

# Lignin extractions from oil palm empty fruit bunch under pressurized and inert conditions

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## Abstract

In this work, lignin was extracted from palm oil empty fruit bunch (EFB) for the first time under pressurized and inert conditions in the presence of deep eutectic solvents (DES). The choline chloride and the oxalic acid were mixed at a ratio of 1:1 to prepare DES, which successfully extracted around 30wt.% of lignin at a relatively mild temperature and pressure. Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (H-NMR) and differential scanning calorimetry (DSC) were used to analyze lignin, whereas X-ray powder diffraction (XRD) was used to investigate the solid residues. FTIR analysis revealed the characteristics of lignin with a major functional group composed of phenolic, aliphatic hydroxyl, and conjugated alkene. The thermal stability of lignin and EFB was confirmed by using DSC. The crystallinity of the solid residue consisting of cellulose was observed to be affected by different temperatures, with the highest value (43.5 %) at 80 °C. The yield of lignin extracted under a pressurized and inert environment shows more than double the value of lignin as compared to the analogue process under atmospheric pressure and also shows comparable lignin yield with microwave-assisted extraction systems. Thus, it provides a new, facile, and efficient approach to the delignification of lignocellulosic biomass.

**Keywords:** Empty fruit bunch (EFB); Lignin; Deep eutectic solvents (DES); High-pressure reactor.

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## 1. Introduction

Lignin is one of the common biopolymers which makes up 10-25% of the lignocellulosic biomass. Lignin is made up of aromatic phenolic compounds that are referred to as monolignols [1]. These compounds include coniferyl alcohol (G-unit), sinapyl alcohol (S-unit), and p-coumaryl alcohol (H-unit). The composition and proportion of these three polymeric components will have a unique combination from plant to plant [2]. Empty fruit bunch (EFB) is a by-product of the palm oil industry and one of the potential sources of lignin. The palm oil industry generates 23% EFB per tonne fresh fruit bunches [3]. Every year, the amount of EFB produced is approximately 127 thousand tonnes [4], thus creating a disposal issue. Utilizing EFB to produce value-added materials might be a partial solution to the problem of waste disposal. Lignin is a natural and sustainable raw material that possesses good chemical and physical

properties. It has the possibility of being used in the synthesis of valuable chemicals and products such as phenolic resins, adhesives, biofuels, and biodispersants [5]. Different lignin functional groups, such as the hydroxyl, aliphatic hydroxyl, phenolic hydroxyl, and methoxyl groups, have an impact on the chemical characteristics and aroma composition of lignin [6,7]. The proportion of hydroxyl groups that make up the aliphatic hydroxyl groups varies depending on the source [8]. There are a few different approaches that can be taken to extract lignin; however, its thermal decomposition is a crucial and rate-limiting phase that must be completed before any technology can be developed in a way that is both cost-effective and sustainable. Methods of lignin extraction such as mechanical, chemical, biological, and microwave heating have been used previously [9-11]. The chemical structure of the extracted lignin differs depending on extraction methods, which have impact on additional alternations. The lignin and

solid fractions were removed using a mechanical approach, which altered their quality and low thermal stability. Biological methods have not yet been fully developed and optimized for industrial-scale lignin extraction. However, chemical techniques, such as acid hydrolysis and alkaline treatment, can be expensive and detrimental to the lignin's structural and chemical characteristics. Therefore, chemical processes provide a substantial barrier to the establishment of a bio-based economy. Nowadays, scientists are focused toward the environmentally friendly isolation of lignin polymers with better conserved features at low temperatures using deep eutectic solvents (DES) [12]. Indeed, utilizing extraction technology with low environmental impact in combination with eco-friendly solvents develops as a vital necessity and viable solution. Among others available green solvents, deep eutectic solvents demonstrate high abilities in the pre-treatment of lignocellulose [13]. DES is a solvent that can be modified so that it works well with a certain type of chemistry. They are non-flammable, have a wide liquid range, and a low vapor pressure [14]. There are several benefits associated with DESs, including the simplicity of their preparation and the low cost of their individual parts. To make DESs, you need to mix together two chemicals, often when they are considerably heated [15]. Compared to conventional solvents like ionic liquids (ILs), this solvent system maintains a relatively low production cost and allows for large-scale applications. The microwave approach with DES also has drawbacks, such as high energy consumption, environmental issues, and equipment corrosion, which reduced process profits. Furthermore, the biological procedure is time-consuming, which limits the process's efficiency. In this study, the pressured heating system's ability to extract lignin from EFB is promoted by the utilization of DESs. The use of DESs in pressure reactors appears to be a promising technique for the extraction of lignin from lignocellulosic biomass. In comparison to more traditional methods of heating, the use of a pressurized heating system facilitates the selective breaking of bonds during the depolymerization of lignin and has a more compact molecular weight distribution. Through the utilization of this technique, the available biomass or agro-residual waste materials can be valorised into valuable materials.

## 2. Materials and methods

### 2.1. Materials and Chemicals

EFB fibers (Dominion Square Sdn. Bhd), distilled water, toluene (ACS reagent 99.5%), absolute ethanol, acetone (ACS reagent 99.5%), choline chloride (Reagent grade 98%), and oxalic acid (Reagent grade 98%) are the materials and chemicals utilised in this work.

### 2.2. Preparation of EFB fiber

The surface dust and contaminants of EFB fiber are removed by washing with distilled water and drying in the sun. Afterwards, a commercial cutting mill was used to turn the dry fibers into a powder (Retsch SM100). Then, the mixture of toluene: ethanol (2:1) is used for 7 h to remove the wax and oil elements from the raw EFB. Finally, the dewaxed fibers were cleaned with distilled water to eliminate extra Soxhlet solvent before being dried at 50 °C and stored in a dry storage.

### 2.3. Lignin extraction from EFB fiber under pressurized inert environment

The lignin in EFB fibers was extracted using DES solvent. Oxalic acid was used as a hydrogen bond donor (HBD) and chlorine chloride as a hydrogen bond acceptor (HBA) in a 1:1 molar ratio to prepare the DES. Then, the mixture was stirred at 90 °C until a transparent solvent was formed. A high-pressure batch reactor was used to extract the lignin from the EFB fiber. 10 g of EFB fiber was mixed with 100 g of DES and placed in a pressure reactor. Under 7 bars of nitrogen atmosphere, the temperature was raised from ambient to the respective extraction temperatures (60, 70, 80, and 90 °C). After 1 h of the extraction process, 50 mL of acetone: water (1:1 v/v) were mixed with the dark-brown liquid. The soluble and insoluble DES fractions have been separated by using vacuum filtration. A rotary evaporator was used to remove volatile acetone from the solution. Finally, centrifugation was used to separate and recover the lignin from the solution. The collected lignin was dried in an oven at 50 °C for 16 h and stored at room temperature.

### 2.4. Lignin extraction from EFB fiber under microwave system

In microwave assisted lignin extraction, 10g of EFB fiber were treated with 100 g of DES. A modified microwave system developed by NV Western Pt. was used to generate microwave radiation. A 90 °C temperature for 60 min was maintained in the microwave system. The dark-brown sample obtained from the process was further treated using similar process details as in the previous section.

### 2.5. Yield calculation of extracted lignin

The yield of lignin extracted from EFB biomass via pressurized reactor system was calculated based on TAPPI T222 (Equation 1)

$$L\% = \frac{m_{\text{isolated}}}{m_{\text{TAPPI}}} \times 10g \text{ EFB} \quad (1)$$

Where L is extracted lignin from EFB in percentage (%);  $m_{\text{isolated}}$  (gm) is the weight of lignin extracted via high-pressure reactor and  $m_{\text{TAPPI}}$  (gm) is the weight of lignin contained in EFB fiber estimated using the TAPPI technique.

### 2.6. Washing the cellulose enriched fractions

The cellulose-enriched fractions obtained after the extraction of lignin were washed repeatedly using distilled water in a beaker, followed by drying in the oven at 50 °C. The dried fractions were mashed with a mortar and pestle until they became powder.

### 2.7. Characterization of lignin and cellulose enriched fractions

Lignin and raw EFB were characterized using Fourier Transform Infrared (FTIR), proton NMR (H-NMR) and Differential Scanning Calorimetry (DSC), while cellulose-enriched fractions were characterized using X-ray Diffraction (XRD). Functional groups of lignin and raw EFB were observed through FTIR (Perkin Elmer Spectrum 100 FT-IR Spectrometer) within a spectral range between 400–4000  $\text{cm}^{-1}$  with 4  $\text{cm}^{-1}$  resolution. DSC (NETZSCH DSC 214-Polyma) was used to determine the glass transition temperature of lignin. The heating rate of the sample was 30

°C/min at temperature ranging from 30-200 °C under nitrogen flow. X-ray diffractometer was used to measure the

crystallinity of the cellulose-enriched fractions in the range  $2\theta$   $10^\circ \leq 2\theta \leq 80^\circ$ . The crystallinity of the cellulose-enriched fractions was calculated from XRD according to the Khan method [16].

$$Crl \% = \frac{A_c}{A_c + A_a} \times 100\% \quad (2)$$

Where  $A_c$  is the crystalline peaks area and ( $A_c + A_a$ ) is the total area of crystalline and amorphous regions.

### 3. Results and Discussions

Table 1 shows the yield of isolated lignin extracted using DES under inert and pressurized conditions. The pressure and time were kept constant at 7 bar and 60 min, respectively, whereas the temperature varied from 60 to 90 °C. It can be seen from the table that the pressurized environment was able to assist the lignin extraction as compared to the analogue test under atmospheric pressure. At a similar extraction temperature of 80 °C, only 11.5 % of lignin was extracted, compared to 23.5 % for the extraction carried out at 7 bars of nitrogen. Furthermore, it was discovered that the reaction temperature has a significant impact on the amount of lignin yield, with an increasing trend from 60 to 90 °C. The optimal reaction temperature is one of the most significant factors influencing the delignification extent in a pressure reactor. Therefore, the percentage of extracted lignin was calculated, and the effect of reaction temperature on the delignification of EFB by ChCl:OA is shown in the table. The lignin extraction increased dramatically from 0 to 30 wt% as the temperature rose from 60 to 90 °C. The high temperature decreases the viscosity and enhances the diffusivity of the DES solvent system by disrupting the H-bond between solvent components. This improves biomass-solvent contact and lignin removal. Various temperature combinations were used in a pressure reactor for the ability to control the reaction and provide influence over the targeted bond breakage of a chemical bond during lignin depolymerization. Inert gas pressure permits the transmission of the heating energy and interior (e.g., inter-atomic link stretching) forces of the molecules, influencing the kinetic and compositional features of the system, which include interaction energy dispersion [17]. At 90 °C, approximately 30% of the lignin yield is extracted from EFB. However, the crystallinity of extracted fractions at 90 °C decreases in pressure reactors due to fiber degradation.

The efficiency of lignin extraction under inert pressurized conditions with the presence of DES as a green and recyclable solvent was also compared to the extraction under the microwave heating process. A comparable extraction yield of lignin was obtained for the microwave-assist extraction process (30.5%) at a temperature of 90 °C for a similar duration. However, microwave assisted heating consumes high energy [18]. A pressure reactor can effectively cleave the bonds between lignin and xylan, increasing the production of lignin. It should be noted that the extraction environments during the delignification process can be controlled using a closed pressurized system and either inert or active gas. An inert gas environment will control any potential oxidation of the produced products and by-products, Arfat et al., 2024

enabling more controllable and tunable characteristics of lignin. Overall, these findings indicate that the DES is a potential solvent for lignin extraction and biomass pretreatment in the presence of pressured inert nitrogen gas. Therefore, lignin extraction from EFB in a pressure reactor can be considered an economical and facile process.

#### 3.1. FT-IR Characterization of lignin and residue

Absorption bands at 3434.94 and 3438.01  $\text{cm}^{-1}$  (between 3200 and 3550  $\text{cm}^{-1}$ ) in Fig. 1. of the FT-IR spectra demonstrate that OH groups of phenolic and aliphatic hydroxyl components are common in both the EFB and the isolated lignin, and that is due to strong intermolecular force bonding of bending vibration. The peak that occurs on raw EFB spectra at 2918.14  $\text{cm}^{-1}$  and the peaks that show on lignin spectra at 2924.12  $\text{cm}^{-1}$  and 2853.51  $\text{cm}^{-1}$  (between 2840 and 3000  $\text{cm}^{-1}$ ) are both ascribed to the C-H stretching vibrations of methyl groups [19]. The cyclic hydrocarbons of lignin peak at 2922-2852  $\text{cm}^{-1}$  and the ether linkage of lignin peaks at 1032.30  $\text{cm}^{-1}$ . The absorptions at 1647.38  $\text{cm}^{-1}$ , 1608.97  $\text{cm}^{-1}$ , 1513.17, and 1463.73  $\text{cm}^{-1}$  reveal the carbonyl group stretching for the methoxyl group of lignin, the methyl group ( $\text{CH}_2/\text{CH}_3$ ) stretching, and the aromatic ring stretching, respectively [20]. However, the absorption spectra of the lignin's guaiacyl structure is found to range between 1328.43 and 1377.39  $\text{cm}^{-1}$ . Lignin's hydroxyphenyl structure shows peaks at 1237.51 and 1165.03  $\text{cm}^{-1}$ .

#### 3.2. <sup>1</sup>H NMR analysis of lignin

The chemical structure of lignin was studied through proton NMR spectrometry using DMSO solvent. Fig. 2. demonstrates the proton NMR spectrometry of extracted lignin sample. The signal between the range (6.5–7.8 ppm) attributed aromatic and vinyl protons in syringyl (S) and guaiacyl (G) units. There are some modest peaks of aliphatic protons in the range (4.4-5.5 ppm). The methoxyl proton generates a sharp signal in the range (3.4-4.0 ppm) which represents G and S unit. Water and DMSO-d<sub>6</sub> solvent are represented by the two clear and significant signals that appear at 3.4 ppm and 2.5 ppm, respectively. The signals for saturated aliphatic proton were shown in the range (2.4-1.0 ppm) [21]. Differential scanning calorimetry (DSC) is used to examine the thermal behaviour of EFB and lignin. The results are shown in Fig. 3. In the case of EFB and lignin, a peak between 40 and 100 °C is observed, which is associated with the loss of water molecules due to evaporation. The areas of the endotherms where the peak temperature is higher than 125.8 J/g for EFB The DSC was operated under a nitrogen atmosphere with a flow rate of 40  $\text{ml min}^{-1}$  and a heating rate of 30  $^\circ\text{C min}^{-1}$  and sample in the range of 2-3 mg was placed in an enclosed aluminium crucible. The sample was heated from room temperature to 120 °C in the first heating cycle and kept isothermal for 6 minutes. Throughout the second heating cycle, the sample was heated to 200 °C. During the second heating cycle, the glass transition temperature ( $T_g$ ) of lignin was found to be 186 °C.

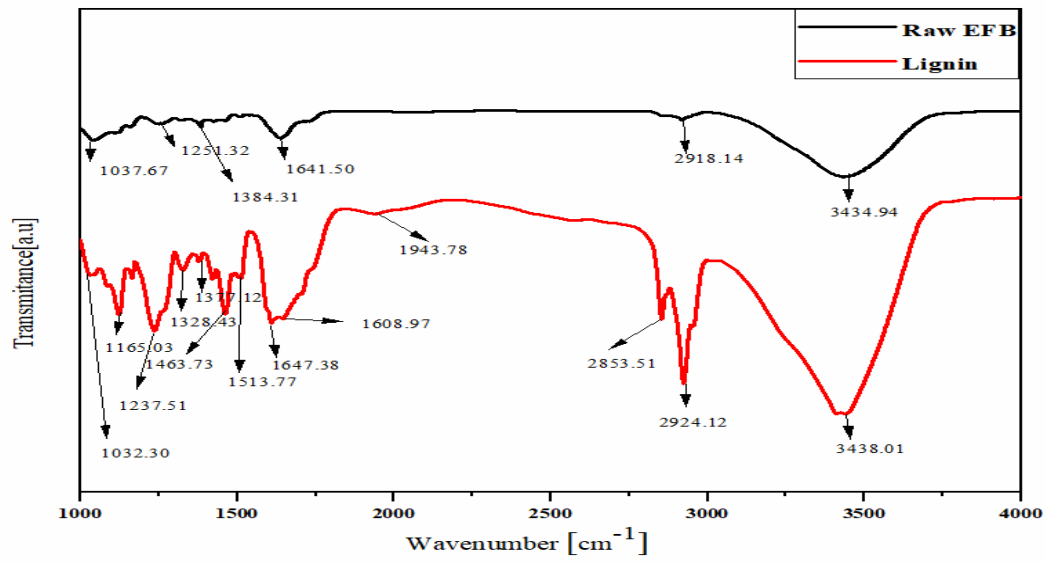


Figure 1: FT-IR analysis of EFB and lignin

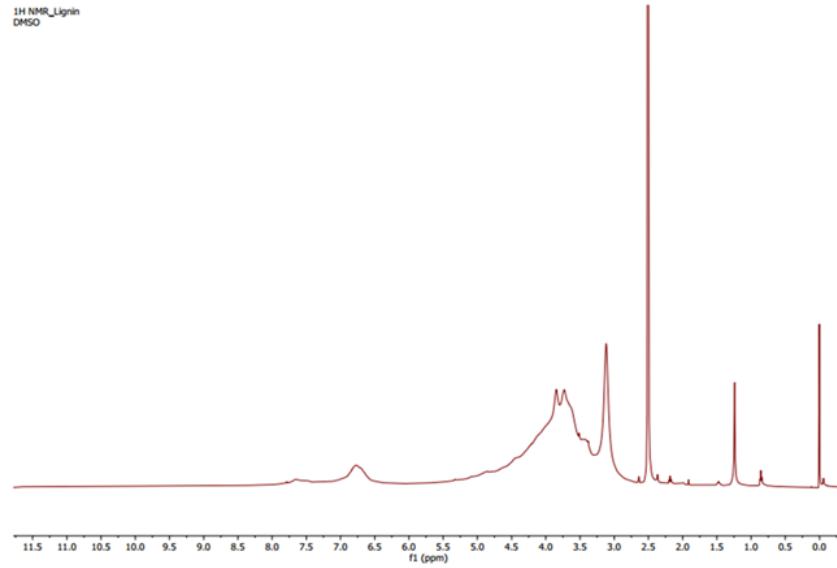


Figure 2: Proton NMR analysis of lignin

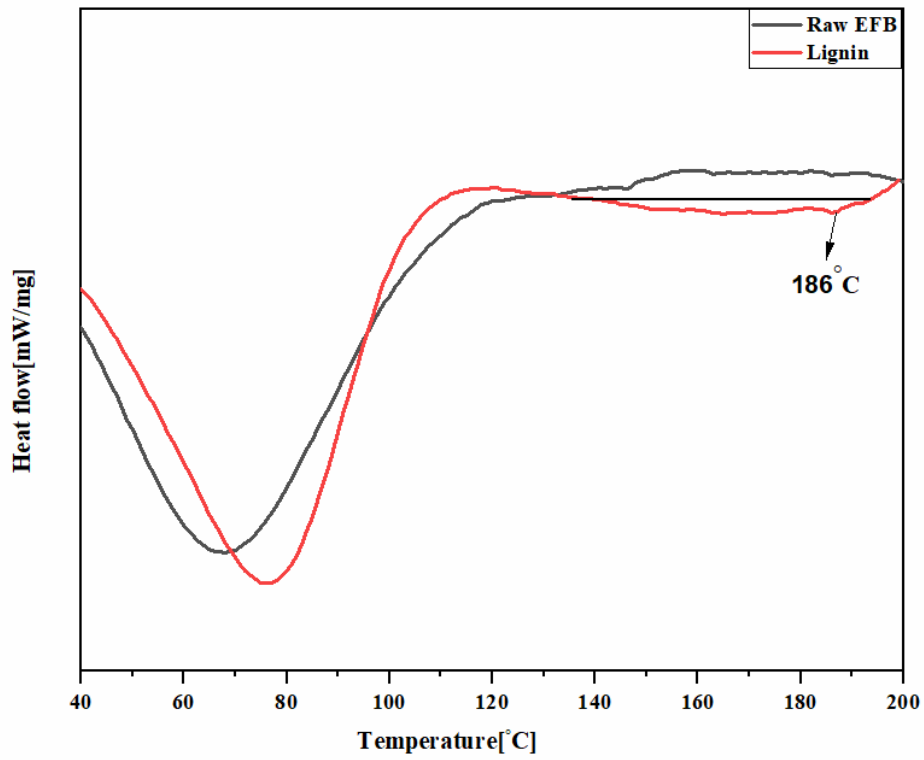


Figure 3: DSC thermogram of yield lignin and raw EFB

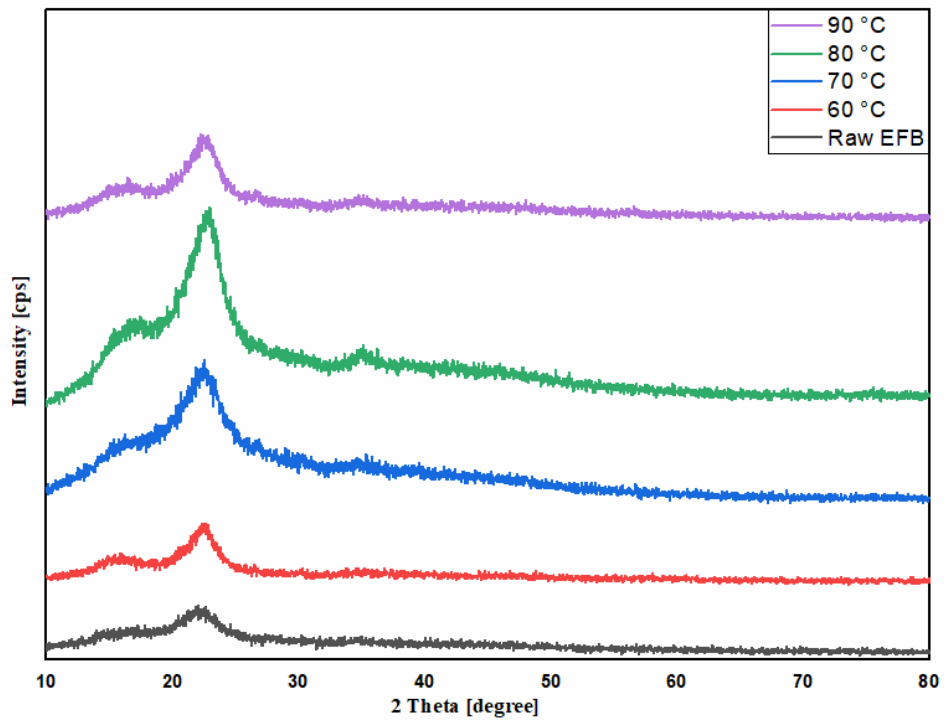


Figure 4: XRD of solid residue

**Table 1:** Yield of lignin obtained from Eq. (1)

Sample	Pressure (bar) (N <sub>2</sub> )	Time (min)	Temperature (°C)	Yield (%)
T60°C	7	60	60	0
T70°C	7	60	70	16.4
T80°C	7	60	80	23.5
T90°C	7	60	90	29.7
P080°C*	Atmospheric	60	80	11.2
M90°C**	Atmospheric	60	90	30.5

\*The treatment carries out under atmospheric pressure in the reactor

\*\*The treatment carries out under microwave-assist process

**Table 2:** The crystallinity calculation of Cellulose Enriched Fractions and Raw EFB

Sample	Ac	Ac+Aa	CrI (%)
Raw EFB	749.26	2217.81	33.79
T60°C	1212.06	3247.84	37.31
T70°C	2630.76	6774.76	38.83
T80°C	3387.81	7793.14	43.47
T90°C	682.18	1962.60	34.76

The high T<sub>g</sub> value of lignin is most likely related to the persistence of the degree of cross-linking polymer, as well as the molecular weight and purity of the extracted lignin, under these moderate conditions [22]. The T<sub>g</sub> temperature is a softening transition temperature for an amorphous substance like lignin. This is a unique explanation of the glass transition temperature of lignin. However, the broad peak (130-190 °C) disappeared after the glass transition region. The T<sub>g</sub> value can be measured by a glass transition region. As a result, extracted lignin is expected to behave more like a linear cross-linked polymer [23].

### 3.4. XRD analysis of cellulose enriched fractions

The crystallinity of cellulose enriched fractions was identified through X-ray Diffraction (XRD) (Fig. 4). All the diffraction patterns revealed peaks in the range of  $2\theta = 18^\circ$  and  $22.7^\circ$ , indicating the typical cellulose I structure. Based on XRD spectra, the crystallinity index (CrI) of raw EFB, T60 °C, T70 °C, T80 °C, and T90 °C was calculated. The peaks at  $18^\circ$  and  $26.6^\circ$  were more defined for DES treated fibers and further magnified in the case of high cellulose content. This is related to the breakdown of lignin and hemicellulose, which increases the crystallinity of DES-treated solid wastes. The high intensity peak demonstrated that the DES treatment effectively removed non-cellulosic components (lignin and hemicellulose) [24]. According to Table 2, the raw EFB has the lowest crystallinity, at 33.79%, because of the presence of non-cellulosic materials in its structure. The sample that is subjected to the reaction at 80 °C has a high degree of crystallinity (43.47%).

## 4. Conclusions

The results show the first successful lignin extraction under a pressurized system with DES as a simple and reactive solvent. Besides, controlling the temperature was

found to be crucial in the delignification process. Indeed, the crystallinity of cellulose residues is also affected, with a more crystalline structure being observed at 80 °C. Cellulose crystallinity characteristics are important for further cellulose valorization processes. The characteristics of lignin and raw EFB are compared by FTIR, while thermogram indicated thermal stability of lignin after the removal of cellulose and hemicellulose from reaction. XRD spectra of the treated solid EFB is more significant in terms of crystallinity and lignin removal. 80 °C is the optimum temperature at which crystallinity is higher of treated EFB than Raw EFB. In further studies various reaction conditions including pressure and reusability of DES can be studied extensively to determine their correlation to improve the yield of lignin.

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## Conflict of Interest

The authors declare that they have no known competing interest.

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