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Pretreatment of Empty Fruit Bunch using Various Choline Chloride-based Acidic Deep Eutectic Solvents

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Research on renewable resources has been extensively conducted, especially on lignocellulosic biomass as it is cheap and abundant. Lignocellulosic biomass has complex polymer arrangements, making the conversion to various products difficult. The conversion requires pretreatment to improve the derivation of biomass components. Deep eutectic solvent (DES) pretreatment is widely used due to its effectiveness and simple preparation step. In this work, various acidic-based DESs were prepared through the combination of choline chloride (ChCl) as hydrogen bonding acceptors (HBA) and organic acids as hydrogen bonding donors (HBD), which include ChCl/lactic acid, ChCl/levulinic acid, ChCl/oxalic acid, and ChCl/sulfanilic acid for empty fruit bunch (EFB) pretreatment. The DESs were characterised using Fourier transform infrared spectroscopy (FTIR) and their density was determined. The acidic-based DESs with different ChCl-to-acid molar ratios of 1:1–1:5, except for ChCl/sulfanilic acid with molar ratios of 2:1 and 3:1, were utilised for the pretreatment of EFB at fixed treatment conditions to observe the effect on biomass structure and lignin degradation. The degradation of lignin was determined based on the data from UV-Vis spectrometry, while the characteristics of raw EFB and selected pretreated EFB samples were determined using FTIR, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The FTIR analysis was also conducted for selected DES before and after pretreatment to observe the changes in chemical functional groups. The results show that the density of the DESs increased with the increasing amount of HBA used. The FTIR, TGA, and SEM results support the characteristics of the pretreated EFB and explain the possible biomass components involved in the pretreatment process. The degradation of lignin was found to be between 15.0% and 81.7%, and high lignin degradation was obtained using ChCl/lactic acid and ChCl/sulfanilic acid. This result shows that ChCl/sulfanilic acid has the potential for biomass pretreatment based on the high lignin degradation and the characteristics of the pretreated samples.

Keywords: Lignocellulosic biomass; deep eutectic solvent; lignin degradation; empty fruit bunch; pretreatment

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Biomass is one of the cheapest, biodegradable, and abundant organic materials available in the world. Regarded as a non-depleting source of energy, it can continuously and sustainably become the largest energy supply in various forms [1]. Biomass is commonly animal and plant derivatives, and the available biomass from plants is lignocellulosic (LC) biomass, such as plant waste from plantation, agriculture, and forest. The utilisation of LC biomass has not yet been fully implemented in most countries in the world by further converting biomass into biochemicals and biofuels. In Malaysia, LC biomass is typically generated from plantations of oil palm, paddy, sugarcane, coconut, pineapple, rubber, and also other wood residues [2]. The statistic shows that the palm oil industry is one of the main industries with the largest share in the agriculture sector in Malaysia. This country is the second largest producer and supplier globally, with 7 million tonnes of crude palm oil produced every year [3, 4]. The waste produced from oil palm industries and plantations is oil palm fronds, oil palm trunks, empty fruit bunches, palm kernel shells, mesocarp fibre, and oil palm mill effluent. The amount of waste produced in Malaysia for the palm oil sector is approximately 20 tonnes per hectare annually, of which 79% of the waste comes from empty fruit

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bunch (EFB) alone [5]. EFB is produced in a palm oil mill after palm fruits are removed from the bunches.

LC biomass has a very complex heterogeneous arrangement of polymers made up of polysaccharides, which are cellulose, hemicellulose, and aromatic polymer (i.e., lignin) [1]. Based on the reported work, EFB has high cellulose, hemicellulose, and lignin content, which contains 23.7%–65.0%, 20.6%–33.5%, and 14.1%–30.0%, respectively [6]. The high content of cellulose and hemicellulose increases the potential as feedstock in numerous industries, such as pulp and paper [5]. Due to the LC complex structure, its chemical composition and reactivity hinder the conversion of LC components and the production of biochemicals and biofuels. Thus, the pretreatment of LC biomass is required to break the complex structure of biomass and remove unwanted chemical structures in biomass. Researchers have extensively reviewed and discussed various pretreatment methods available, which are physical pretreatment, chemical pretreatment, biological pretreatment and combination of pretreatment [3, 7]. However, some of the pretreatment methods are expensive and unavailable for larger scales, while some have high operation and maintenance costs, high energy consumption, and low efficiency [5, 7]. Chemical pretreatment shows high efficiency in the treatment process. Among the chemical pretreatment process, deep eutectic solvents (DESs) are an emerging new type of green solvent with the advantages of using a simple preparation process and as a potential treatment for high lignin degradation [3, 7, 8].

The preparation of DES has been reported as a simple process that only requires a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) during the reaction without the formation of side products [9]. The HBA can be a quaternary ammonium salt, and the HBD is commonly from amines, amides, carboxylic acids, and polyols groups. Choline chloride (ChCl) is commonly used as an HBA in preparing DES with various HBDs. Some of the DESs that have been studied in recent years for biomass pretreatment are ChCl:lactic acid [10], ChCl:oxalic acid [11], ChCl:citric acid [10], ChCl:urea [12], ChCl:formamide [13], and ChCl:glucose [14]. ChCl has been used with various HBDs to prepare DESs. Lactic acid is one of the HBDs from the carboxylic group that is commonly studied for biomass pretreatment. As stated by Xu et al. [15], ChCl/lactic acid is the most effective and commonly used DES in removing lignin from LC biomass material.

This study aims to pretreat EFB using various DESs and focuses on the acidic type of DESs using ChCl-based DESs for EFB pretreatment. This includes a new acidic DES (i.e., ChCl/sulfanilic acid). Different molar ratios of HBA and HBD in preparing DESs were studied in EFB pretreatment to observe the effect on EFB structure and lignin degradation. The raw and pretreated EFB were characterised using Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) to study the change of morphology and chemical properties.

EXPERIMENTAL

Chemicals and Materials

Choline chloride ($C_5H_{14}ClNO$, ≥98%, Sigma Aldrich), lactic acid ($C_3H_6O_3$, 90%, Merck), oxalic acid ($C_2H_2O_4 \cdot 2H_2O$, Merck), levulinic acid ($C_5H_8O_3$, 98%, Sigma Aldrich), and sulfanilic acid ($C_6H_7NO_3S$, ≥98%, Merck) were utilised without any additional purification. EFB was used as the main raw material in the pretreatment process. Dirt and foreign particles were removed by cleaning EFB with water, which was then sun-dried for 8 h. Then, the EFB was cut into smaller pieces, dried in an oven overnight, and stored in a closed container. The EFB has an estimated composition of 49.97% cellulose, 23.27% hemicellulose, 22.86% lignin, and 3.9% other components.

Synthesis of DESs and Pretreatment of EFB

Three different acidic-based DESs were prepared by mixing ChCl with lactic acid, oxalic acid, and levulinic acid, respectively, at molar ratios of 1:1–1:5 (ChCl: acid) by heating and stirring each mixture at 80 °C using a magnetic stirrer hot plate at 300 rpm until a homogeneous mixture was obtained [10]. Meanwhile, another acidic-based DES was prepared from sulfanilic acid and ChCl via mixing at molar ratios of 2:1 and 3:1 (ChCl:acid) and heating at 140 °C using a magnetic stirrer hot plate at 300 rpm until a homogeneous mixture was formed. The different conditions used for the preparation of ChCl/sulfanilic acid are based on the screening process conducted. The DESs produced were preserved in a desiccator.

As for EFB pretreatment, all the prepared DESs were used for the pretreatment of EFB at fixed reaction conditions of 0.4 g EFB, reaction temperature of 120 °C, reaction time of 6 h, and continuous stirring at 300 rpm. These reaction conditions were selected based on the selected conditions from previous studies [13, 14, 16]. The reaction was conducted in a Schott bottle. The slurry product was washed with water and filtered to collect liquid product, while the solid product was further washed with sodium hydroxide and filtered to remove the degraded lignin. It was then rinsed with water before drying the solid sample in the oven at 80 °C overnight.

Analysis and Characterisation

The density of DES was determined by pouring the solvent into a volumetric flask (10 mL) until the calibrated mark, and Eq. (1) was used to calculate

DES density. The measurement was conducted by measuring the DES weight in a volumetric flask at 25 °C. The procedure followed the method used in previous work for the determination of DES density [17].

$$\text{Density } (\rho) = m/V \tag{1}$$

Where m is the DES weight (g) in a volumetric flask and V is the DES volume (mL).

UV-Vis spectroscopy was used to determine the lignin degradation of the pretreated EFB. First, 0.1 g EFB was thoroughly mixed for 5 min with 20 mL of aqueous 0.02 mol/L potassium permanganate ($KMnO_4$) and 5 mL of 2.0 mol/L sulfuric acid. The lignin content and degradation were quantified using the method reported by Wan Omar and Amin [18]. The mixture was filtered with Advantec filter paper 110 mm to separate the EFB from the solution. Then, the filtrate was measured with a LAMBDA 750 UV/Vis/NIR spectrophotometer (PerkinElmer, Inc) by analysing the samples between 200 and 800 nm, where the reading was recorded at 546 nm. The lignin content was determined based on the Kappa number. The Kappa number was calculated using Eq. (2), and the lignin content in the sample was determined using Eq. (3). Then, the percentage of lignin degradation was calculated using Eq. (4).

$$K = \frac{a}{w}\left(1 - \frac{A_e}{A_o}\right) \tag{2}$$

$$\text{Lignin content, L (wt.\%)} = 0.15K \tag{3}$$

$$\text{Lignin degradation (removal) (wt.\%)} = \frac{L_i - L_a}{L_i} \times 100\% \tag{4}$$

Where K is the Kappa number, a is the volume of $KMnO_4$ used, w is the weight of sample used, A_o is the spectral intensity of blank sample, A_e is the spectral intensity after the addition of sample, L_i is the lignin content of the untreated sample, and L_a is the lignin content of the treated sample.

A scanning electron microscope from Hitachi (SU3500) was used to observe the structure of EFB and pretreated EFB samples at 300× magnification. TGA was conducted to study the thermal degradation of raw EFB and selected pretreated EFB samples using a Mettler Toledo TGA/DSC 1 STAR system in the range of 150–850 °C (10 °C min^{-1}) under nitrogen flow. FTIR was used to identify the chemical bonds of raw EFB and selected pretreated EFB samples and to detect any changes of different functional groups in the EFB structure before and after pretreatment. A Perkin-Elmer Spectrum One FTIR spectrometer was used to conduct the analysis at an IR range of 600–4000 cm^{-1}. In addition, FTIR analysis was also conducted on the prepared DESs before and after pretreatment to observe any changes in chemical bonding.

RESULTS AND DISCUSSION

Density of Synthesised DESs

Based on DES preparation, the result in Figure 1 shows that the density of the DESs increased as the molar ratio of HBA to HBD increased. The nature of HBD affects the density of the DESs as the respective HBD used in this work has a different density. ChCl/oxalic acid obtained a higher density than ChCl/levulinic acid and ChCl/lactic acid. The prepared DESs are made up of different alkyl chain lengths of ChCl/carboxylic acids, and a previous study explains that the alkyl chain length of HBD affects and reduces the density of DES [19]. A previous report supports the result of ChCl/levulinic acid which has a lower density than ChCl/lactic acid and ChCl/oxalic acid. Florindo et al. [19] stated that the long alkyl chains of acids used correspond to an increase in molar volume, which reduces the density. As compared to ChCl/sulfanilic acid, the different chemical structure of the DES with a C6 ring structure provides different density results. As observed for respective DES preparation, different molar ratios of HBA and HBD affect the DES density. The major cause of the reduced density is the amount of ChCl in the DES structure. Figure 1 illustrates that the increase of HBA concentration reduced the DES density, while the increase of acid molar ratio (as HBD) showed opposite results. The increase of acid used increases the density of DES as the free space between the DES reduces [17, 20]. The result of ChCl/sulfanilic acid in Table 1 also shows that the density of ChCl/sulfanilic acid-2 is lower than ChCl/sulfanilic acid-1 due to the increasing amount of HBA. Shafie et al. [17] reported that the increasing amount of ChCl decreased the density of DES due to the interaction of hydroxyl groups in the acid structure with chlorine anion (Cl^-), which caused more hydrogen bond interaction, formed different sizes of complexes, and changed the density of DES. This explains that the density of DES increases as the concentration of HBD increases.

Lignin Degradation

The lignin content of raw and pretreated EFB samples was analysed to determine the lignin degradation caused by the pretreatment using DESs. Based on the results obtained in Figure 2(a), the percentage of lignin degradation is between 31.7% and 75.0% for ChCl/lactic acid, ChCl/oxalic acid, and ChCl/levulinic acid. ChCl/lactic acid with a molar ratio of 1:2 shows high lignin degradation, followed by ChCl/oxalic acid with a molar ratio of 1:3 and ChCl/levulinic acid with a molar ratio of 1:3. The results show that increasing the molar ratio increased the degradation of lignin. However, the lignin degradation decreased at high molar ratios. The molar ratio with high HBD is proper for pretreatment. This is because more acidic solvents with stronger hydrogen bonding resulted in high lignin removal [21]. However, the high acidity of DES caused the sample to clump together when pretreated with DES [22], thus reducing the degradation process. High lignin degradation of 75% was obtained using ChCl/lactic acid. Based on the observation, the samples pretreated using ChCl/lactic acid with a molar ratio of 1:2, ChCl/oxalic acid with a molar ratio of 1:3, and ChCl/levulinic acid with a molar ratio of 1:3 obtained EFB biomass with bright brown colour. A previous study obtained low lignin extract for the DES pretreatment of corncob using ChCl/levulinic acid [11]. Low lignin removal was obtained using ChCl/levulinic acid for the pretreatment of moso bamboo [23]. From Figure 2(b), the lignin degradation of EFB using ChCl/sulfanilic acid-2 and ChCl/sulfanilic acid-1 is 76.7% and 81.7%, respectively. Both ChCl/sulfanilic acid DESs show high lignin degradation after the pretreatment process. Based on the observation of the

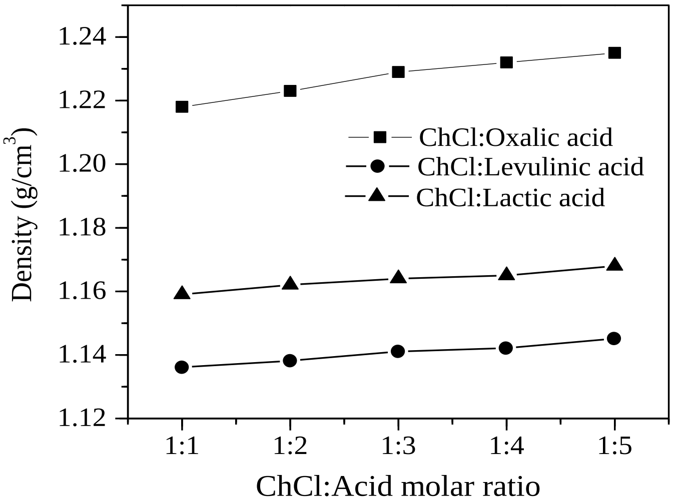

Figure 1. Densities of ChCl/lactic acid, ChCl/oxalic acid, and ChCl/levulinic acid at different molar ratios.

Table 1. Densities of ChCl/sulfanilic acid at different molar ratios.

ChCl:Sulfanilic acid	Density (g/cm^3)
ChCl/sulfanilic acid-1 (2:1)	1.26
ChCl/sulfanilic acid-2 (3:1)	1.23

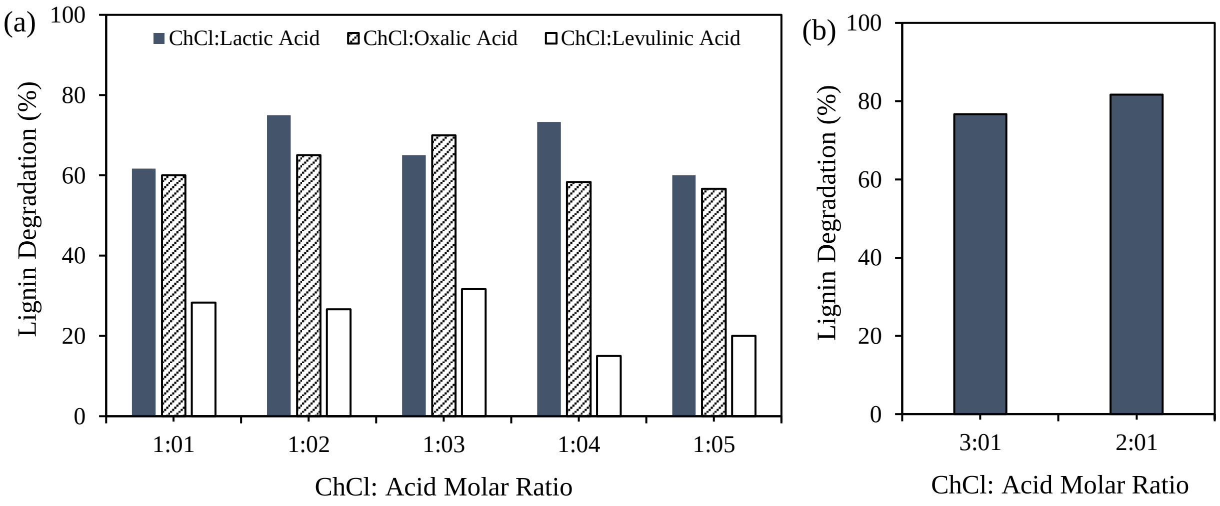

Figure 2. Lignin degradation of (a) ChCl/lactic acid, ChCl/oxalic acid, and ChCl/levulinic acid and (b) ChCl/sulfanilic acid at different molar ratios.

samples after pretreatment, the pretreated EFB using ChCl/sulfanilic acid has a dark surface, which can be related to the degraded lignin on the pretreated surface. As determined by Yiin et al. [5], dark spots formed on the dried EFB pulp due to the lignin compound deposited on the sample surface. Selected samples of the pretreated EFB using ChCl/lactic acid, ChCl/oxalic acid, and ChCl/levulinic acid and also both ChCl/sulfanilic acid-1 and ChCl/sulfanilic acid-2 were further analysed to study the sample characteristics.

Characterisation of Raw and Pretreated EFB

The SEM images of raw EFB and selected pretreated EFB samples are shown in Figure 3. Figure 3(a) illustrates smooth, rigid, and packed raw EFB. This indicates that the majority of cellulose is coated in lignin and hemicellulose, and it is evidently proved by Li et al. [8]. After pretreatment, the surface morphology of EFB changes due to the chemical treatment using DES. The changes in surface morphology were observed for all pretreated samples, which resulted in ruptured and irregular structures of the samples. This is due to the high temperature used during pretreatment, which could eliminate most contaminants and impurities on the EFB surface [24]. A similar finding was reported previously, where the sample showed a ruptured surface after pretreatment [25]. Li et al. [8] also determined that after the pretreatment, the disrupted structure of lignin and hemicellulose exposed the cellulose, resulting in fragmented fibre bundles. From the SEM result in this work, the fibre structure of cellulose can be observed for the samples pretreated using ChCl/lactic acid and ChCl/sulfanilic acid. As stated by Ling et al. [23], the exposure

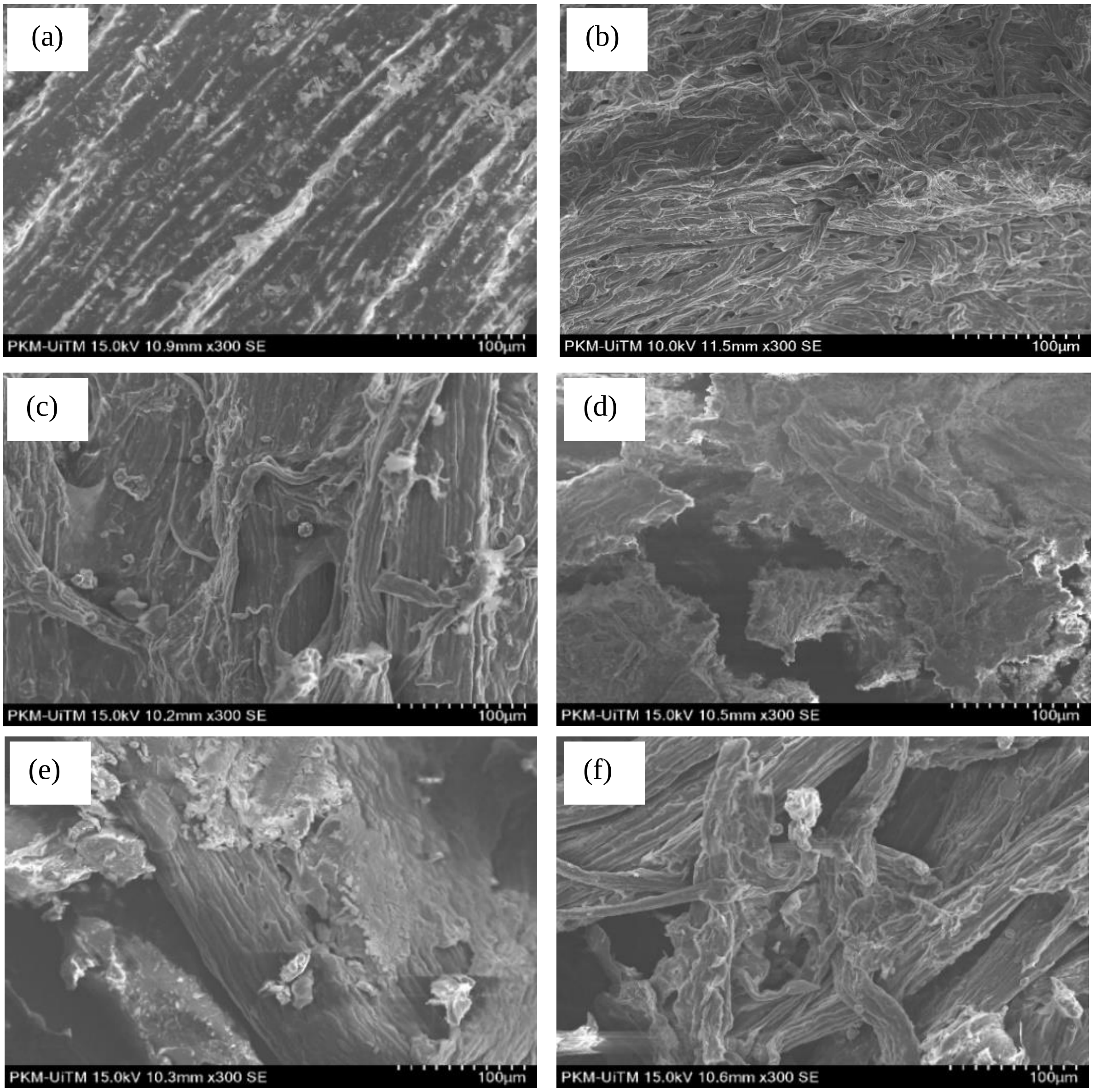

Figure 3. SEM images of (a) raw EFB and pretreated EFB samples using (b) ChCl/lactic acid, (c)

ChCl/levulinic acid, (d) ChCl/oxalic acid, (e) ChCl/sulfanilic acid-1, and (f) ChCl/sulfanilic acid-2.

of microfibrils occurs due to the removal of lignin and hemicellulose matrix. A similar observation was obtained for the sample pretreated using ChCl/levulinic acid, where the fibre structure was exposed. However, from the lignin degradation result, the low degradation percentage is possibly because high lignin content is deposited on the sample. This explains that pretreatment occurs when using ChCl/levulinic acid, but the DES cannot fully remove lignin during the process. Ling et al. [23] also determined that ChCl/levulinic acid demonstrated a weak ability to remove lignin, possibly due to the mild pretreatment conditions applied.

The raw EFB and pretreated EFB samples were further characterised via TGA to study the degradation of major components based on thermal degradation. The results of differential thermal gravimetric analysis (TGA-DTG) of the samples are shown in Figure 4. Based on the TGA-DTG curves, major decomposition was observed at a temperature range of 200–400 °C. At this temperature range, major components such as hemicellulose, cellulose, and lignin are decomposed. However, slow decomposition of lignin was reported in the range of 200–500 °C, and the decomposition increased slightly above 700 °C [26]. Thus, the major decomposition peak between 200 and 400 °C is mainly related to hemicellulose and cellulose components. The decomposition of EFB shows high degradation at 330 °C, which is related to the cellulose component in the EFB structure. Due to the complex structure arrangement, the degradation of respective components was not clearly observed. The temperature range was used to distinguish component degradation. As shown by the DTG curves of the pretreated samples, the degradation peak was reduced, and some peaks shifted to the left due to the low degradation of the sample caused by the removal of components (e.g., lignin) during pretreatment. The pretreated samples of ChCl/lactic acid, ChCl/oxalic acid, and ChCl/sulfanilic acid showed high degradation peaks around 300–330 °C, which are related to cellulose components. No clear peak was observed for hemicellulose (200–280 °C), which could be explained by the removal of hemicellulose and lignin during pretreatment. However, for the sample pretreated using ChCl/levulinic acid, the degradation peak of cellulose is significantly reduced, which explains the possible dissolution of cellulose in the DES during pretreatment. This could be due to the pretreatment conditions that use slightly higher temperatures (usually below 100 °C) and long reaction time for the pretreatment using ChCl/ levulinic acid. This result is also supported by the observation of the degradation peaks of hemicellulose (the peak observed between 200 and 280 °C) and lignin (a small peak observed between 500 and 600 °C) in the DTG curves. The lignin available in the sample can be related to the low lignin degradation reported in this work and weak lignin removal from previous studies [11, 23].

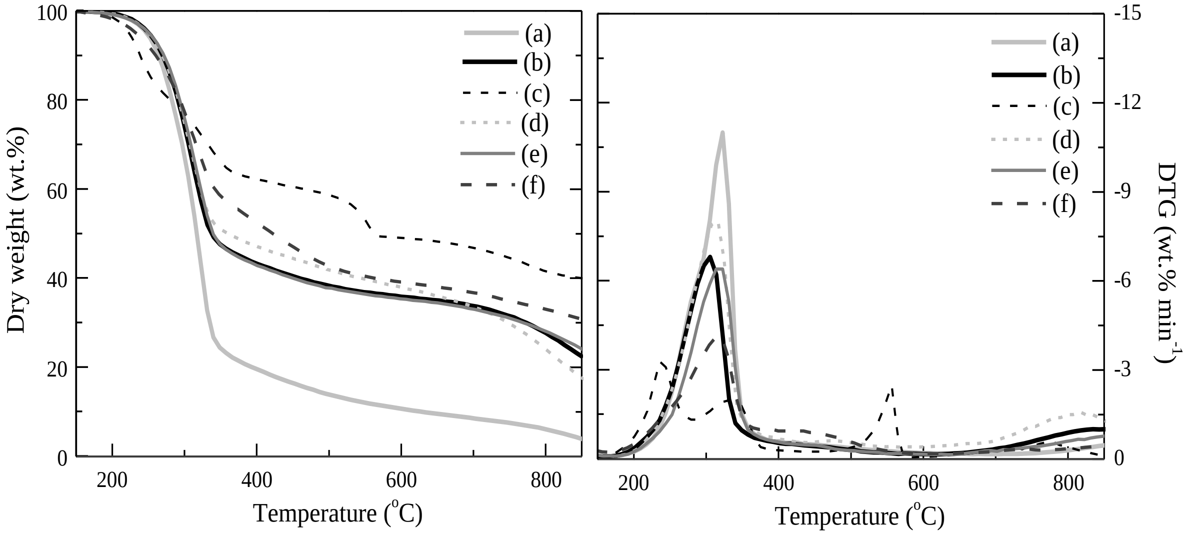

Figure 4. TGA (left) and DTG (right) curves of (a) raw EFB and pretreated EFB samples using (b) ChCl/lactic acid, (c) ChCl/levulinic acid, (d) ChCl/oxalic acid, (e) ChCl/sulfanilic acid-1, and (f) ChCl/sulfanilic acid-2

Figure 5 displays the FTIR spectra of raw EFB and selected pretreated EFB samples using respective DESs. The corresponding functional groups and the change in chemical bonding caused by the pretreatment using respective DESs are discussed in this part. Based on the peaks observed, the peaks related to O-H and aliphatic C-H groups are recorded around 3000–3500 cm^{-1} and 2790–2900 cm^{-1}, respectively. Around 3000–3500 cm^{-1}, the O-H functional group observed is related to the cellulose, hemicellulose, and lignin structures of EFB and also to the pretreated samples. The aliphatic C-H stretching vibration can be found in methyl and methylene groups for the complex biomass structure. The peaks mentioned have been reported previously by Harun et al. [27] and Huang et al. [28]. The wider and broader peaks between 3000 and 3500 cm^{-1} indicate the stretching vibration of O-H, in which more hydroxyl groups are released as the non-fibrous material (e.g., lignin) is eliminated. Li et al. [8] also found that the peak shifted towards higher frequencies when more hydroxyl groups were released, and non-fibrous material was discarded.

There are other important chemical functional groups that can be used as references for peak identification of raw EFB and pretreated EFB samples in this study. The C=O stretching in lignin and hemicellulose was identified around 1620–1685 cm^{-1} [29]. The peak identification of pure components (e.g., cellulose) might be difficult as the pretreated sample possibly contains remaining lignin and hemicellulose. However, the peak intensity can be compared to resemble the peak intensity of pure cellulose to confirm the cellulose structure, as carried out by [27]. Some important peaks, such as the C-O-C of the glycosidic bond of cellulose from the previous work, can be used to compare with the pretreated EFB samples in this work. C-O-C asymmetry stretching of glycosidic bond in cellulose structure was observed at 1167 cm^{-1} in raw EFB and pretreated EFB samples using ChCl/lactic acid and ChCl/sulfanilic acid. This C-O-C stretching related to cellulose structure was reported previously around 1158 cm^{-1} [29] and 1140–1160 cm^{-1} [27]. In addition, the detection of C-H bending vibration in CH_2 of cellulose was observed around 1400 cm^{-1}, which is similar as reported by Li et al. [30].

The C-O (C-C-O and C-OH) and C-C stretching vibration of all three major components were detected around 1000–1100 cm^{-1}. These peaks can be observed for raw EFB and pretreated EFB samples treated using ChCl/levulinic acid and ChCl/oxalic acid. This explains that the pretreatment conducted using the stated DESs does not provide high removal of components, such as lignin and hemicellulose.

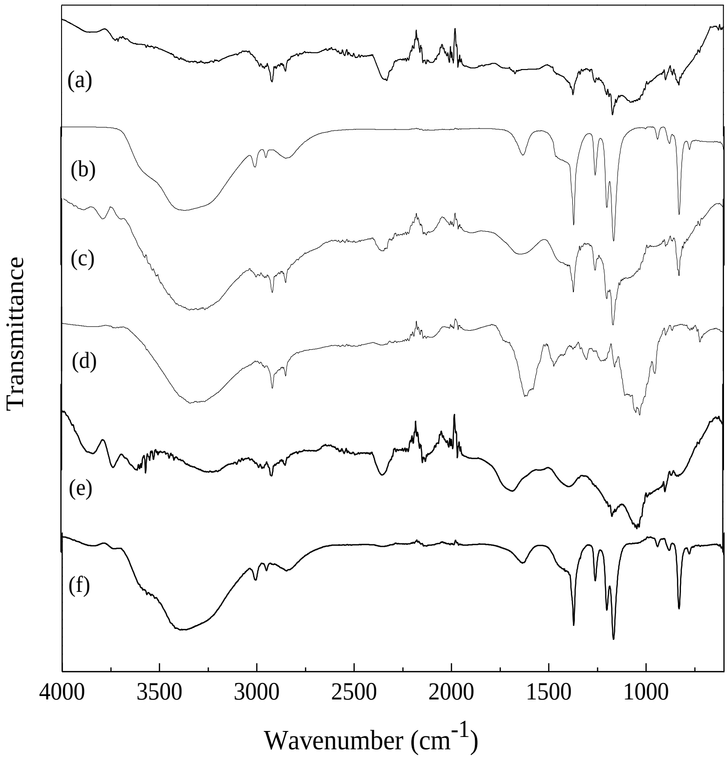

Figure 5. FTIR spectra of (a) raw EFB and selected pretreated EFB samples using (b) ChCl/sulfanilic acid-2, (c) ChCl/sulfanilic acid-2, (d) ChCl/oxalic acid, (e) ChCl/levulinic acid, and (f) ChCl/lactic acid

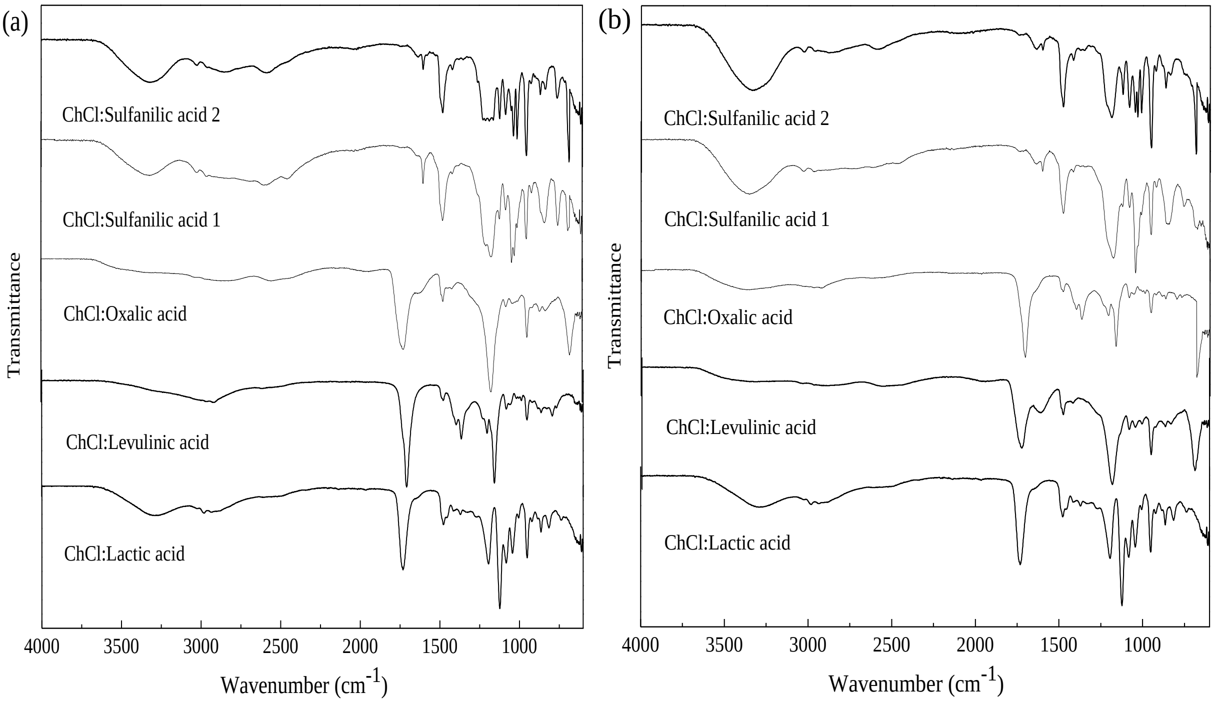

Figure 6. FTIR spectra for selected DES (a) before and (b) after pretreatment of EFB

FTIR Analysis of DESs Before and After Pretreatment

Figure 6 displays the FTIR spectra of the selected DESs before and after the pretreatment of EFB. FTIR is used to study the chemical structure of the DESs prepared in this work, and the changes in the functional groups are related to the existing components from EFB pretreatment in the DES mixture. Figure 6(a) shows broad peaks between 3100 and 3500 cm^{-1} for ChCl/sulfanilic acid and ChCl/lactic acid. The wide peak of ChCl/lactic acid indicates that the hydroxyl group is present in the DES structure. Two hydroxyl groups are present in the lactic acid structure, while the -OH of carboxyl group involves in the esterification with the -OH group of ChCl. Thus, lactic acid still has the hydroxyl functional group after the esterification with ChCl, as shown in the FTIR spectrum. However, for levulinic acid and oxalic acid, the hydroxyl group is involved in the esterification with ChCl; hence, no hydroxyl peak could be observed in the FTIR spectra. Besides, these broad peaks are also related to the hydrogen bond in the amine group observed for ChCl/sulfanilic acid. The peak is clearly observed in ChCl/sulfanilic acid due to the N-H group of sulfanilic acid structure in DES.

The peak stretching around 1750 cm^{-1} indicates the C=O carboxylate groups of esters in the DES structure. This peak can be observed in the spectra of ChCl/lactic acid, ChCl/levulinic acid, and ChCl/oxalic acid. A similar finding was found by Al-Risheq et al. [31]. However, this peak was not observed in ChCl/sulfanilic acid due to the absence of C=O in the DES structure. Al-Risheq et al. [31] reported that C-O stretching, O-H bending, and C-H stretching were detected between 1000 and 1450 cm^{-1}. The spectra around 1180–1250 cm^{-1} display the stretching vibration of C-N, which can be related to the ChCl and sulfanilic acid in the DES structure. The stretching vibration of C-N was detected at 1246 cm^{-1} [32]. The C-O stretching detected around 1100–1180 cm^{-1} is related to the ester linkage between ChCl and acid in the synthesised DES. The possible detection of C-O for ChCl/sulfanilic acid could explain the esterification between the -OH from the sulfonic group and the -OH of ChCl. The reaction between the sulfonic group and the -OH group was reported previously in other studies [33, 34]. However, a detailed mechanism study is required to confirm the reaction between both chemicals, and some studies stated that ChCl and HBD (e.g., sulfanilic acid) are mainly connected by hydrogen bonds [32, 35].

By comparing Figure 6(a) and (b), minor alterations in the peak structure could be seen. After pretreatment, the peaks between 3100 and 3500 cm^{-1} of the DES become wider and broader. Additional hydroxyl groups are formed after the pretreatment, making the O-H stretching vibration peaks broader [8]. The hydroxyl group from degraded lignin is discharged and washed away with the DES. This can be related to the small increase of C=O peak intensity around 1600–1640 cm^{-1}, which can be referred to as lignin and hemicellulose, and a small increase of C-O peak intensity for all three major components between 1000 and 1100 cm^{-1}. Based on the overall peaks in the spectra, it can be said that the recovered DES after pretreatment does not affect the structure of the initial DES because most of the original FTIR peaks are present in the DESs after pretreatment.

CONCLUSION

The acidic DESs used for the pretreatment of EFB show significant results in removing lignin from the EFB precursor. Different molar ratios of various acidic DESs were employed in this work to study their effect on EFB pretreatment, especially for two molar ratios of new ChCl/sulfanilic acid. As presented in this work, ChCl/lactic acid shows the ability to pretreat biomass and provides cellulose-rich biomass after pretreatment. Similar output was obtained by the sample treated with ChCl/sulfanilic acid. The characterisation of the pretreated samples reflects the results of the degradation of lignin obtained in this work, where high lignin degradation was obtained for the samples pretreated with ChCl/lactic acid and ChCl/sulfanilic acid. The SEM images of the samples pretreated with ChCl/lactic acid and ChCl/sulfanilic acid also show a fibrous structure of cellulose. Besides, the degradation peak of cellulose in the pretreated samples via TGA and the FTIR spectra of the samples pretreated using ChCl/lactic acid and ChCl/sulfanilic acid show a high possibility of cellulose availability in the structure after the removal of other components, such as lignin and hemicellulose. More analysis should be conducted to support the result of the samples pretreated using potential DES for biomass pretreatment, such as ChCl/sulfanilic acid.

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