Effectiveness of Green Chemical Solvent-based on Triethylammonium Methanesulfonate Ion Liquid for the OPEFB Pretreatment Process

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Abstract: Many studies have explored the pretreatment of lignocellulosic biomass based on oil palm empty fruit bunch (OPEFB) which is categorized as potential biomass waste for bioethanol production. Before proceeding further to obtain bioethanol, several steps such as pretreatment to increase organic constituents are needed. The ionic liquids (ILs) were commonly investigated by many researchers for lignocellulosic pretreatment because it is easy solubilization property, non-toxic, and not harmful impacts on the environment. Therefore in this study, the hypothesis and main objective were to observe the effectiveness of triethylammonium methanesulfonate ion liquid (TMS IL) in the OPEFB lignocellulose pretreatment process. Three variations were studied to obtain optimization of the pretreatment process, such as times duration, IL composition, and temperature. Based on these results, we observed the effectiveness of the time duration for OPEFB pretreatment of 20 hours. Furthermore, it was applied to determine the optimization of IL composition and temperature showing that using 91% (1:1:10) at 120°C for 20 hours has provided good performance for the OPEFB lignocellulose pretreatment process. TMS IL has exhibited the ability to reduce hemicellulose and lignin contents to 7.35% and 17.80%, whereas cellulose was increased by 54.24%. This has the opportunity to be projected to a larger scale for bioethanol production based on OPEFB lignocellulose.

Key words: OPEFB, pretreatment, lignocellulose, TMS, bioethanol

1 Introduction

Nowadays, oil palm plantations have a highly developed potential for palm oil production and renewable resource to replace fossil energy and reduce environmental deterioration¹. In Indonesia, it is very abundance grown to produce palm oil as known as crude palm oil (CPO)²,³. During processing, it also produces biomass waste such as oil palm empty fruit bunches (OPEFB), which can be a raw material for bioethanol production⁴,⁵. Lignocellulosic biomass such as OPEFB is a major waste from the oil palm industry that contains fibrous lignocellulose biomass and other organic constituents. In the community, OPEFB is only utilized as compost, paper making, organic fertilizer and briquettes⁶,⁷. In fact, it can be developed as bioethanol production because it contains 40-50% cellulose and 24-40% hemicellulose, which are potential as main raw materials for energy production⁸,⁹.

Bioethanol production is not as easy as imagined because it has to go through several stages such as pretreatment and fermentation process depending on organic constituents¹⁰,¹¹. Several studies have focused on modifying the pretreatment process by using acidic, alkali, organosolv, ion liquids, and enzymatic which goal to destruct lignocellulose structure to obtain high organic constituents from
cellulose or hemicellulose\textsuperscript{12–15}. However, the use of acidic, alkali, organosolv, and enzymatic techniques have disadvantages properties besides apart from depending on the ambient condition and lead to environmental deterioration\textsuperscript{16, 17}.

The effectiveness of pretreatment technologies has been applied by using ionic liquids because of easy solubilization property, non-toxic, removal of wax facilitated the significant rearrangement of internal structure and transformation of crystal cellulose an amorphous one, resulting in better enzymatic hydrolysis\textsuperscript{23}. According to Mohtar et al.\textsuperscript{19} reported that the 1-butyl-3-methylimidazolium chloride ([bmim] [Cl]) ion liquid has shown effective to extract lignin compound and increasing cellulose content. With the same ion liquid used by Nargotra et al.\textsuperscript{20} has shown the high potential for biofuel production based on cellulose constituent. Meanwhile, Liu et al.\textsuperscript{18} also reported that the use of 1-butyl-3-methylimidazolium acetate ([BMIM] Ac) ion liquid has higher potential solubilization property and transformation of crystal cellulose. Application of unique capability ionic liquids have a deconstruction of complex polysaccharides and removing lignin under ambient reaction conditions\textsuperscript{21, 22}. Exploration of novel ionic liquids feedstocks for biorefineries has been a continuous promising practice.

Therefore in this study, we tried to observe the OPEFB pretreatment process by using TMS IL that has provided a sustainable alternative to more common lignin degradation processes and proton transport reactions had a significant impact on the degradation efficiency\textsuperscript{23}. Regarding previous work, including TMS IL for pretreatment of OPEFB biomass, favourable conditions at high temperatures of 150°C, many variations in concentration, and duration of time\textsuperscript{24}. But it also needs to be confirmed as a standard methodology for establishing a pretreatment process for OPEFB biomass waste based on TMS IL. This advantage can be used as an alternative treatment in dissolving cellulose biomass into glucose (nanocellulose) in OPEFB because it does not harm the environment and as a substitute for organic solvents in the lignocellulose pretreatment process\textsuperscript{25}. Therefore, the pretreatment method using TMS IL is considered under green chemistry, this makes the process viability even more significant and has the opportunity to be projected to a larger scale.

2 Methods

All materials are purchased from Sigma-Aldrich. The TMS IL test for OPEFB biomass pretreatment was applied to three variable variations such as time duration, IL composition, and temperature. First, we determine the effectiveness of the time duration for the pretreatment process using time variations of 14, 17, and 20 hours with an IL composition of 83% (1:1:4) (OPEFB:H\textsubscript{2}O:TMS) w/w at 120°C. After that, the composition of TMS IL was improved to 83% (1:1:4); 85% (1:1:5) and 91% (1:1:10) by using the optimal duration of time obtained and the temperature of 120°C. Finally, we also determine the optimal temperature used by varying 50, 80, 100, 120, and 150°C to obtain the effectiveness of OPEFB biomass pretreatment using TMS IL. During IL performance tests, we perform IL recovery to separate TMS from lignocellulosic biomass by filtering OPEFB and followed by adding methanol as a solvent using a vacuum filter. Furthermore, methanol and TMS are separated using a rotary evaporator with temperatures below 60°C. The final step, IL is washed using distilled water and centrifuged for 15 minutes at 4°C at a rotational speed of 10,000 rpm to separate TMS from organic constituents. Organic constituents were analyzed using high-performance liquid chromatography (HPLC) and UV-Vis spectrophotometer which refers to the National Renewable Energy Laboratory (NREL) procedure.

3 Results and Discussion

3.1 Study of untreated OPEFB

The initial stage of OPEFB biomass analysis before the pretreatment process, we determined the OPEFB organic constituents to evaluated the effectiveness of pretreatment using TMS IL. The analysis was carried out using HPLC where the sample size used was 30 mesh for all treatments because a smaller sample size would maximize contact between IL and lignocellulose so that lignin could be reduced, while cellulose and hemicellulose could be hydrolyzed optimally. OPEFB biomass is very difficult to destruct, so in this case we destruct by using a crusher to obtain the small particle size. Based on Table 1, we summarize the results of treatment variation of this study. Under the untreated OPEFB shows that the high lignin content followed by cellulose and hemicellulose in OPEFB biomass waste. It has the potential to be used as a biomass material for bioethanol production because of its containing cellulose before the pretreatment process. The level of organic constituents such as cellulose, hemicellulose and lignin were obtained of 27.40%, 12.87%, and 34.61%, respectively. Although lignin is also presented with high content, this is serious work to reduce lignin level in the pretreatment process. In addition, lignin can also inhibit the hydrolysis process because it has a complex molecular structure that will impact the difficulty of the hydrolysis process and requires a long time to reduce levels of lignin and hemicellulose. Previous studies have also been reported by Nieves et al.\textsuperscript{26} that the untreated material contained 24.6% lignin and dominated the type of lignin in acid-insoluble waste. Whereas, Hamzah et al.\textsuperscript{27} obtained 43.8% cellulose, 16.4% lignin, and 35.0% hemicellulose.
3.2 Time optimization

To observe the optimal time effort in the pretreatment process, where the initial pretreatment was applied by using TMS IL in a ratio of 1:1:4 (83%) at a temperature of 120°C with a variation of time 14, 17, 20 hours. High-temperature and time applications are expected to increase cellulose content and reduce lignin level during pretreatment. According to Li et al.\textsuperscript{27}, temperature selection for the delignification process is between 100-130°C to obtain high cellulose content. Furthermore, we separated the sample with IL using a rotary evaporator followed by inserting the methanol solution. The residual sample was evaporated to reduce the water content to less than 10%.

To identify organic constituents into OPEFB biomass after pretreatment, it was hydrolyzed by 2 stages. First, we used a 72% H\textsubscript{2}SO\textsubscript{4} solution under low temperature and the second it diluted using 84 mL of distilled water at high temperature. According to Chen et al.\textsuperscript{28} reported that acid hydrolysis combined with temperature can damage the β-1,4-glycosidic bonds in cellulose structure. This is the most effective process for producing nanocellulose. After that, analysis of organic constituents from OPEFB biomass was carried out using HPLC and UV-Vis Spectrophotometer. HPLC has been used to determine cellulose and hemicellulose levels while UV-Vis spectrophotometer is used to determine lignin level. The results obtained in the pretreatment variation process using TMS ion liquid can be seen in Table 1.

Table 1 The results of treatment variation of this study.

| Variable study | Treatment variation | Organic Constituents of OPEFB biomass (%) |
|----------------|---------------------|-----------------------------------------|
|                |                     | Cellulose      | Hemicellulose | Lignin      |
| Untreated OPEFB|                     | 27.40          | 12.87         | 34.61       |
| Times optimization | 14 h 83 (1:1:4) 120°C | 32.89 ± 2.76  | 11.31 ± 0.49  | 28.71 ± 1.53 |
|                | 17 h 83 (1:1:4) 120°C | 35.81 ± 1.53  | 12.63 ± 0.84  | 28.46 ± 0.38 |
|                | 20 h 83 (1:1:4) 120°C | 37.23 ± 1.05  | 11.69 ± 2.30  | 26.20 ± 2.12 |
| OPEFB Pretreatment using TMS ion liquid | Composition TMS ion liquid | 83 (1:1:4) 20 120°C | 53.41 ± 2.06 | 9.75 ± 0.45  | 27.42 ± 3.11 |
|                | 85 (1:1:5) 20 120°C | 54.24 ± 2.62  | 7.35 ± 1.03   | 17.80 ± 3.10 |
|                | 91 (1:1:10) 20 120°C | 28.76 ± 2.47  | 10.90 ± 0.90  | 27.82 ± 1.66 |
|                |                     | 32.73 ± 2.69  | 20.27 ± 1.78  | 27.55 ± 2.46 |
|                |                     | 47.53 ± 1.97  | 14.90 ± 0.40  | 28.46 ± 0.38 |
|                |                     | 54.24 ± 2.62  | 7.35 ± 1.03   | 17.80 ± 3.10 |
|                |                     | 29.60 ± 5.39  | 0.46 ± 0.61   | 59.18 ± 0.60 |

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Fig. 1 Results of time optimization of TMS IL in the OPEFB pretreatment process.

Referring to Table 1, we extract values from time variation versus organic constituents which goal to observe the effectiveness of the OPEFB pretreatment process using TMS IL as shown in Fig. 1. Based on Fig. 1 it can be seen that the difference in the level of the organic constituents which is the role of TMS IL performance. Prolonged times during the pretreatment process has increased cellulose content followed by hemicellulose, although not significantly. While effective condition shows a decrease in lignin content.
level together with a long pretreatment process. Based on this result, we concluded the effectiveness time variation for the OPEFB pretreatment process of 20 hours. This is evidenced by comparing the levels of lignocellulosic biomass before pretreatment and cellulose content increased by 9.83%, while lignin levels decreased by 8.41% and hemicellulose decreased by 1.18%.

Chemical pretreatment using TMS IL has rendered selective functionality in biomass degradation. IL selectively solubilize hemicellulose and some chemicals solubilize lignin components. In fact, lignin in lignocellulosic biomass is the main obstacle during the biomass pretreatment process. The role of pretreatment process using TMS IL to remove lignin content is necessary to enhance cellulose which later can be utilized as bioethanol production. Lignin is degraded into simple alcohol compound products such as p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. However, the pretreatment was effectively removing and recovering hemicellulose portions as soluble sugars in aqueous solution. The hemicellulose is reduced because it can be easily hydrolyzed by dilute acid, alkali, or enzymes under mild conditions. Due to its high thermochemical sensitivity, hemicellulose degradation can easily occur to form unwanted coproducts (furfurals and hydroxymethyl furfurals), which inhibits the fermentation process for bioethanol production. Thus, if we can mobilize the contents of hemicellulose and lignin, the cellulose can be increased to form nanocellulose.

Based on Fig. 2A, the presence of triethylammonium ions in TMS IL to produce Bronsted acid (H+) as a catalyst source to protonation of oxygen atoms in β-1,4-glycosidic bonds in the cellulose chain. This aims to form nanocellulose as a sugar monomer for future fermentation into bioethanol production. In addition, Fig. 2B depicts the role of methanesulfonate ions in TMS IL during the esterification process occurred in between methanesulfonate ions and hydroxyl groups to yield “cellulose methanesulfonate”. This is one treatment for increasing cellulose content to simple molecules.

3.3 The composition variation of TMS IL

Previously in time variation, we used 83% TMS (1:1:4) had shown increased cellulose levels and decreased lignin and hemicellulose. Thus, we try to increase variations in the concentration used of TMS IL to observe the optimization of IL used towards concentration variations of 85% (1:1:5) and 91% (1:1:10) based on the weight of OPEFB, with a heating temperature of 120°C for 20 hours. The analysis results from the OPEFB pretreatment process by using TMS IL with various concentrations can be seen in Fig. 3.

![Fig. 2](image-url) The role of TMS IL in the OPEFB lignocellulose pretreatment process (A) acid hydrolysis of cellulose into nanocellulose based on Triethylammonium group, and (B) Formation of sulfate group on the nanocellulose from methanesulfonate.
By varying the composition of TMS IL shows that the effectiveness of the lignocellulosic pretreatment was performed using 91% IL by weight of OPEFB. Explicitly, the cellulose content has increased to 54.24% due to the amount of ion liquid percentage given is greater, so the reaction rate to produce H⁺ is also richer to more easily break lignin bonds and provide catalyst access to hydrolyze cellulose. In addition, the role of H⁺ ions can bind –OH groups from phenyl propane units in lignin to facilitate the degradation process.

3.4 Temperature variations

Afterwards, we also continued this experiment on the performance of temperature variations that refer to the optimal time for 20 hours and the composition of IL 91% during OPEFB pretreatment. The temperature variation effect is applied at 50°C, 80°C, 100°C, 120°C and 150°C for 20 hours. Based on Fig. 4 shows that differences in the content of organic constituents between cellulose, hemicellulose and lignin. Below 120°C shows a significant increase in cellulose content. Lignin has stabilized between 50-100°C but decreases when the temperature is raised to 120°C. Uniquely, at 150°C lignin also presents high content. It is due to the lignin and hemicellulose play a role in the formation of pseudo-lignin structures at high-temperature. In addition, chemical structure damage also occurs in cellulose and hemicellulose at high temperatures, while lignin can still survive because it has a complex molecular structure. We also suspect TMS IL can only work at temperatures below 130°C. For this reason, we concluded to obtain high cellulose and low lignin during OPEFB pretreatment using effective TMS IL at temperatures between 100-130°C.

4 Conclusion

Ionic liquids are promising green chemistry solvents with unique properties. It is useful for lignocellulosic biomass pretreatment to improve the organic constituents. We demonstrated the application of TMS IL in OPEFB pretreatment process shown excellence to reduce hemicellulose and lignin contents to 5.52% and 16.81%, whereas cellulose was increased by 26.84%. This has the opportunity to be projected to a larger scale for bioethanol production using TMS IL based on OPEFB biomass.

Author Contributions

M.N. and A.H. performed all the experiments. H.A. coordinated the study. M.A.F. contributed the analytic tools. M.M. and D.P. writing the manuscript. D.M., Z.A. and L.O.A. processed the research data. All authors have read and agreed to the published version of the manuscript.

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Conflict of Interest

All authors declare that there is no conflict of interest in this paper.
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