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Research Article

Comparison of the Deep Euteutic Solvent (DES) Solvent for Extracting Lignin from the Lignocellulosic Material of Pineapple Leaves

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ABSTRACT

Background: Lignocellulosic biomass is one of the materials that has the potential to produce cellulose. Lignocellulose material consists of lignin, hemicellulose and cellulose so that the three materials must be separated first to get pure cellulose. The main problem faced in the process of separating cellulose is the difficulty of separating lignin. One of the processes in separating lignin is by pretreatment of lignocellulosic material. **Methods:** In this study, Deep Euteutic Solvent (DES) choline (ChCl) as a hydrogen bond acceptor was synthesized and eight hydrogen bond donors (HBD) were mixed. Eight types of DESs, i.e. , choline chloride-acetic acid (ChCl-AA), ChCl: formic acid (ChCl-FA).), choline chloride: Lactic acid (ChCl-LA), choline chloride:Citric acid (ChCl-SA), choline chloride: Glycerol (ChCl-G), choline chloride: Ethylenglycol (ChCl-EG), choline chloride: Sorbitol (ChCl-S), and choline chloride: Urea (ChCl -U) with a ratio of 1: 2 were investigated. Each. DES solvent was applied as a pretreatment for the lignocellulosic material of pineapple leaves. The results of the pretreatment formed were characterized by the Infra Red spectroscopic method to determine the typical functional groups. **Result:** The results showed that the pretreatment process using DES solvent resulted in a decrease in lignin levels in pineapple leaf powder, the highest in DES with linear saturated acid-based HBD, formic acid at 32.05%, glycerol at 30.18% and then in alpha hydroxy-based HBD, acetic acid at 29.90%. Meanwhile, the FT-IR results show that ChCl-FA has a high delignification ability during pretreatment. Pineapple leaves that have been pretreted with DES solvent can be a potential raw material for the next conversion process. This study presents DES as an effective and easy pretreatment method for lignin extraction.

Key words: Pineapple leaves, Deep eutectic solvent, Pretreatment, Lignocellulose.

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INTRODUCTION

Lignocellulose is biomass derived from plants and its availability is quite abundant, especially as agricultural, plantation and forestry waste.[1] Lignocellulosic biomass has potential as a source of energy (such as ethanol fuel).[2] Lignocellulose is a biomass that has a high cellulose content.[3] The lignocellulosic biomass can be used for various chemical and energy raw materials and their derivative products.[4] The dominant source of lignocellulosic material which has been used for the production of cellulose raw materials and which has been modified into cellulose derivatives is bagasse[4,5], oil palm empty bunches[5-7], water hyacinth leaves[8,9], corncob[10-12], cotton[13], peanut shells[14], roselle fiber[15], Betung Bamboo[16], and alang-alang.[17] Apart from these raw materials, pineapple leaf waste is another leading lignocellulose that can be utilized. Indonesia is the third largest producer of pineapples after the Philippines and Thailand. Indonesia produces pineapples with a contribution of around 23% to the Southeast Asia region.[18] Total pineapple production in Indonesia in 2016 amounted to 1,396,153 tons.

Lignocellulosic biomass is composed of three main polymers, namely lignin, hemicellulose, and cellulose. Cellulose forms a skeleton surrounded by hemicellulose and lignin and is firmly bound to one another.[19] The use of cellulose as raw material is often disrupted by the presence of lignin. Lignin is difficult to degrade because it has a complex structure. Lignin is composed of 3 types of phenylpropanoid compounds, namely cumaryl alcohol, coniferile alcohol and synapyl alcohol. The three are arranged randomly to form an amorphous (irregular) lignin polymer. Lignin must be removed, to obtain cellulose with high purity through the delignification process.[20] The delignification process can be carried out using physical, chemical, physicochemical and biological methods.[21] Biological or enzymatic methods cannot be applied directly to lignocellulosic raw materials because lignin inhibits the penetration of fungi or enzymes into the cell walls of the lignocellulosic material.[22] Therefore it is necessary to remove some of the lignin and hemicellulose, so that the cellulose fibers become more accessible to the enzymes. The method that can be done to increase the efficiency of the overall process is pretreatment.[23] Pretreatment will change the structural biomass by releasing some of the lignin components to expose the cellulose fraction in the biomass.[24]

Lignocellulose pretreatment can be grouped into four methods, ie: chemical, physical, physico-chemical, and biological pretreatment. Recently, the pretreatment process with methods based on green chemistry continues to be developed to reduce production costs and avoid adverse effects on humans and the environment. The use of Ionic liquds (ILs) solvent for lignocellulosic biomass pretreatment is widely used because of the nature of the solvent which is more environmentally friendly

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and more efficient.[25] ILs are able to remove lignin and reach the crystallinity structure of cellulose which can increase accessibility and enzymatic digestibility. However, the use of ILs is still limited because of their high price, low biodegradable properties, and the possibility of being toxic.[4]

Lignocellulose pretreatment using Deep Eutectic Solvents (DES) has been carried out on several biomass such as rice straw[26], corn stalks[27], corn cobs[28], and lactuca sativa.[29] DES has received attention as a suitable alternative solvent because of its non-toxic nature, biocompatibility, ease of synthesis, and the availability of relatively inexpensive components allowing for large applications.[30] DES is an alternative solvent and has been proven effective in removing lignin and hemicellulose bonds, and reducing the crystallinity of cellulose in the pretreatment process.[31] DES is usually formed by combining quaternary salts such as Choline chloride (ChCl) which act as acceptors and hydrogen bond donors such as alcohols or carboxylic acids.

To date, there has been no research on the application of DES to extract lignin from pineapple leaves. In this study, eight different DES were used, ie: choline chloride-acetic acid (ChCl-AA), ChCl: formic acid (ChCl-FA), choline chloride: Lactic acid (ChCl-LA), choline chloride:Citric acid (ChCl-SA), choline chloride: Glycerol (ChCl-G), choline chloride: Ethylenglycol (ChCl-E), choline chloride: Sorbitol (ChCl-S), and choline chloride: Urea (ChCl-U) with a ratio of 1: 2 each. Then, their performance was evaluated, and characterized by Fourier transform infrared spectroscopy (FT-IR).

MATERIAL AND METHODS

Material preparation

The material used in this study is pineapple leaves obtained from pineapple plantations, Subang, Indonesia. The pineapple leaves used are ripe pineapple leaves after the pineapple harvesting process. Pineapple leaves washed with water, cut into small pieces and aired for 5 days, then powdered using a blender. The powder is sieved using a 60 mesh sieve. Furthermore, the extractive process is carried out on the biomass to remove extractive substances.[32] Extractive free biomass is stored in a tightly closed container for pretreatment use.[33]

The chemicals used in this study were acetic acid (Merck, 99–100% purity), choline chloride (Sigma Aldrich, ≥98% purity), citric acid (R&M Chemicals, ≥99% purity), formic acid (Merck, Purity). 98–100%), lactic acid (R&M Chemicals, purity ≥85%), maleic acid (Merck, purity ≥99%), malic acid (Sigma Aldrich, ≥99%), pro pionic acid (Merck, purity ≥99%), sodium hydroxide (Merck, ≥97% purity) and succinic acid (Sigma Aldrich, Bioreagent class) and all other reagents used in the experiment were analytical grade.

Deep eutectic solvent (DES) synthesis

DES is formed by combining quaternary salts as acceptors and hydrogen bond donors such as alcohols or carboxylic acids. In this study, ChCl was used as a hydrogen bond acceptor and eight hydrogen bond donors were mixed as follows, namely choline chloride-Acetic acid (ChCl- AA), choline chloride: Formic acid (ChCl-FA), choline chloride: Lactic acid (ChCl-LA), choline chloride:Citric acid (ChCl-SA), choline chloride: Glycerol (ChCl-G), choline chloride: Ethylenglycol (ChCl-EG), choline chloride: Sorbitol (ChCl-S), and choline chloride: Urea (ChCl-U) with a ratio of 1: 2 each. ChCl and hydrogen donor molecules are heated at 60 ° C at 150 rpm until homogeneous or the liquid formed is colorless / transparent (Abbott et al., 2003). Then the mixture is heated on a hot plate until it reaches a reaction temperature of 80˚C and homogenized using a magnetic stirrer with a stirring speed of 500 rpm for 2 hours.[27] After that, the hot plate was turned off and the deep eutectic solvent (DES) obtained was cooled to DES temperature and stored in a vacuum desiccator with silica gel for further use.

Pretreatment of pineapple leaf using DES

The pretreatment procedure was carried out on extractive free pineapple leaf powder. Pineapple leaf powder and DES were mixed in a ratio of 1:10 according to weight then heated and incubated at 130° C for 4 hours.[27,26] Then, 35 ml of hot water was added to precipitate and regenerate the pineapple leaf cellulose under strong stirring conditions of 5800 rpm for 20 minutes. The solid fraction was separated using filter paper then the solid obtained was washed with 35 ml of hot water (85 ° C) 4 times. Then dried using an oven at a temperature of 105ºC until constant weight.[26] The results of pretreatment using DES then determined the levels of cellulose, hemicellulose and lignin as well as physical analysis such as FTIR.

CHARACTERIZATION

Chemical characterization

Pineapple leaves weigh as much as 10 grams was extracted with 300 ml of ethanol- benzene mixture (1: 2) for 8 hours. The extraction was washed with 96% ethanol, until the solution was clear, and aerated. Then dried in an oven at a temperature of 55 ° C-60 ° C until the weight is constant.[32] The holocellulose content (cellulose + hemicellulose) of the sample was calculated using sodium chlorite solution acidified at 70 ° C for 1 hour, and the process was repeated until the final sample turned white.[34] Then, holocellulose was treated with 17.5% by weight of NaOH and 10% acetic acid overnight at 80°C to obtain cellulose. The difference between the values of holocellulose and cellulose gives the hemicellulose content of the pineapple leaf samples. The lignin content of the samples was analyzed according to Klason Lignin.[35] All measurements were carried out in triplicate. The chemical composition is calculated from the residue before and after pretretment and the changes in the chemical composition of cellulose, hemicellulose, and lignin are calculated.

FTIR Spectroscopy

The infrared spectrum of the sample was measured using FTIR at a wave number of 4000-400 cm-1. FTIR analysis was performed on extractive free pineapple leaf powder before and after pretreatment.[36,37] The spectrum output is recorded in transmission mode as a function of the wave number.

RESULTS AND DISCUSSION

DES synthesis

In this study, 8 types of DES were synthesized from ammonium Choline Chloride (ChCl) and Hydrogen Bond Donor (HBD) salts such as acetic acid, formic acid, lactic acid, citric acid, glycerol, ethylene glycol, sorbitol and urea. DES is obtained by heating ChCl and HBD salts at a certain molar ratio simultaneously to a temperature of 80 ° C and while stirring using a magnetic stirrer for 2 hours, after the heating process is complete, a colorless liquid called DES is obtained. DES is a chemical solvent that can be designed according to its use. Through the manufacturing process, a DES with certain characteristics can be produced.[38] The physical properties of DES differ depending on the molar ratio salt and its constituent HBD.[39] Examination of the physical characteristics of DES includes examination of shape, pH, density and viscosity. The results of physical characterization examinations can be seen in table 1.

From the results of the research, after the heating process is complete all DES is in the form of a clear liquid (colorless liquid). At room temperature all DES is still liquid even though there is a DES which changes to a thicker and white color (cloudy), namely DES ChCl:U, as shown in figure 1. DES which is a clear liquid at room temperature indicates that the freezing point of DES is below room temperature

Table 1: Characteristics of DES.

Code	DES	DES form	pH	Density (g/mL)	Viscosity(cps)
ChCl:AA	ChCl: Acetic acid (1:2)	clear	3.95	1.05	108.22
ChCl:FA	ChCl: Foric acid (1:2)	clear	3.45	1.02	110.08
ChCl:LA	ChCl: Lactic acid (1:2)	clear	4.57	1.15	139.51
ChCl:SA	ChCl:Citric Acid (1:2)	clear	4.65	1.16	141.05
ChCl:G	ChCl: Glycerol (1:2)	clear	6.95	1.17	200.66
ChCl:EG	ChCl: Ethylene glycol (1:2)	clear	7.02	1.11	30.36
ChCl:S	ChCl: Sorbitol (1:2)	clear	6.75	1.37	11300
ChCl:U	ChCl: Urea (1:2)	clear	7.12	1.59	725

Figure 1: DES synthesized results from various variations of HBD.

(28°C ± 2°C) because no change in the shape of DES has occurred.[40] Meanwhile, DES which is cloudy shows that DES has a freezing point value above room temperature (28°C ± 2°C) because at room temperature the DES form turns thicker and white.[39] The results of all form DES can be seen in figure 1.

pH is one of the important characteristics of a liquid. The strength of the acid or base of DES is strongly influenced by the constituent components of DES, especially HBD, so that DES with alkaline, neutral or acidic pH can be produced.[38] In previous research on the biocompatibility of DES as a biocompatible and biodegradable solvent conducted by it was found that DES with amine, alcohol and sugar based HBD did not inhibit bacterial growth because DES has a pH value in the neutral pH range. and vice versa DES with organic acid-based HBD can inhibit bacterial growth caused by changes in pH.[41] The DES pH value tested was far below the optimal pH (6.5-7.5). This research that has been carried out is in line with Zhao's research, namely that DES with alcohol-based HBD (ethylene glycol, glycerol), sugar (sorbitol) and amines (urea) has a pH in the neutral pH range while DES with organic acid-based HBD has a pH below neutral.

Density is one of the important physical properties of ionic liquids in general and in particular for DES.[40] DES density is usually determined gravimetrically and the molar ratio of the salt and HBD constituent DES has a significant effect on the resulting DES density. In this study, the resulting DES density value is greater than the density of water and is between 1.02 g / mL - 1.59 g / mL . The research conducted is in line with the research of Garcia's research, in general DES shows a density value of 1.0–1.35 g / mL, while DES made from metal salts such as $ZnCl_2$ as a hydrogen bond acceptor has a density of 1.3– 1.6 g / mL.[42]

DES viscosity is one of the most important analyzes because the application of DES is highly dependent on its viscosity value.[43] By knowing the viscosity value of DES, it will be easier to make DES with an optimum molar ratio suitable for certain applications and can also save energy in the DES manufacturing process.[39] In the application of DES solvents, the development of DES with low viscosity is desirable because DES has the potential to be environmentally friendly media. DES with high viscosity is not recommended because it has limitations in actual applications such as liquid- liquid extraction and electrochemical reactions. The viscosity of the DES eutectic mixture is mainly influenced by the chemical properties of its constituent components, namely salt and HBD. Viscosity is strongly influenced by the interaction of hydrogen, van der Waals and electrostatic bonds.[44] The lower the DES viscosity value, the better DES is used as a solvent.[43] In this study, DES with organic acid HBD had a value between 100-300 cps, HBD based on sorbitol and urea had a value greater than 300 cps while DES based on ethylenglycol had the lowest viscosity with 30.36 cps. The high DES viscosity is caused by the presence of excess hydrogen bonds which cause van der Walls interactions and excess electrostatic interactions between the two components resulting in lower mobility of the molecules in DES. This will affect the composition of the eutectic mixture of DES, such as the characteristics of the resulting DES will be different.[45] According to Zhao's research, the large number of hydroxyl groups in HBD will cause excess hydrogen bonds, thereby increasing the attractive forces between molecules and making the liquid thicker.

Pretreatment of pineapple leaf using DES

Pretreatment is the initial stage in the lignocellulose bioconversion process. The pretreatment process aims to reduce various compounds that can inhibit the rate of hydrolysis such as lignin, reduce the degradation of holocellulose resulting in high total carbohydrates, reduce cellulose crystallinity, and increase the enzyme contact surface.[28] The pretreatment process for the purpose of lignin delignification is aimed at increasing the accessibility and enzymatic digestibility of the berlignocellulosic material so that high levels of cellulose will be obtained.[26] Deep Eutectic Solvents (DES) are one of the solvents that have received attention as a suitable alternative solvent compared to ILs. DES is usually synthesized by combining quaternary salts such as Choline chloride (ChCl) which acts as an acceptor and Hydrogen Bond Donors (HBD) such as amines, alcohols or carboxylic acids. The interaction between ChCl and HBD occurs through hydrogen bonds

between the salt halide anions and donor hydrogen groups.[42] The reason it is called a Deep Eutectic Solvent (DES) is when two components are mixed together in the right ratio, the eutectic point of the mixture is obtained. This eutectic point is the lowest melting point resulting from the molar ratio of the two components.[46] DES has promising solvent properties compared to ILs, namely having low volatility, wide liquid range, non-toxicity, biocompatibility, ease of synthesis, and availability of relatively inexpensive components that allow for large applications.[30] This study focuses on the effect of HBD variations as a constituent of DES on the levels of cellulose, hemicellulose and lignin of pineapple leaf. In this study, raw pineapple leaves (without pretreatment) contained 10.67% lignin, 40.13% cellulose and 18.50% hemicellulose. From the results of pretreatment using DES solvent, the largest decrease in lignin levels was found using ChCl:FA (1:2) with lignin content obtained at 7.25% while the lowest reduction in lignin levels was using ChCl:EG (1:2) with lignin content of 8, 45%. From the results of pretreatment using DES solvent, the largest cellulose content was obtained using ChCl:FA (1:2) with cellulose content obtained by 53.50% while the lowest cellulose content using ChCl:S (1:2) was 40.91%. From the results of pretreatment using DES solvent, the largest decrease in hemicellulose was obtained using ChCl:FA (1:2) with a hemicellulose content obtained of 10.01% and the lowest hemicellulose content decreased using ChCl:S (1:2) with a hemicellulose content obtained of 12.81%.The results of chemical composition of pineapple leaf with and without DES pretreatment can be seen in figure 2.

The percentage of lignin reducing in the pretreatment process using DES can be seen in figure 3. The results of the research conducted are similar to the research reported by Tan, Ngoh and Chua (2018), the percentage of lignin reduction in DES with HBD based on alpha hydroxy lactic acid is greater than that of malic acid and citric acid.[47] The results of the research conducted are similar to the research reported by Tan, Ngoh and Chua (2018), the percentage of lignin reduction in DES with HBD based on alpha hydroxy lactic acid is greater than that of malic acid and citric acid. In this study, the percentage of lignin reduction in DES with HBD was 27.65% lactic acid and 25.68% citric acid. In the alpha-hydroxy (AHA) based DES group such as lactic acid, malic acid and citric acid, it was found that monocarboxylic acids achieved higher lignin extraction yields than di- and tricarboxylic acids.[48] Despite having the same functional type groups (OH and COOH), there was a difference in performance between the AHA-based DES. This may be due to the number of COOH groups present. The addition of COOH groups to malic acid and citric acid allows the formation of more hydrogen bonds with HBA.[49] D'Agostino et al. (2011) explained that in DES dicarboxylic acid there are two COOH groups that can form a broad dimer chain, which limits the mobility of solvent molecules. The lower solvent mobility may have weakened the solute-solvent interaction with lignin resulting in a decrease in the lignin extraction efficiency.[50]

The results of this study indicate that the percentage of lignin reduction in the formic acid treatment process is 32.05% while acetic acid is 29.90%. The results of this study are similar to those reported by Tan that the addition of chain length from C1 to C4 will decrease lignin extraction. DES solvents with HBD based on linear saturated acids such as formic acid and acetic acid significantly affected the lignin extraction ability. Short alkyl chains, OH groups and double bonds in HBD carboxylic acids enhance the performance of DES. The longer the alkyl chain, the lower the lignin extraction.[48] The results of this study also showed the percentage reduction in lignin levels using ChCl:lactic acid was 27.65%, and ChCl:urea was 20.62%. The results of this study are similar to those reported by Thi and Lee (2019), where lactic acid

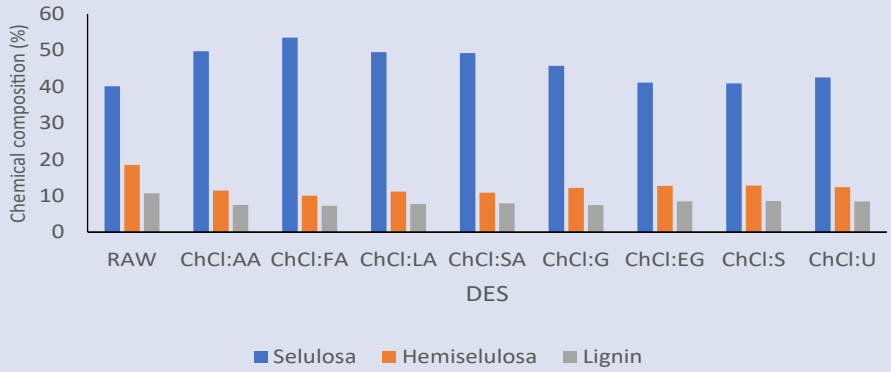

Figure 2: Chemical Composition of Pineapple Leaf with and Without DES pretreatment.

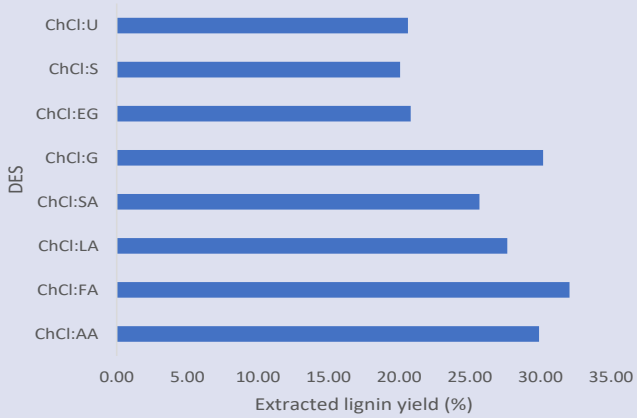

Figure 3: The efficiency of reducing the percentage of lignin in the pretreatment process using DES.

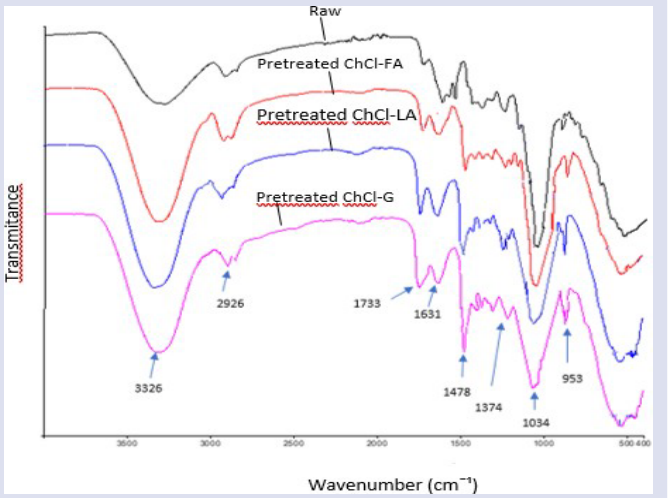

Figure 4: FTIR spectrum of the biomass samples before and after treatment with DES in a ratio of 1:10 (Operating conditions: at 130 ° C for 4 hours).

was shown to have the best performance in the pretreatment process compared to urea. This was due to the disruption of the highest biomass structure during ChCl lactic acid pretreatment which increased the accessibility of cellulose. In addition, it is known that ChCl-lactic acid has the lowest viscosity which contributes to a better pretreatment process between biomass and DES.[3]

Fourier Transform Infrared (FTIR) spectra of pineapple leaf

FTIR spectra assignment is carried out to find out information related to chemical bonds present in pineapple leaf. The chemical bonds are indicated by different peaks. FTIR on pretretmented pineapple leaf fibers showed changes in absorption intensity at peak biomass characteristics associated with stretching of O-H, C-H and C = O bonds in cellulose, hemicellulose and lignin components. The ability to disrupt the biomass structure due to higher infrared radiation absorption at several significant peaks such as 3326, 2926, 1733, 1631 and 1034 cm^{-1}. [3] FTIR test on the pretretment process of pineapple leaf can be seen in figure 4.

The FTIR test results of pineapple leaf fiber before and after pretreatment using DES solvent showed that there was a vibration stretching of the O-H bond at the peak of the wave 3326 cm^{-1} and stretching the vibration of the C-H bond at 2926 cm^{-1}. The peak at wave number 1733 cm^{-1} shows the stretching of the carbonyl ester[51], the vibration of C = C aromatic ring at the peak of the wave 1478 cm^{-1}, CH deformation in the inner aromatic CH group at 1035 cm^{-1}, and CH deformation in the group External aromatic CH at 953 cm^{-1}. [52,53] Lignin is indicated by the presence of peaks in the range 1500- 1600 cm^{-1} with the aromatic group C = C.[53] The peaks at the wavelengths of 3326 cm^{-1} and 2926 cm^{-1} can be used to explain changes in the structure of cellulose.[53,51] The signal is strong at 1700 cm^{-1} because the unconjugated C = O indicates the presence of the hydroxyl and carbonyl functional groups. This spectrum is related to the effectiveness of lignin removal.[48] In the research, the degree of delignification can be analyzed at peaks of 1034, 1631 and 1478 cm^{-1}. At the peak of 1030 cm^{-1}, ChCl-FA, ChCl-LA and ChCl-G provide the highest infrared absorption due to the high vibration bending of the C-H unit guaiacol in the lignin unit.[3] High delignification capabilities also occurred at the peaks of 1631 and 1478 cm^{-1}. [3] It can be concluded that ChCl-FA, ChCl-LA and ChCl-G are effective in removing lignin.[51]

CONCLUSION

The biochemical characterization of pineapple leaves showed a high content of cellulose and hemicellulose with significant lignin content. In the pretreatment process using DES solvent resulted that the highest reduction in lignin levels in pineapple leaf powder was in DES with linear saturated acid-based HBD, formic acid at 32.05%, glycerol at 30.18% and then in alpha hydroxy-based HBD, acetic acid at 29.90%. Further research needs to be done on the development of a methodology to achieve the effectiveness of the DES solvent used.

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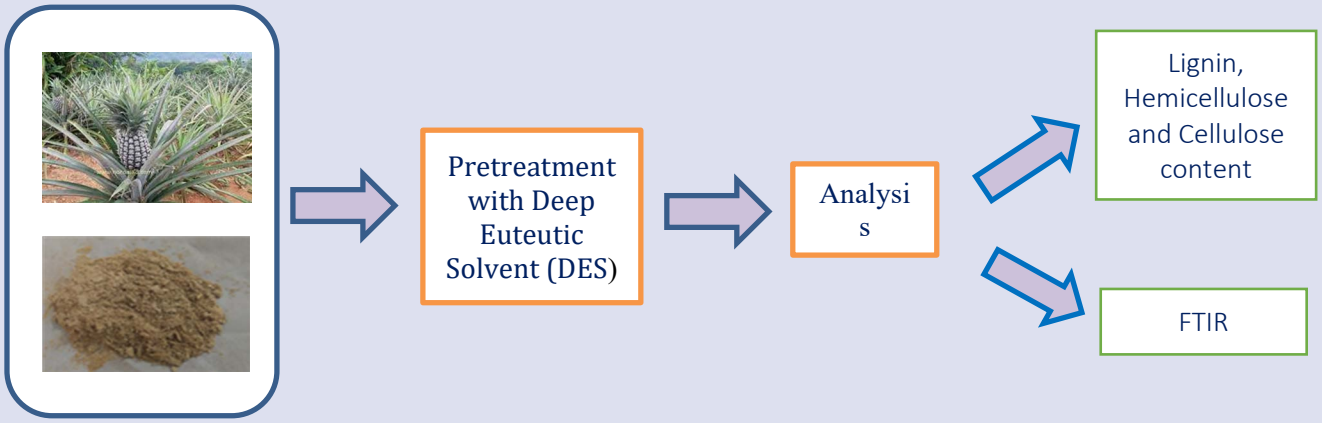
GRAPHICAL ABSTRACT



SUMMARY

- The biochemical characterization of pineapple leaves showed a high content of cellulose and hemicellulose with significant lignin content.
- In the pretreatment process using DES solvent resulted that the highest reduction in lignin levels in pineapple leaf powder was in DES with linear saturated acid-based HBD, namely formic acid at 34.75%, then in alpha hydroxy-based HBD, namely lactic acid by 30.44% and glycerol by 30.38%.

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