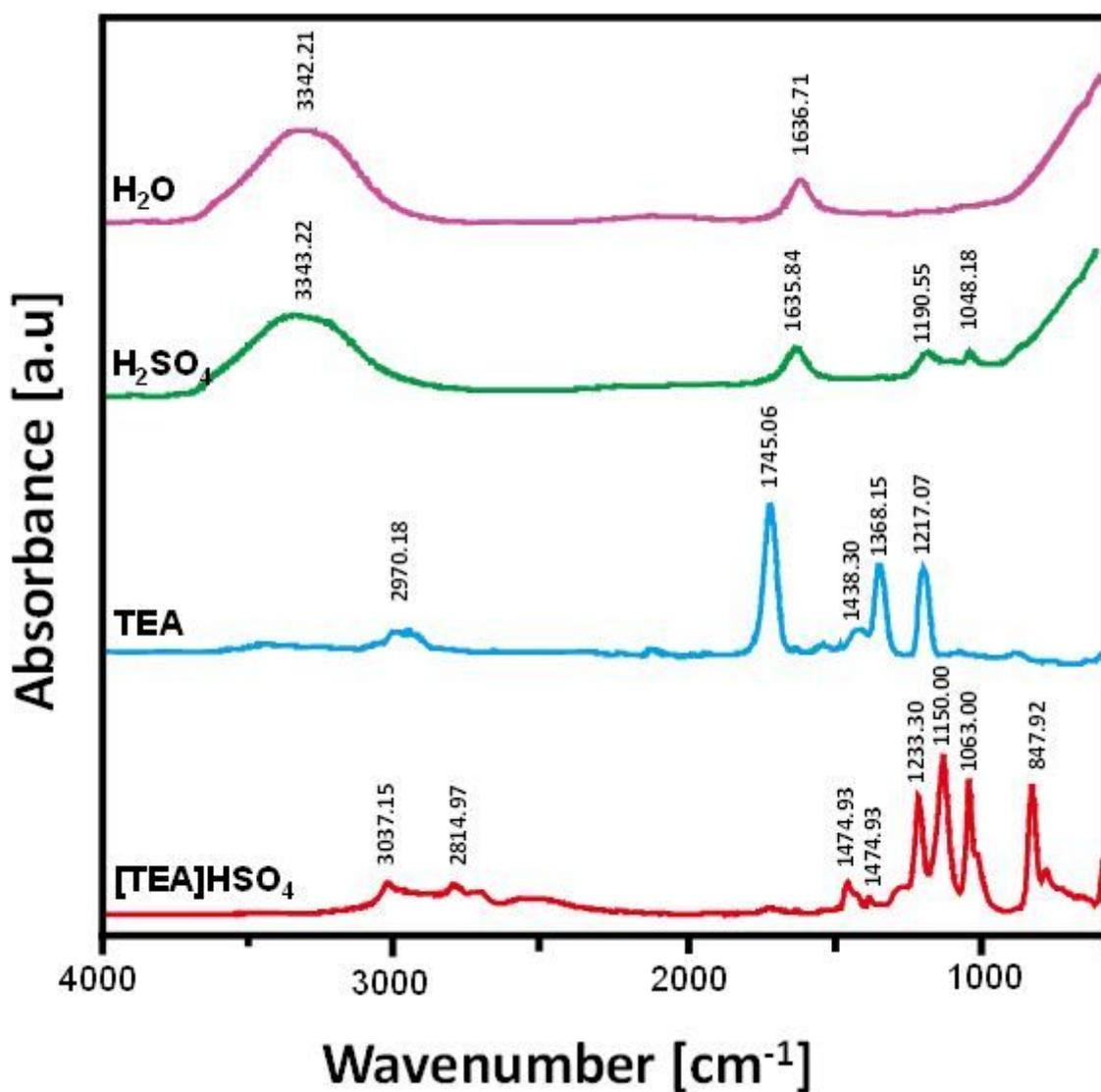


Figure 2

IR spectrum of [TEA][HSO₄] constituents

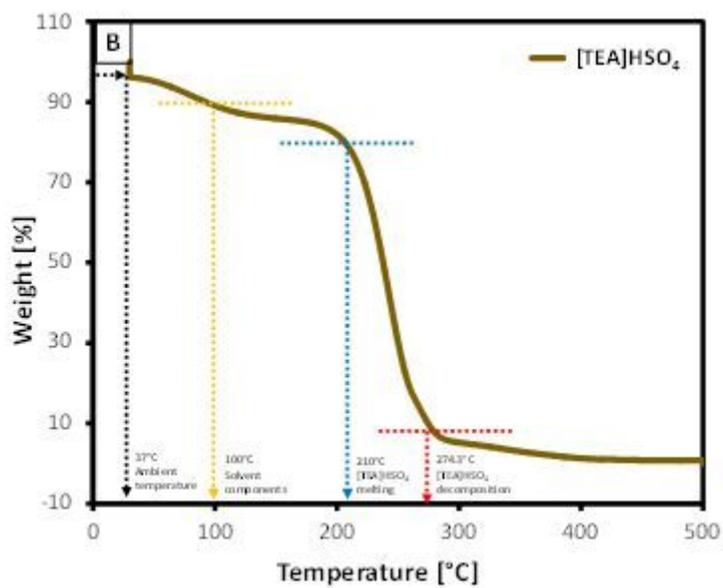
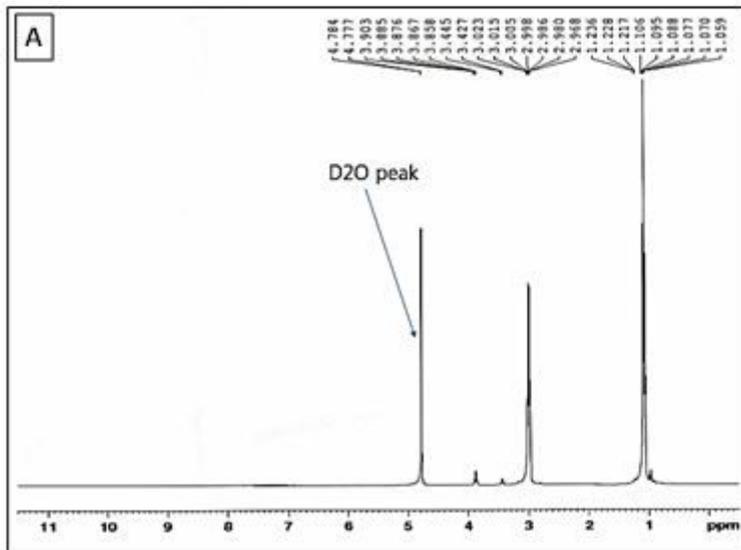


Figure 3

The $^1\text{H-NMR}$ spectrum (A) and thermal analysis (B) of $[\text{TEA}][\text{HSO}_4]$ ionic liquid

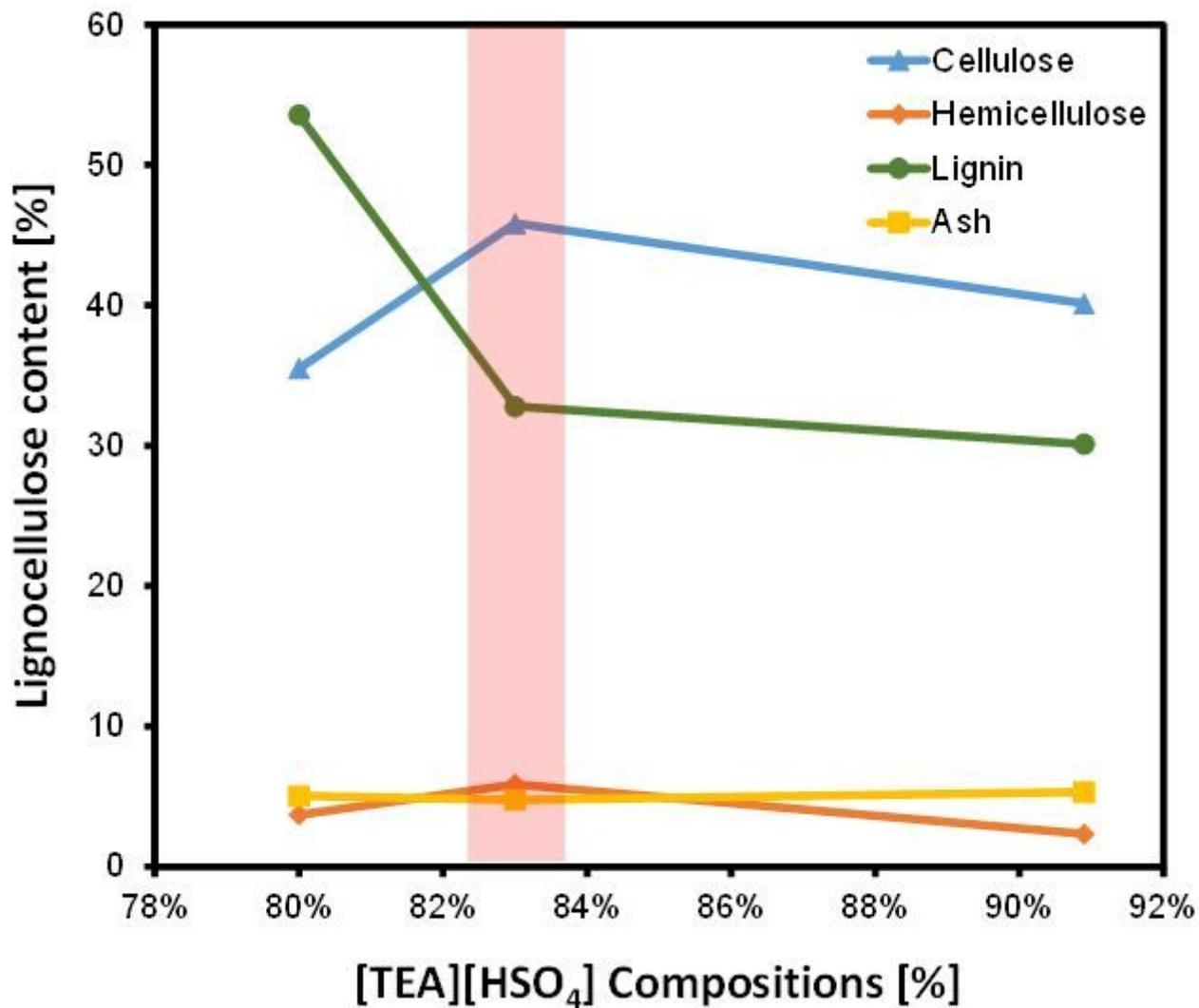


Figure 4

The optimal concentration used for OPEFB lignocellulose pretreatment

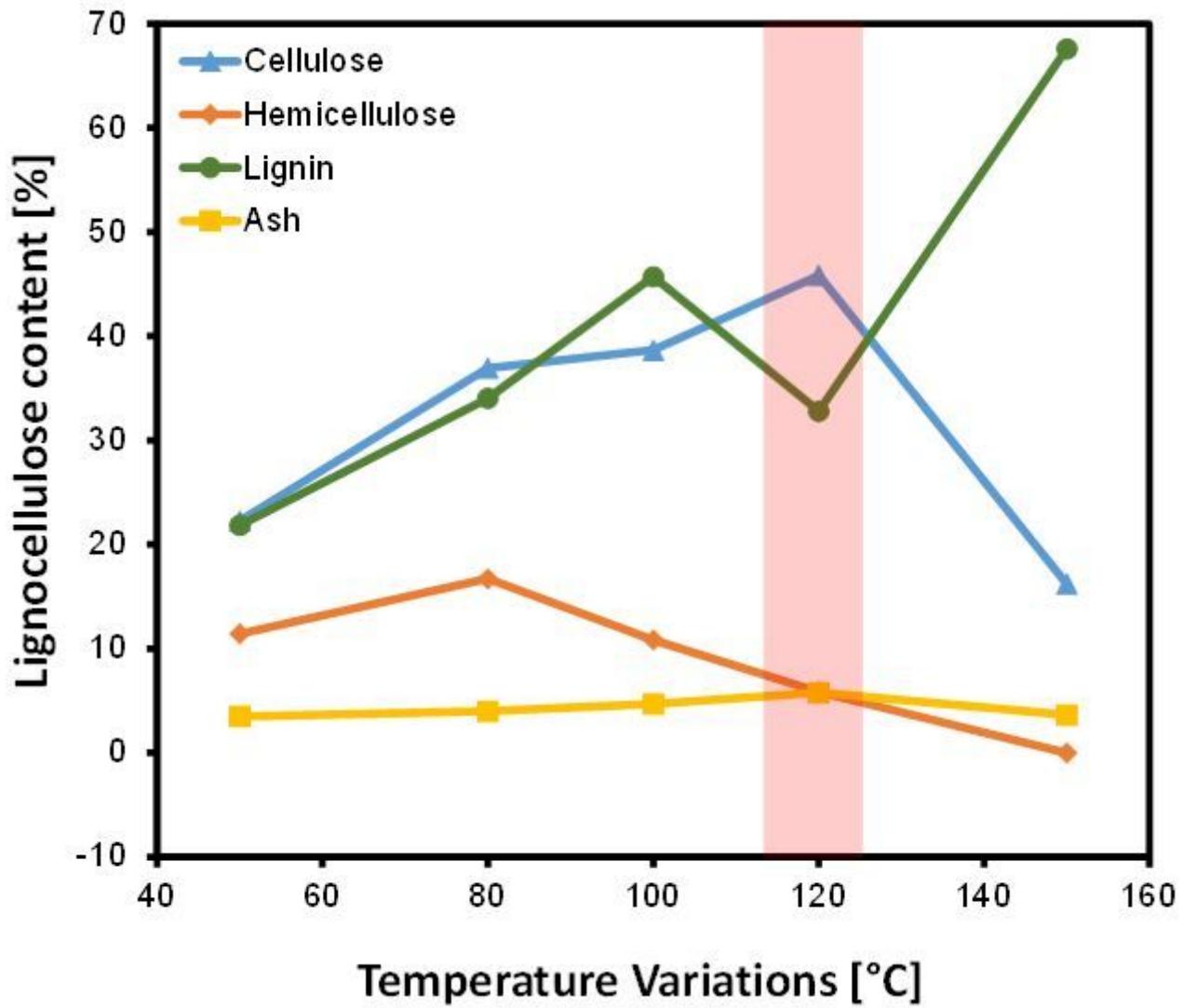


Figure 5

Temperature variation during the pretreatment process using [TEA][HSO₄]

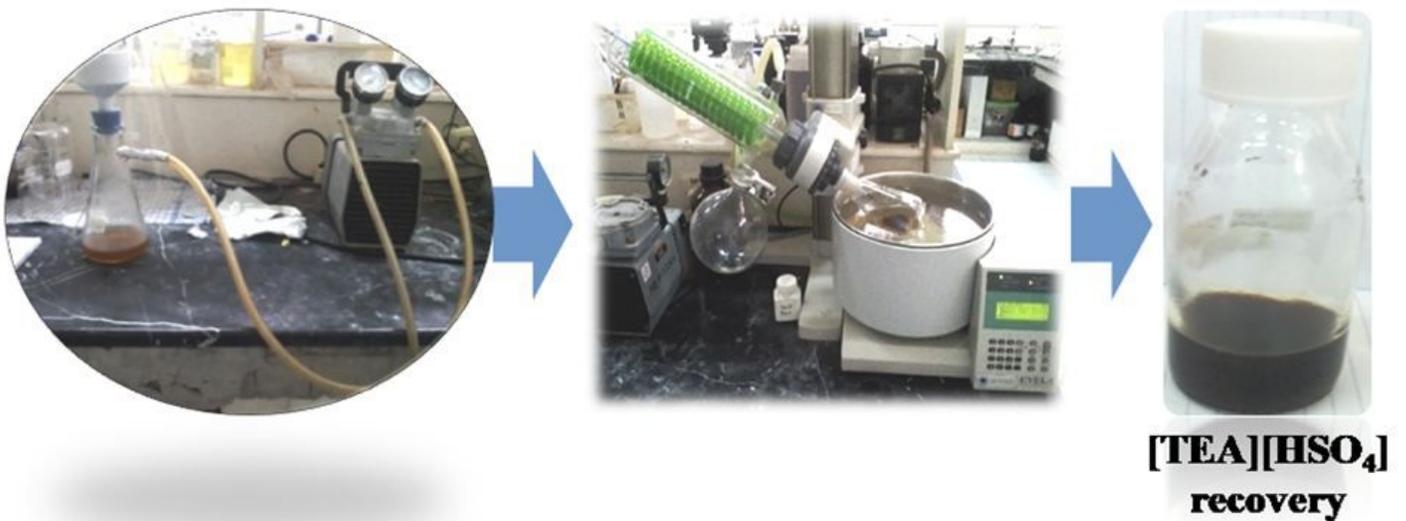


Figure 6

The recovery process of [TEA][HSO₄] ionic liquid