Applied Science and Engineering Progress, Vol. 20, No. 1, 2027, 8190

Research Article

DES Molar Ratio and Time-Driven Delignification of Pineapple Peel: Achieving Exceptional Lignin Removal and Cellulose Enrichment

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DOI: 10.14416/j.asep.2026.06.004
Received: 24 January 2026; Revised: 11 March 2026; Accepted: 27 May 2026;

Abstract

This study examined the influence of Deep Eutectic Solvent (DESs) molar ratio and reaction time on the delignification of pineapple peel as a lignocellulosic biomass. Lactic acid was employed as the hydrogen bond donor (HBD), while choline chloride, betaine hydrochloride, and glycine were used as hydrogen bond acceptors (HBAs). The DESs molar ratios investigated were 1:4, 1:6, 1:8, and 1:10. Delignification was conducted at 121°C for 1, 2, and 3 h. The lignin, hemicellulose, and cellulose contents before and after delignification were determined using the Chesson–Datta method. Structural and morphological modifications of the biomass were evaluated by FTIR, SEM, and XRD analyses. The highest lignin removal was achieved using betaine:lactic acid DES with a molar ratio of 1:6 for 1 h. Under this condition, lignin removal reached 96.87%, with hemicellulose and cellulose contents of 7% and 79%, respectively. These results indicated that betaine:lactic acid DES effectively disrupts lignin bonds in pineapple peel compared to other DESs without damaging cellulose.

Keywords: Deep Eutectic Solvent, Delignification, Pineapple Peel, Cellulose, Lignin Removal

1 Introduction

Lignocellulosic biomass, characterized by its renewable abundance, chiefly encompasses polysaccharides like cellulose and hemicellulose, along with the intricate aromatic polymer lignin [1], [2]. Due to its low cost and frequent classification as waste, lignocellulosic biomass presents a promising and cost-effective alternative energy source. This biomass holds potential for transformation to be converted into high-value biochemicals including enzymes, organic acids, biopolymers, and biochar, as well as a variety of biofuels like bioethanol, biodiesel, and biogas [3]–[5]. Structurally, lignocellulosic biomass consists of crystalline cellulose fibers embedded within a complex hemicellulose–lignin matrix that restricts the accessibility of cellulolytic enzymes and consequently hinders the direct conversion of the cellulose into fermentable sugars without prior pretreatment [6], [7]. The recalcitrant nature of plant cell walls is mainly attributed lignin carbohydrate complexes, which act as physical and chemical barriers restricting enzymatic penetration [8]. Effective delignification requires lignin solubilization coupled with hemicellulose degradation, which fractures the complex polymeric architecture and enhances cellulose reactivity [9].

Pineapple (*Ananas comosus*), a tropical fruit from the Bromeliaceae family, boasts distinctive flavor and aroma profiles, exceptional nutritional density, and economic accessibility [10], [11]. Pineapple peel is a viable feedstock for biomass-based energy conversion processes since it is a lignocellulosic biomass consisting of hemicellulose, lignin, cellulose [12]. In Indonesia, pineapple productivity increased at an average annual rate of 10.99% during the period 2014–2023, reaching its highest level in 2023 at 149.63 tons per hectare [13]. Dried pineapple peel contains significant lignocellulosic components, including 19.8% cellulose and 11.7% hemicellulose, along with moisture (86.7%), carbohydrates (10.54%), ash (0.48%), fat (0.02%), and crude fiber (1.66%) [14]. The substantial cellulose composition of pineapple peel establishes it as a promising feedstock for fermentable sugar production toward renewable fuels [15]. However, lignin in pineapple peel limits enzymatic accessibility to cellulose and hemicellulose, making delignification necessary to enhance carbohydrate availability [16], [17]. Delignification entails the selective removal of lignin from lignocellulosic matrices, thereby enabling structural modification of biomass to improve subsequent hydrolysis into constituent monomers [18], [19]. The process expands surface area within the lignocellulosic matrix, thereby improving enzyme accessibility to cellulose and hemicellulose components [20]–[22]. Diverse lignin removal strategies facilitate enhanced cellulose and hemicellulose accessibility. Physical pretreatment methods are carried out through mechanical size reduction, including milling, crushing, grinding, and extrusion [23]–[25]. Chemical pretreatment methods commonly involve the use of acids and alkalis [26], [27]. Physicochemical pretreatment methods combine physical-chemical approaches, such as steam explosion and microwave irradiation [28]–[30]. Microbial pretreatment, leveraging fungi and bacteria, modifies lignocellulosic biomass structure before hydrolysis with enzymes [31], [32].

In recent years, DESs have attracted growing interest as eco-friendly alternatives to traditional solvents. Researchers and industries alike value them for their versatility across various fields of chemistry. These include organic synthesis, catalysis, extraction processes, and even membrane fabrication [33]. Owing to their comparable physicochemical properties, DESs have been widely proposed as promising substitutes for ionic liquids (ILs) in biomass delignification processes, particularly due to their high thermal stability, negligible volatility, low vapor pressure, and adjustable polarity [34], [35]. DESs are generally biodegradable, low-cost, non-toxic, easy to prepare, less energy consumption and recyclable [36], [37], [38]. These characteristics make DESs selective solvents for delignification processes without significantly damaging the main carbohydrate components of lignocellulosic biomass [39]. To make DESs, acids and bases, either Brønsted or Lewis, are mixed at exact molar ratios [40], [41]. The produced liquid phases demonstrate substantially reduced freezing points compared to the individual precursors [42]. These solvents are formed through hydrogen bonding interactions between HBDs include amides, carboxylic acids, and other substances that donate protons or electrons, such as urea, thiourea, glycerol, and oxalic acid and HBAs include quaternary ammonium or phosphonium salts [43], [44]. The physicochemical characteristics of DESs can be customized as needed by varying the ratio of HBA to HBD [45].

DES delignification has been explored for lignocellulosic biomass, its application to pineapple peel—particularly using betaine hydrochloride-based DES—remains underexplored, representing a significant opportunity for valorizing this abundant agro-industrial waste. This study investigated the delignification of pineapple peel using DESs synthesized from choline chloride, betaine hydrochloride, and glycine as HBAs, with lactic acid as the HBD. Investigations were conducted into the effects of DES type, molar ratio, and reaction time on lignin removal while changed in lignocellulosic composition and structural characteristics were further analyzed for the selected optimal sample.

2 Materials and Methods

2.1 *Raw Materials*

Pineapple peel samples were gathered from Cinta Manis Village in the Banyuasin Regency of Indonesia. The samples were oven-dried for 12 h at 105 °C to eliminate residual moisture. The dried samples were then pulverized using a blender and sieved to produce uniformly sized particles with a mesh size of 60. Choline chloride (≥99%), betaine hydrochloride (≥99%), glycine (≥99%), and lactic acid (90%) were procured from Merck and Sigma-Aldrich.

2.2 *DESs Synthesis*

In molar ratios of 1:4, 1:6, 1:8, and 1:10, DES were produced by combining HBAs such as glycine, betaine hydrochloride, and choline chloride with lactic acid as the HBD. Components were mixed in a three-necked round-bottom flask equipped with a condenser and thermometer, then heated to 80 °C on a hotplate under continuous magnetic stirring at 500 rpm for 30 min. The synthesized DESs were stored in Schott bottles prior to use.

2.3 *Delignification*

25 mL of DESs were combined with 10 g of 60-mesh pineapple peel at molar ratios of 1:4, 1:6, 1:8, and 1:10. The mixtures were heated for 1, 2, 3 h at 121°C in an autoclave. After the delignification, the solid residues were filtered and rinsed with distilled water (around 5 – 10 L) until the pH was neutral (7.0 – 7.3). The neutralized samples were then oven-dried at 105 °C for 6–8 h prior to compositional analysis.

2.4 *Compositional and Morphology Analysis*

The lignin, cellulose, and hemicellulose contents were measured both before and after delignification using the Chesson-Datta method [46]. A Thermo Scientific Quanta 650 SEM, a Bruker Alpha II FTIR spectrometer with spectra covering a wavenumber range of 4000–500 cm^{-1} obtained using 24 scans at a resolution of 8 cm^{-1}. A Panalytical XRD system used to determine the Crystallinity Index (CrI). The system was operating at 40 kV and 30 mA using Cu Kα radiation with a wavelength of 1.5406 Å were used to analyze each sample morphology. The following formula was used to determine the CrI based on Hermans method [47]:

$$\text{CrI} = \frac{\text{Acryst}}{\text{Atotal}} \text{ x } 100\% \tag{1}$$

A_{cryst} = area of the crystalline peaks

A_{total} = total area under the diffraction pattern

3 Results and Discussions

3.1 *Effect of DESs molar ratio on delignification*

This study aimed to observe the lignin removal from pineapple peel. The DESs used were Gly:LA, ChCl:LA and Betaine:LA with molar ratios of 1:4, 1:6, 1:8, and 1:10, and 1, 2, and 3 h reaction times. The molar ratio of HBA to HBD has a significant impact on the rate of lignin removal during delignification using DESs [48]. The experimental data provided in Table 1. The result showed that the optimal ratio for Gly:LA, ChCl:LA, and Betaine:LA DESs was 1:6. In terms of lignin removal, The delignification time, temperature, and DES molar ratio were the most important factors [49]. The molar ratio's impact shows that the DES solvent becomes more acidic as the lactic acid level rises [50], [51]. When the HBD ratio is increased, lactic acid can provide more H^+ ions to facilitate protonation as a catalytic mechanism [52]. Higher availability of protons improves lignin solubilization by strengthening the DES-lignin interactions and encouraging the breakage of bonds that bind lignin to the lignocellulosic matrix [53]. This is consistent with Li *et al.,* [54] who report that increasing of HBA:HBD ratio in ChCl:LA-based DES enhanced the cleavage of lignin–hemicellulose bonds in rice straw biomass.

Numerous prior investigations have explored the efficacy of DESs for biomass delignification. For instance, previous studies observed on corncob, lignin removal ranging from 64.7% to 93.1% as the ChCl:LA molar ratio increased from 2:1 to 15:1 [55]. In contrast, in sugarcane bagasse, a low ChCl:LA molar ratio of 1:2 resulted in relatively high residual lignin due to insufficient H^+ availability to effectively cleave β-O-4 lignin bonds. [52]. These results highlight the adaptability of DES formulations for targeted fractionation of lignocellulosic constituents. The mechanism of DES pretreatment entails distrupting the intermolecular bonding within lignocellulose [56] and reducing cellulose particle size [57].

However, excessively high lactic acid ratios can lead to over-acidification and trigger lignin condensation reactions [58]. Following ether bond cleavage, new C–C bonds are formed between lignin fragments during lignin condensation, producing more condensed lignin with a higher molecular weight [59], [60]. Condensed lignin tightly encapsulates cellulose, inhibiting cellulase access and adsorbing the enzyme, thereby reducing cellulose conversion [61]. As shown in Table 1, lignin condensation was observed at high temperatur used (121°C) and 1 : 6 molar ratio of ChCl : LA. The lignin content decreased from 39.87% to 11.28% (Table 1). While this condition, the cellulose consentrated into 71%. The optimal molar ratio (1:6) caused further increases in DES acidity, which not only accelerates lignin removal [62] but also enhanced cellulose concentration by selective delignification. The decreasing HBA proportion while increasing HBD leads the primary DES mechanism to shift from lignin separation toward cellulose hydrolysis, causing substantial cellulose dissolution into the DES filtrate [63]. Therefore, the HBA:HBD molar ratio determines DES performance, making the identification of an optimal molar ratio a key factor for improving delignification efficiency [64].

3.2 *Effect of reaction times on delignification*

The reaction time in the delignification process is a critical parameter when using DES, as it governs the extent of contact between the solvent and the lignocellulosic matrix. According to Figure 1, delignification using Gly:LA DES reached an optimum at 2 h, whereas ChCl:LA and Betaine:LA DESs reached their optimum at 1 h. This indicated a significant increase in lignin removal, followed by a gradual decrease if the reaction time exceeded the optimum. Specifically, as shown in Figure 1a, the optimum reaction time for Gly:LA DES is 2 h. Resulting from the comparatively elevated viscosity of Gly:LA, arising from the establishment of robust hydrogen-bonding interactions among the amino and carboxyl moieties of glycine and the hydroxyl functionalities of lactic acid [65], [66]. Prolonged reaction duration facilitates superior lignin solubilization by overcoming DES-biomass matrix penetration barriers [67]. In a comparable

Table 1. Lignocellulosic composition of pineapple peel

DES type	Molar ratio	Reaction time (h)	Composition (%)		
			Cellulose	**Hemicellulose**	**Lignin**
Untreated pineapple peel			21.00	32.00	39.87
Gly : LA	1:4	1	37.00	19.00	23.88
		2	41.00	25.00	20.53
		3	40.00	19.00	26.96
	1:6	1	53.00	8.00	29.96
		2	56.00	2.00	20.39
		3	24.00	17.00	34.12
	1:8	1	37.00	6.00	34.27
		2	40.00	13.00	32.54
		3	28.00	29.00	29.05
	1:10	1	38.00	14.00	26.01
		2	45.00	3.00	33.07
		3	40.00	31.00	23.62
ChCl : LA	1:4	1	54.00	3.00	11.47
		2	48.00	6.00	32.13
		3	64.00	13.00	12.83
	1:6	1	71.00	11.00	11.28
		2	50.00	2.00	34.89
		3	56.00	11.00	13.19
	1:8	1	55.00	14.00	26.45
		2	46.00	15.00	31.70
		3	43.00	18.00	30.08
	1:10	1	36.00	26.00	25.90
		2	38.00	22.00	30.78
		3	33.00	19.00	36.84
Betaine : LA	1:4	1	54.00	6.00	32.92
		2	50.00	2.00	30.87
		3	23.00	3.00	34.26
	1:6	1	79.00	7.00	11.79
		2	25.00	2.00	28.58
		3	27.00	3.00	16.96
	1:8	1	51.00	15.00	22.80
		2	46.00	6.00	37.45
		3	37.00	5.00	30.21
	1:10	1	53.00	6.00	32.04
		2	52.00	8.00	29.79
		3	36.00	6.00	29.84

finding, Liu *et al.,* [68] reported that in wheat straw pretreated with triethylbenzyl ammonium chloride (TEBAC)/lactic acid DES, cellulose content decreased from 66% at 2 h to 48.7% at 12 h due to prolonged pretreatment.

In contrast, Betaine:LA and ChCl:LA DESs exhibit relatively lower viscosity and higher acidity, allowing protons (H^+) to more easily cleave lignin bonds [50], [69]. The previous study found that delignification of birchwood with reaction times ranging from 10 to 120 min, yielding maximum lignin extraction in 60 min reaction time [70]. While the delignification with DES for 62 min achieved 88.35% cellulose conversion and a significant reduction in lignin content from 27.44% to 9.93% for pineapple peel [71]. Previous studies demonstrated that extended reaction times enhance cellulose enrichment through delignification. For instance, ChCl:LA DES pretreatment of Napier grass at a 1:4 molar ratio, 80°C for 5 h, achieved 71% cellulose concentration alongside 68% lignin removal [72].

Hemicellulose and amorphous cellulose can break down over extended reaction times into low-molecular-weight substances that are soluble in the solvent [73]. Excessively long reaction times can reduce solid yield as carbohydrate components in lignocellulosic biomass dissolve and degrade [64]. Additionally, extending the delignification time did not significantly increase cellulose content but increased energy consumption [74]. These results indicated that for pineapple peel biomass, a short reaction time (1 h) with ChCl- or Betaine-based DES was sufficient to achieve lignin removal above 90% without excessive cellulose degradation.

3.3 *Effect of HBAs on delignification*

DESs are commonly recognized as environmentally friendly solvents because of their capacity to effectively dissolve and fractionate lignin from lignocellulosic biomass. The most researched kind of DESs are acidic ones, which are often made up of organic acids like lactic acid as the HBD combined with HBA [75]. The carboxylic acid groups in lactic acid supply more protons for cleaving glycosidic, ester, and ether bonds than the hydroxyl groups in glycerol, hence increasing the solubility of hemicellulose and lignin [76]. Lignin fractionation also requires HBAs since halide anions help break β-O-4′ linkages, which stop lignin condensation [77]. Chloride ions (Cl^-) from the HBA may compete with hydroxyl groups in lignin and carbohydrates to create hydrogen bonds and promote the disintegration of ether bonds in lignin carbohydrate complexes (LCCs) [78]. The hydroxyl groups in lignin and carbohydrates form hydrogen bonds with chloride ions in DES, which break LCC links through competitive interactions [48]. Based on Table 1, the most effective DES for pineapple peel delignification was Betaine:LA at a 1:6 molar ratio for 1 h. Under these conditions, the highest lignin removal of 96.87% was achieved, reducing lignin content to 11.79% while increasing cellulose content to 79% compared to other conditions.

Prior studies demonstrated that hydrothermal pretreatment of rice straw with Betaine:LA DES at 170 °C for 1 h achieved 96% hemicellulose solubilization, 81.3% lignin removal, and 72% cellulose recovery [79], alongside efficiencies exceeding 64% lignin removal and cellulose contents surpassing 85% at 120 °C [80]. Similarly, Betaine:LA DES facilitated 80.1% lignin degradation in bamboo during pretreatment at 140 °C over 6 h [81], 53% lignin removal from willow biomass after 3 h of reaction, and 79% from maize straw [82]. Betaine may easily establish eutectic interactions with HBDs due to its polar functional groups and asymmetric structure [83]. In addition to nitrogen and chloride ions, betaine hydrochloride also includes carboxylic acid groups (-COOH), which provide strong hydrogen-bond interactions and efficient electron-donating and accepting capabilities [75], [84].

Table 1 shows that ChCl also effectively acted as an HBA, achieving 95.70% lignin removal. As illustrated in Figure 2. Chloride anions are present in both ChCl and betaine hydrochloride. When the highly electronegative Cl^- ions create hydrogen bonds with the hydroxyl groups in lignin and carbohydrates, the internal hydrogen-bond network of the lignocellulosic matrix may be damaged [85]. Strong intra- and intermolecular hydrogen interactions stabilize the glucose chains coupled via β-(1,4)-glycosidic connections in natural cellulose [86], [87]. Delignification with DES creates new hydrogen bonds between the hydroxyl groups (-OH) of the polysaccharide and the DES by severing these initial intermolecular hydrogen bonds [88], [89].

DESs hydrogen-bond basicity, which reflects the solvent's capacity to function as an HBA, reduces both intra- and intermolecular hydrogen bonds in cellulose [90]. Additionally, molecules like imidazole and morpholine, as well as anions that may function as HBAs such as OAc^-, $(MeO)_2PO_2^-$, Cl^-, and $HCOO^-$, are excellent candidates for DES production [91]. The absence of a carboxylic acid moiety in ChCl—unlike in betaine hydrochloride—limits its ability to supply protons for hydrogen bond formation. [92]. The maximum cellulose recovery in Gly:LA was only 56%, which was less than that of DESs based on betaine hydrochloride and ChCl. Glycine betaine possesses lower hydrogen-bond basicity compared to species containing Cl^-, owing to its lack of halide constituents. Gly:LA only eliminated around 58.4% of the lignin, whereas ChCl: LA-based DES could reach a maximum delignification degree of about 90.4% [73]. Higher delignification efficiency is the result of ChCl:LA's increased capacity to permeate the lignocellulosic matrix due to the presence of halide ions. Despite possessing a carboxyl group (-COOH) capable of hydrogen bond formation, glycine proves less effective at disrupting lignin ether bonds and lignocellulose complex (LCC) linkages

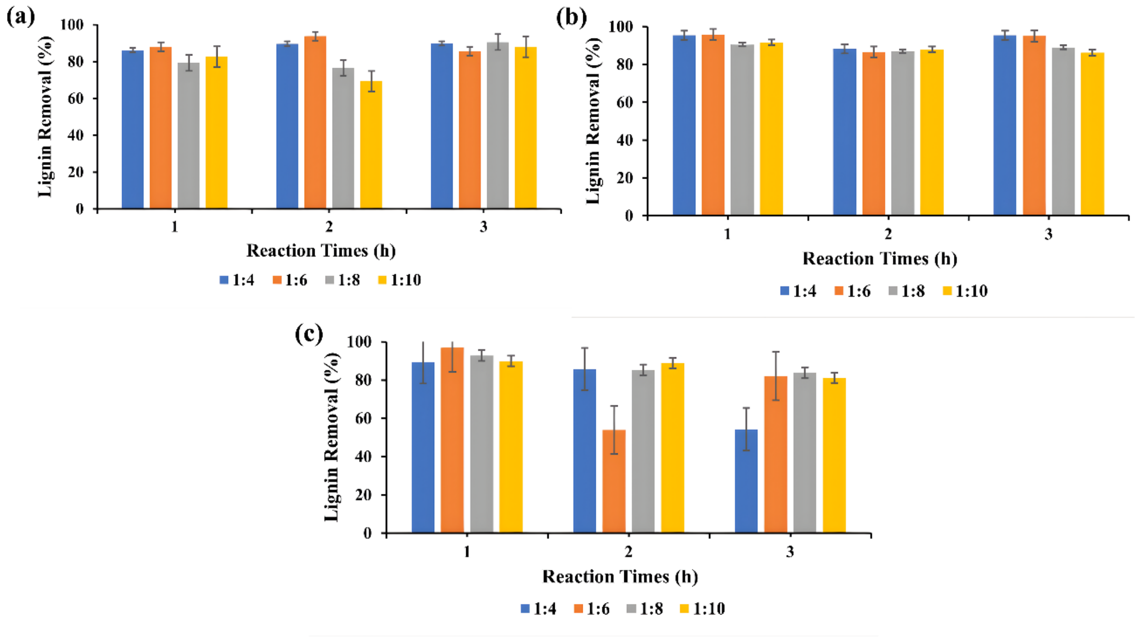

Figure 1. The reaction times effect of (a) Gly:LA, (b) ChCl:LA, and (c) Betaine:LA on lignin removal from pineapple peel

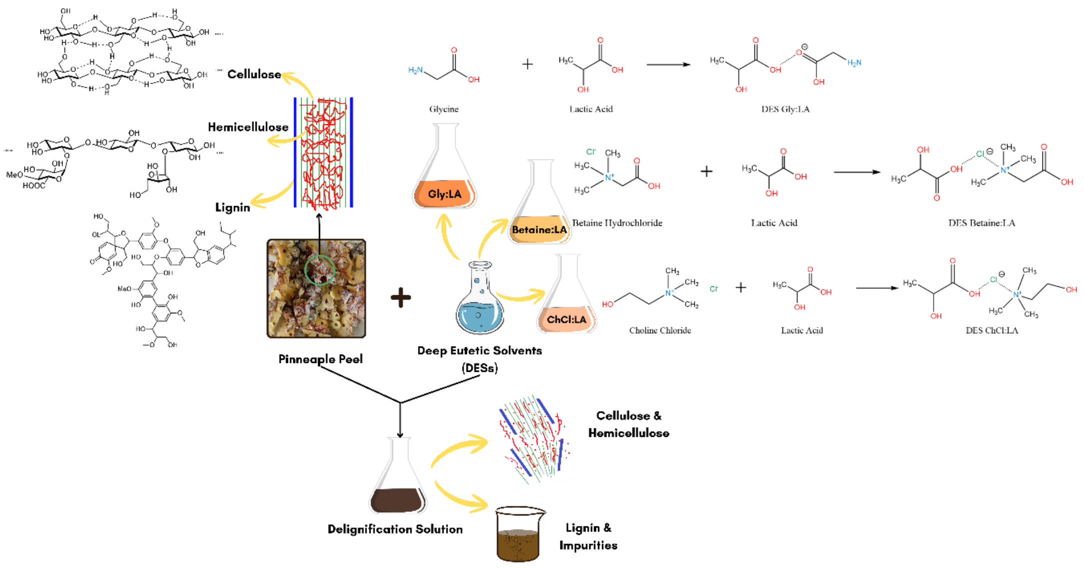

Figure 2. Delignification process using Gly:LA, ChCl:LA, and Betaine:LA.

than DES formulations containing Cl^-. Consequently, the delignification mechanism in Gly:LA relies primarily on HBD acidity, without halide anions to reinforce lignin disruption.

3.4 *SEM analysis of the pineapple sample*

SEM was used to observe the surface morphology of pineapple peel before and after delignification. The surface morphologies of pineapple peel before and after delignification DESs are shown in Figure 3. The untreated pineapple peel exhibited an irregular structure with a rough, fibrous, non-homogeneous, and porous surface, reflecting an intact lignocellulosic matrix [93].

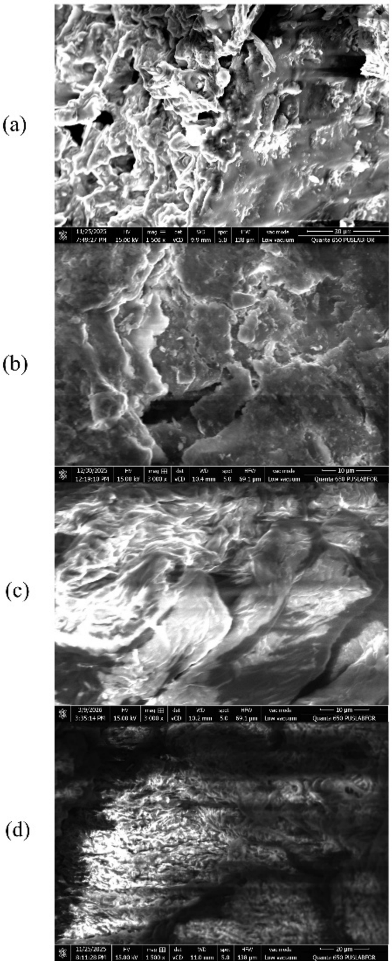

Figure 3. SEM images of pineapple peel (a) untreated and (b) Betaine:LA 1:6 1 h (c) Glycine:LA 1:6 2 h (d) ChCl:LA 1:6 1 h

The biomass surface underwent discernible structural changes following delignification. The delignified sample revealed a more homogeneous and refined surface structure than its untreated counterpart, consistent with crystalline cellulose presence [94] and a decrease in the amorphous percentage as a result of the removal of lignin and a portion of the hemicellulose. The increased CrI after delignification reflects the dominance of highly organized cellulose arrangements [95]. The comparatively smooth morphological characteristics imply that the DES breaks lignin bonds alone, sparing the cellulose framework from serious structural harm. These structural changes promote greater cellulose accessibility for reactive agents like enzymes, augmenting enzymatic hydrolysis efficacy and subsequent bioconversion yields [96], [97].

3.5 *FTIR analysis of the pineapple sample*

The FTIR spectra of untreated and delignified pineapple peels are shown in Figure 4. The delignified sample's FTIR spectrum showed several absorption bands with reduced intensity, suggesting that delignification using DESs led to a notable drop in lignin concentration along with the dissociation of lignin–cellulose connections.

Alcohol groups' C–O stretching vibrations, which originate from the polysaccharide structures of cellulose and hemicellulose, are responsible for the absorption band at about 1025 cm^{-1} [98]. A decrease in the amorphous hemicellulose proportion is shown by the band's decreased intensity following delignification. C–O vibrations linked to syringyl lignin units are responsible for the lower intensity in the 1200–1275 cm^{-1} area, which indicates a drop in lignin concentration during delignification [99], [100]. Since aryl–alkyl ether connections, primarily β–O–4 couplings, bind syringyl lignin units to aliphatic side chains, the breakage of syringyl lignin linkages during delignification is shown by the reduction in the C–O band at 1239 cm^{-1}. Additionally, the O–H deformation vibrations of phenolic groups, which are typical of free hydroxyl (phenolic) groups in lignin structures, are attributed to the absorption band at about 1368 cm^{-1} [101]. This band's decreased intensity during delignification indicates lignin breakdown and disintegration, demonstrating the effectiveness of the delignification process.

In the wavenumber regions of 1728 and 1627 cm^{-1}, which are associated with C=O stretching vibrations of ester or carboxylic acid groups (present in hemicellulose and lignin) and conjugated carbonyl or aromatic structures of lignin, respectively [63],

[88]. This demonstrates the disintegration of lignin components that include carbonyl groups as well as the ester linkages that link lignin to hemicellulose. In addition, the strength of the absorption band at 2926 cm⁻¹ is reduced during DES delignification. This band corresponds to the C-H stretching vibrations of methyl and methylene groups ($-CH_2$ and $-CH_3$), which are often found in lignin and hemicellulose chains [102]. The presence of aromatic phenols (Ph-OH) and aliphatic alcohols ($R-CH_2-OH$) in the untreated sample yields an absorption band at 3294 cm⁻¹ due to their O-H stretching vibrations. Changes in the O-H band's intensity during DES delignification show that the lignocellulosic matrix's hydrogen bonding has been broken. By forming new hydrogen bonds with these -OH groups, the DES weakens the links between lignin and carbohydrates and makes lignin removal easier.

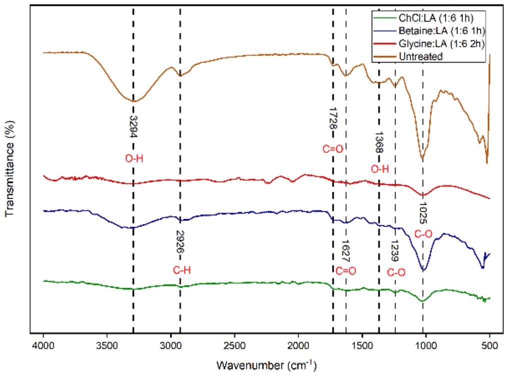

Figure 4. FTIR spectra of pineapple peel before and after delignification using DES

3.6 *XRD analysis of the pineapple sample*

One typical analytical approach for determining the atomic arrangement in both crystalline and amorphous materials is XRD, which uses X-rays that are distributed in different directions [103]. XRD analysis provides important information in studies of lignocellulosic biomass pretreatment, particularly regarding cellulose structure and its degree of crystallinity [104]. The relative percentage of crystalline and amorphous fractions in lignocellulosic biomass is expressed quantitatively using the CrI [105]. As illustrated in Figure 5, the XRD analysis showed that the crystalline phase of cellulose type I was represented by a major diffraction peak at $2\theta \approx 21.85°$ in untreated pineapple peel [62].

After delignification, the XRD patterns showed diffraction peaks at $2\theta \approx 21.8°$, 34,5°, and 44,7°, which correspond to the (110), (200), and (004) crystal planes, respectively, confirming the characteristic structure of cellulose type I [106], [107]. Cellulose type I is the native crystalline form in which cellulose chains are arranged in a parallel manner, while the (110), (200), and (004) planes indicate certain lattice planes inside the unit cell of cellulose type I that may be identified by XRD [108].

The calculated CrI values showed noticeable differences among the treatments. The determination of CrI used equation (1). Delignification with ChCl DES (1:6, 1 h) increased the CrI to 53.55%. A higher crystallinity index was observed for the Betaine DES treatment (1:6, 1 h), reaching 57.88%. In contrast, the Glycine DES treatment (1:6, 2 h) resulted in a CrI of 40.12%, which was comparable to the untreated sample. The increase in CrI indicates that DES-mediated treatment preserved cellulose crystallinity without altering its native polymorphic structure [109]. This result is in line with research by Liu *et al.,* [110] who found that corn stover treated with ChCl:OA DES increased its CrI to 57.8%. Similarly, Zhao *et al.,* [111] observed an increase in CrI to 53.9% in wheat straw using ChCl:monoethanolamine DES. Lin *et al.,* [97] also reported similar findings for bamboo residues, when delignification using ChCl :LA DES increased the CrI to 53%, without compromising crystalline cellulose integrity. DES-mediated delignification effectively eliminated amorphous constituents, including lignin and hemicellulose [112]. As a result, the proportion of crystalline cellulose became more dominant, which is consistent with the delignification results showing high lignin removal and high cellulose recovery [113], [114].

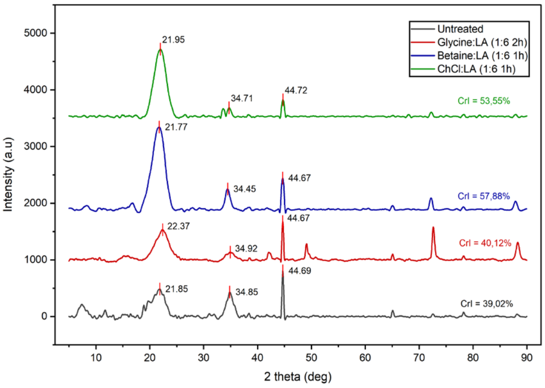

Figure 5. XRD patterns of pineapple peel before and after delignification using DES

4 Conclusions

Lactic acid-based DESs pretreatment of pineapple peel demonstrated substantial efficacy, primarily dictated by the HBA:HBD molar ratio and reaction time. The optimum molar ratio for all DESs Glycine:LA, ChCl:LA, and Betaine:LA was identified as 1:6, which resulted in the highest lignin removal, accompanied by an increase in cellulose content due to the reduction of amorphous components. The optimum reaction time was 1 h for the ChCl:LA and Betaine:LA systems, while a longer reaction time of 2 h was required for Glycine:LA to achieve lignin removal above 90% without excessive cellulose degradation. Among the DESs evaluated, the Betaine:LA-based system exhibited superior performance, achieving lignin removal of up to 96.87% with cellulose and hemicellulose contents of 79% and 7%, respectively. This outcome underscores its greater effectiveness for pineapple peel delignification compared to choline chloride- and glycine-based DESs. The present findings establish the potential scalability of DES pretreatment for pineapple peel biorefineries, with 95.70% lignin removal supporting economically feasible cellulose valorization. Subsequent research will prioritize optimization of enzymatic hydrolysis efficiency, DES recycling protocols, and comprehensive life-cycle assessments to affirm industrial practicality.

Acknowledgments

The authors sincerely thank the Directorate of Downstreaming and Partnership, Directorate General of Research and Development, Ministry of Higher Education, Science, and Technology, for funding through the Basic Research scheme (Contract No. 187/C3/DT.05.00/PL-BATCH II/2025, 14 July 2025).

Author Contributions

A.M.J.: conceptualization, investigation, data analysis, reviewing, and editing; M.Y.: funding acquisition, project administration; G.K.A.: data collecting, writing an original draft. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

Declaration of generative AI and AI-assisted technologies in the writing process

The authors declare no AI tool is used in this study.

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