

Sustainable Biomass-to-Energy Transformation: Choline Chloride Based Deep Eutectic Solvent for Lignin Extraction and Liquefaction

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Biomass is often renowned as one of the inexpensive and largest sources of non-depleting energy in the world, attributed to its great potential for continuous and sustainable supply of energy in the form of biofuels and various value-added products. With the increasing demand to preserve the environment, the use of green solvents, such as deep eutectic solvents (DESs), is desirable, given their capability to reduce the generation of hazardous substances. In this work, choline chloride based DESs have been used to extract lignin from biomass. The structure and thermal stability of the extracted lignin are analysed using Fourier-transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA), respectively. FT-IR spectra revealed that chemical properties of lignin were determined through absorbance peaks corresponding to hydroxyl and C-H stretching, as well as the presence of carbonyl moieties and phenolic groups. TGA analysis of lignin showed weight loss peaks at 66 °C, 256 °C, and 319 °C, with major weight loss at 200 - 350 °C due to lignin degradation and release of monomeric phenols, resulting in a final residue consisting of non-volatile solids associated with condensed aromatic structures and lignin ash at 740 °C. The extracted lignin was then subjected to subcritical water-supercritical CO₂ hydrothermal liquefaction (HTL) and converted into bio-oil. In this context, HTL proves its benefits by providing the highest yield of 77.41 % using optimum parameters of lignin-to-water ratio (1:5), pressure (20 MPa), temperature (275 °C) and time (60 min). The functional groups of bio-oil derived from the extracted lignin were analysed using FT-IR, which proves the functional groups (phenols, carboxylic acid, ketones, carboxylic acid, esters and aromatic groups) present in the bio-oil. Detailed information regarding the HTL of lignin derived from biomass, which circumvents the need for energy-intensive drying procedures, is critical in mitigating the challenges posed by the abundance of biomass residues.

1. Introduction

As the search for a viable renewable energy source continues, many studies have been conducted over the years that have proven the potential of biomass. One of the potential sources of biomass is the Empty Fruit Bunch (EFB) which comes from oil palm mills. EFB has a high potential to be converted into renewable energy due to its characteristics as lignocellulosic biomass; it is mainly composed of polysaccharides (cellulose and hemicelluloses) and an aromatic polymer (lignin). Typical lignocellulosic biomass consists of 30 - 60 % cellulose, 20 - 40 % hemicellulose and 15 - 25 % lignin (Zoghلامي and Paës, 2019). The lignin, cellulose, and hemicellulose in lignocellulosic biomass are clustered in a complex three-dimensional structure that renders it resistant to chemicals and microbial assault and difficult to hydrolyse (Yiin et al., 2015). Therefore, pretreatment processes are needed to unleash the trapped potential in lignocellulosic biomass.

For biomass pretreatment, environmentally friendly solvents such as ionic liquids (ILs), deep eutectic solvents (DESs) or low-transition-temperature-mixtures (LTTMs) are commonly used (Yiin et al., 2021). In DESs/LTTMs-related studies, Choline Chloride (ChCl) is deemed to be the most common quaternary ammonium salt employed as the proton acceptor. The widespread interest in ChCl has resulted in an exponential increase in the number of studies on ChCl-based DESs throughout the years due to its inexpensive cost and other properties such as biodegradability and non-toxicity, which satisfy the green chemistry criteria (Yiin et al., 2021). Likewise, DESs have been widely introduced to substitute the conventional pretreatment technologies (Kottaras et al., 2017). The pretreatment of lignocellulosic biomass with malic acid-based DESs resulted in excellent delignification selectivity, enhanced enzymatic hydrolysis, and thermal degradation of biomass (Yiin et al., 2018).

HTL is one of the most promising techniques for producing liquid biofuel, as it can transform wet biomass directly and effectively into biocrude, with high heating values while avoiding the energy-intensive drying step (Ni et al., 2022). Supercritical CO₂ is commonly added to subcritical/supercritical water which dissociates carbonic acid, acting as a natural catalyst in hydrothermal reactions. The yield and composition of bio-oil, however, are affected by process variables such as reaction temperature, pressure, residence time, heating rate, solvent, and catalyst employed (Gollakota et al., 2018). Research on using DESs to delignify biomass has mainly focused on extracting lignin and its thermal stability, neglecting the potential for value-added products from green solvents-extracted lignin through HTL technology (Yiin et al., 2022). This will be the first attempt to convert the DESs-extracted lignin into bio-oil using subcritical and supercritical water HTL for conversion of EFB derived lignin into bio-oil. As discussed herein, this paper aims to extract high purity lignin from oil palm EFB, investigate its structure and thermal stability, and convert the lignin into bio-oil using subcritical water-supercritical CO₂ HTL under different reaction time with the examination of the functional groups of bio-oil.

2. Materials and experimental details

2.1 Biomass pretreatment

The source of oil palm EFB was obtained from an oil palm mill at Serian, Kuching, Sarawak, Malaysia. The EFB was washed with water and dried in an oven at 100 °C for 72 h. The dried biomass was then cut into smaller pieces, ground using the FRITSCH Cutting Mill, and sieved to achieve a particle size of 500 µm.

2.2 DESs synthesis

The starting materials, proton donor-DL-malic acid and proton acceptor-choline chloride, with a purity of ≥ 99.5 % and ≥ 98 %, respectively, were obtained from Robert Scientific Co. The proton donor and proton acceptor were thoroughly mixed with magnetic stirring to ensure contact between the solid crystals. A DES was then produced in a weight ratio of 2:4:2 (w/w/w) for DL-malic acid-choline chloride-water and stirred while heating slowly until a transparent liquid mixture without any solid particles was formed.

2.3 Delignification of biomass using DESs and recovery of the used DESs

The processed biomass was pre-treated using DESs at a ratio of 1:20 (w/w) at a temperature of 85 °C for a duration of 3 h using an oil bath and stirred magnetically. The resulting mixture was washed to precipitate lignin. The DESs after being used for delignification were recovered using a rotary evaporator under vacuum pressure of 72 mbar, 38 rpm and water bath temperature of 50 °C.

2.4 Characterisation of EFB derived lignin

Fourier-Transform infrared spectroscopy (FT-IR) and thermogravimetric analyser (TGA) analyses were conducted to obtain a deeper understanding of the structure and thermal stability of lignin. The FT-IR analysis of extracted lignin was conducted using PerkinElmer spectrometer across a range of 500 to 4,000 cm⁻¹ with a resolution of 4 cm⁻¹. Approximately 7 mg of lignin sample was weighed and transferred into a standard ceramic crucible, which was subsequently placed in a Hitachi SII. The sample was heated from room temperature to 1,100 °C at a rate of 20 K/min in a nitrogen atmosphere with a flow rate of 20 mL/min to minimize oxidation of the sample. A curve of weight loss against temperature was obtained.

2.5 Subcritical water-supercritical CO₂ HTL of EFB derived lignin

The extracted lignin and distilled water, at a specified lignin-to-water ratio (1:5), were loaded into an inconel batch reactor. The effect of reaction time on HTL of lignin was examined with a fixed temperature of 275 °C and pressure of 20 MPa (Chan et al., 2018). The reactor was placed into a reactor furnace with mechanical stirring and cyclic horizontal swing span of 2 cm at a frequency of 60 cycles/min. Fourier-Transform infrared spectroscopy (FT-IR) was also used to analyze the functional groups of the bio-oil.

3. Results and discussion

3.1 Characteristics of EFB derived lignin

3.1.1 Structural analysis of lignin

FT-IR is used to determine the chemical properties of lignin as it simultaneously collects spectral data in a wide spectral range, enabling a significant advantage in measuring intensity over a narrow range of wavelengths at a time. Figure 1 shows the absorbance peaks at $3,350\text{ cm}^{-1}$ and $2,900\text{ cm}^{-1}$ corresponding to the total hydroxyl groups and C-H stretching in methyl, methylene, and methoxyl groups, respectively (Wang et al., 2017). The faint signal at $1,800\text{ cm}^{-1}$ was attributed to the C=O stretching of the carbonyl moiety of hemicellulose impurities (i.e., conjugated aldehydes and carboxylic acid) that may be present in lignin (Prasadini et al., 2023). According to Prasadini et al. (2023), no significant differences between lignin types of pretreatments were noticed in the aromatic region ($1,505\text{ cm}^{-1}$ to $1,610\text{ cm}^{-1}$), which implied less or no ultrasonication and pretreatment impact. The following peaks were also unaffected by pretreatment: $1,458\text{ cm}^{-1}$ (O-H in-plane bending), $1,420\text{ cm}^{-1}$ (aromatic ring vibration combined with C-H in-plane vibration), $1,321\text{ cm}^{-1}$ (bending vibration of C-H and C-O bonds) and $1,230\text{ cm}^{-1}$ (C-O-C bond) (Xu and Wang, 2015). A peak was observed at $1,115\text{ cm}^{-1}$, assigned to condensed phenolic groups (Gilca et al., 2015).

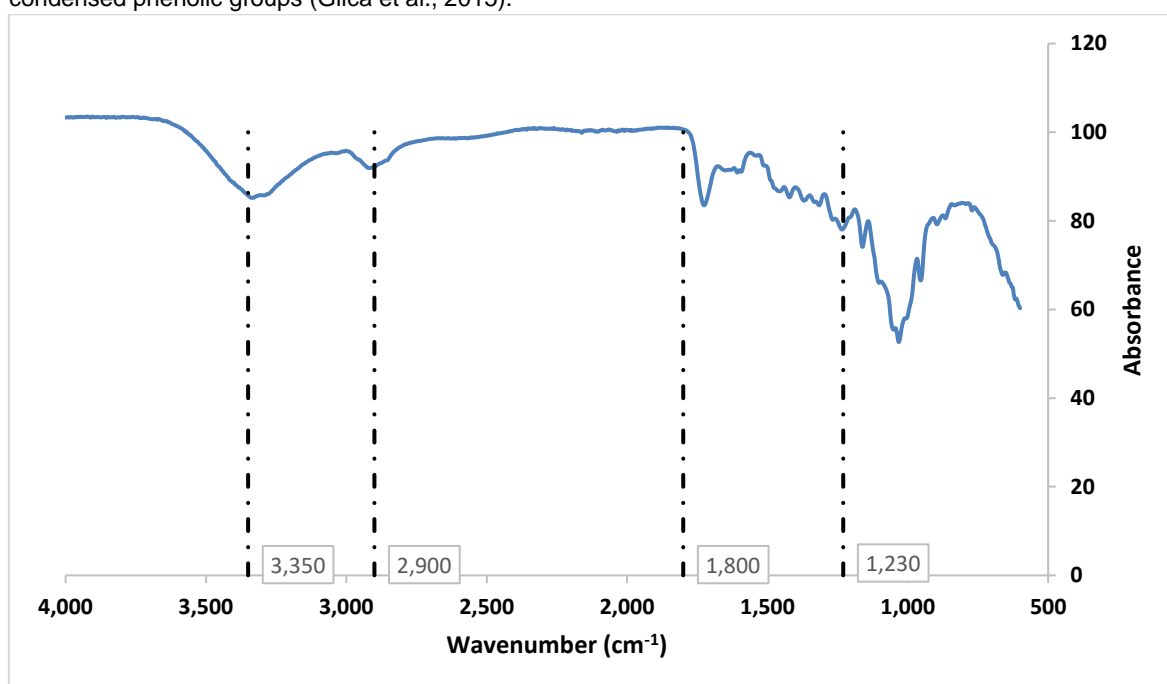


Figure 1: FT-IR Spectra analysis of EFB derived lignin

3.1.2 Thermal properties of lignin

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves obtained from TGA revealed the compositional characteristics of lignin, as presented in Figure 2. Lignin degrades as a heterogeneous polymer across a large temperature range due to various functional groups having differing degrees of thermal stability (Laurichesse and Avérous, 2014). The lignin exhibits a degradation curve trend similar to that reported by Tan et al. (2020) for the extraction of lignin with different solvents. In the present study, three steps of thermal degradation were observed at 66 °C , 256 °C and 319 °C . The initial weight loss peak at 66 °C is due to loss of absorbed water (Coral Medina et al., 2016), and the weight loss was approximately 4 %. The major weight loss ($\sim 50\%$) occurs in the range of $200 - 350\text{ °C}$, which is due to the degradation of the lignin structure (Alriols et al., 2009). Monomeric phenols would be changed into the vapour phase at this temperature because the inter-unit connections between phenolic hydroxyl, carbonyl groups, benzylic, and hydroxyl groups would be fragmented (Mohamad Ibrahim et al., 2011). At 319 °C , the third peak for lignin appeared, which is associated with the breakdown of carbohydrates (Narapakdeesakul et al., 2013). The weight loss continues to degrade from 350 to 740 °C resulting in a final residue of approximately 6 %. The weight remained constant at 800 °C , which was attributed to non-volatile solids associated with highly condensed aromatic structures and lignin ash

(Coral Medina et al., 2016). The findings indicate that most of the lignin components turned into volatiles during the second stage of degradation.

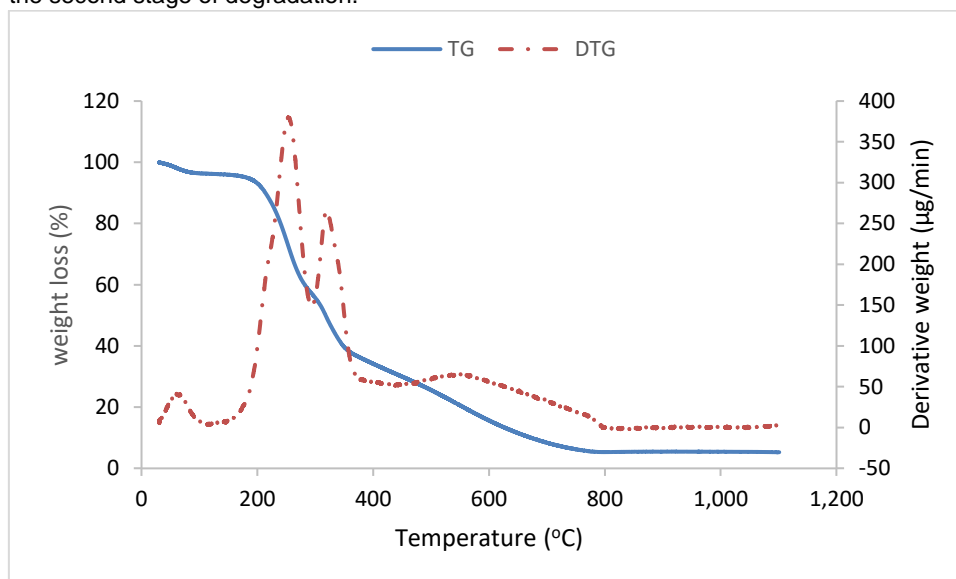


Figure 2: TG and DTG curves of EFB derived lignin

3.2 Yield and functional groups of bio-oil

Table 1 shows the effect of time on the yield of bio-oil through HTL of lignin. The highest yield observed was 77.41 wt% at a time of 60 min. The yield of bio-oil yield was found to be low at 30 min, which indicates that a minimum time of 60 min is required to achieve the high yield. The amount of yield decreased with a reaction time of more than 60 min. This phenomenon can be attributed to the longer space time, resulting in a longer residence time of lignin inside the reactor, which leads to breakdown of more lignin into bio-oil. It is important to note that changing the space time affects the solvent composition (i.e., the lignin-to-water ratio), inside the reactor, which might influence reaction performance (Kristianto et al., 2019).

Table 1: Effect of time in Production of Bio-oil

Run No.	Lignin (g)	Water (g)	Pressure (MPa)	Temperature (°C)	Time (min)	Mass of bio-oil (g)	Yield (%)
1	0.25	1.25	20	275	30	0.0305	14.35
2	0.25	1.25	20	275	60	0.1645	77.41
3	0.25	1.25	20	275	120	0.0951	38.02
4	0.25	1.25	20	275	240	0.0170	8.00

FT-IR analysis was used to determine the functional groups of the bio-oil. The FT-IR spectra of the bio-oils as shown in Figure 3 were consistent and similar, suggesting that similar types of functional groups were present in the bio-oils produced within the range of time, except for run number 4, which had the longest reaction time and showed different absorption peaks than the others. This might be due to the longer time spent inside the reactor, which caused a change in the solvent composition (Kristianto et al., 2019). The characteristic absorption peak from 3,600 to 3,200 cm^{-1} was attributed to O-H stretching, indicating the presence of phenols and carboxylic acid (Chan et al., 2018). The absorption band from 3,000 to 2,800 cm^{-1} demonstrated the distinctive C-H stretching found in bio-oils (Sun et al., 2011). The absorption peaks between 1,780 and 1,640 cm^{-1} were caused by C=O stretching, indicating the presence of ketones, carboxylic acid, and esters. The presence of aromatic groups was revealed by the peaks at 1,680 to 1,580 cm^{-1} , which indicates C=C stretching. The existence of phenolic compounds and esters was evidenced by the peaks at 950-1,300 cm^{-1} (C-O stretching). The peaks located between 675 and 900 cm^{-1} reflected the C-H bending vibration, which might be related to the presence of substituted aromatic groups (Sun et al., 2011).

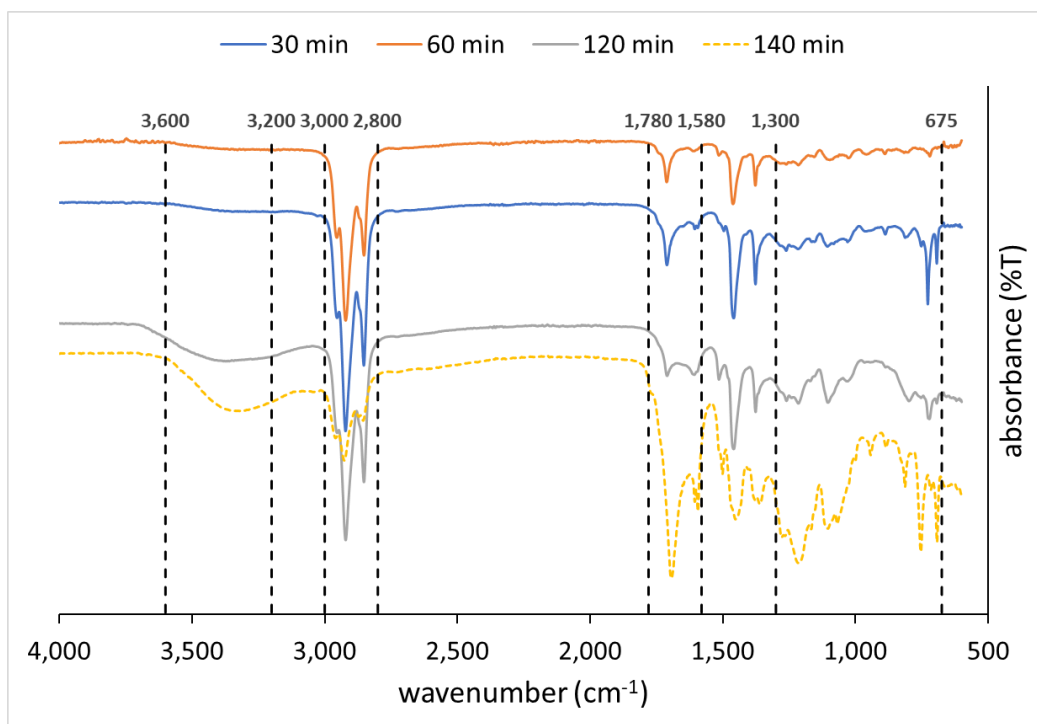


Figure 3: FT-IR analysis of bio-oil produced from EFB derived lignin

4. Conclusions

DEs in this study have shown its potential as a viable alternative to traditional pretreatment techniques for extracting and hydrothermal liquefying lignin from oil palm EFB with recoverability of > 90 %. TGA revealed that the EFB derived lignin had three thermal degradation phases at 66 °C, 256 °C, and 319 °C, and contained several functional groups such as phenolic, carbonyl, benzylic, and hydroxyl at temperatures ranging from 200–350 °C. The lignin also had several absorbance peaks that correlated with the presence of essential functional groups such as hydroxyl, methyl, methylene, methoxyl, and phenolic. The highest bio-oil yield of 77.41 % was obtained through subcritical water-supercritical CO₂ HTL of lignin using optimal parameters of lignin to water ratio of 1:5, pressure of 20 MPa, temperature of 275 °C, and a reaction time of 60 min. FT-IR spectra of the bio-oil obtained from HTL of EFB derived lignin demonstrated the presence of functional groups such as phenols, carboxylic acid, ketones, carboxylic acid, esters, and aromatic groups. Further investigation into the influence of process parameters, reaction mechanisms, and HTL kinetics on lignin degradation chemistry in green solvent delignification is necessary to balance the abundant supply of biomass leftovers while also improving biomass-to-energy conversion by meeting required future process and end products and optimizing product yields.

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