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INFLUENCE OF DEEP EUTECTIC SOLVENT (DES) ON CLEAVAGE SPECIFICITY OF LIGNIN-DERIVED OIL PALM BIOMASS

(Pengaruh Pelarut Eutektik Dalam Terhadap Kespesifikan Lignin Terbitan Biojisim Kelapa Sawit)

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Abstract

Carbon fibre is widely used in industry, but its high cost limits its use. Interestingly, lignin has the potential to serve as a carbon fibre precursor with properties similar to those of polyacrylonitrile (PAN) and pitch-based precursors. Oil palm frond (OPF), lignocellulosic biomass composed of cellulose, hemicellulose and lignin, is an attractive source of biomass for lignin extraction. This study proposes lignin extraction from OPF using a deep eutectic solvent (DES). DESs are eutectic mixtures of hydrogen bond acceptors (HBAs) and donors (HBDs) with much lower melting points than their constituents. This study used choline chloride (ChCl) and glycerol as HBA and HBD because they are easy to prepare, have low toxicity and are biodegradable and ecologically benign. Lignin extraction from OPF was conducted in a batch reactor at different reaction temperatures (130 °C–170 °C) and reaction times (3–6 h) using a 1:3 molar ratio of ChCl:Glycerol. The results show that DES can extract lignin with low particulate matter content (4.53%) at a higher reaction temperature (170 °C) and longer reaction time (6 h). However, extracted lignin with low ash and volatile matter contents was obtained at a lower reaction temperature (130 °C) and shorter reaction time (3 h). The carbon content of the extracted lignin was significantly influenced by the reaction temperature and reaction time, with a lower reaction temperature and moderate reaction time capable of producing lignin with a carbon content of >50%

Keywords: carbon fibre, lignin, deep eutectic solvent, oil palm biomass

Abstrak

Gentian karbon digunakan secara meluas dalam industri, walaupun penggunaannya dihadkan oleh kos prekursor yang mahal. Lignin mempunyai potensi sebagai prekursor untuk gentian karbon dengan sifat yang setanding dengan poliakrilonitril dan prekursor berasaskan pitch. Pelepah kelapa sawit, sejenis biojisim lignoselulosa yang mengandungi selulosa, hemiselulosa, dan lignin merupakan sumber biojisim yang menarik untuk pengekstrakan lignin. Penyelidikan ini mencadangkan pengekstrakan lignin daripada pelepah kelapa sawit menggunakan pelarut eutektik dalam (DES). DES ialah campuran eutektik yang terdiri daripada penerima ikatan hidrogen (HBA) dan penderma ikatan hidrogen (HBD) dan mempunyai takat lebur yang jauh lebih rendah daripada

juzuk masing-masing. Kajian ini menggunakan kolin klorida dan gliserol sebagai HBA dan HBD kerana ia mudah disediakan, mempunyai ketoksikan yang rendah, boleh terbiodegradasi, dan tidak berbahaya dari segi ekologi. Pengekstrakan lignin daripada pelepah kelapa sawit dijalankan dengan menggunakan reaktor kelompok pada suhu tindak balas (130 °C–170 °C) dan masa tindak balas (3–6 jam) yang berbeza bersama dengan kolin klorida dan gliserol pada nisbah molar 1:3. Kajian ini membuktikan bahawa DES mampu mengekstrak lignin dengan bahan zarah yang rendah (4.53%) pada suhu tindak balas yang lebih tinggi (170 °C) dan masa tindak balas yang lebih lama (6 jam). Walaubagaimanapun, lignin dengan kandungan abu dan bahan meruap yang rendah diperolehi pada suhu tindak balas yang rendah (130 °C) dan masa tindak balas yang singkat (3 jam). Kandungan karbon di dalam lignin yang diekstrak dipengaruhi oleh suhu tindak balas dan masa tindak balas, dengan suhu tindak balas yang lebih rendah dan masa tindak balas sederhana mampu menghasilkan lignin dengan kandungan karbon lebih daripada 50%.

Kata kunci: gentian carbon, lignin, pelarut eutektik dalam, biojisim kelapa sawit

Introduction

The exceptional mechanical, electrical and thermal properties of carbon fibre have led to its widespread use in various fields, including military and aerospace engineering, construction and medicine [1]. The global market for carbon fibre is predicted to quadruple in a decade, reaching over $3 billion and exceeding 100,000 tonnes [2]. However, the rapid growth of industrial applications of carbon fibre hinges on the material's affordability without compromising its physical properties. The high cost of carbon fibre is directly proportional to the cost and yield of the precursor from which it is derived. A large proportion of carbon fibre is manufactured using wet and solution-spun PAN, an expensive precursor that accounts for 51% of the price of carbon fibre. Significant research is being conducted on the synthesis of low-cost carbon fibre because of the growing demand for the commercialisation of carbon fibre in various sectors.

Lignin, an aromatic polymer found in nature, has recently attracted considerable attention because of its low price, high carbon content and bio-renewability. Lignin is a promising replacement for petroleum-based PAN for producing carbon fibres because of its high carbon content (60%–65%) [3]. In addition to cellulose and hemicellulose, lignin is a key component of lignocellulosic biomasses. Lignin is a by-product of the paper industry that cannot be recycled; its decomposition produces furans and dioxins, which deplete atmospheric oxygen [4]. Lignin's aromatic compounds, availability of phenolic and aliphatic hydroxyl groups, high carbon content, thermal stability and abundance make it a superior choice for synthesising carbon fibres compared with cellulose and other renewable carbon sources.

According to Chen et al. [5], lignin valorisation necessitates the effective extraction of lignin with properties amenable to further processing. Condensed lignin and/or pseudo-lignin resulting from traditional pretreatment methods, such as dilute acid and steam explosion, are unusable for further processing. Research into lignin valorisation has led to the development of pretreatment technologies that utilise ionic liquids and organic solvents derived from biomass. DESs are ionic solvents composed of HBA and HBD, which combine to form a eutectic with a significantly lower melting point than its constituents [6]. Most DESs are produced by reacting ChCl (as HBA) with HBDs, such as amines, carboxylic acids and polyols. DES has been suggested as a promising solvent for processing lignocellulosic biomass, especially for lignin valorisation [7–9].

Currently, lignocellulosic treatments are used to produce high-quality cellulose. Nonetheless, the separation of lignin from a native structure has received less attention, making it difficult to obtain homogeneous lignin with the requisite structure and molecular weight [10]. Recent studies have shown that ChCl and acid-based DES effectively extract lignin from lignocellulosic biomass. Lignin extracted from biomass using DES has distinct structural characteristics, such as a lack of ether linkages and a low molecular weight distribution [8, 11]. Hydrogen bonds in DES molecules are crucial for lignin extraction. Di Marino et al. [12] hypothesised that increasing the amount of water in the biomass could improve the solubilisation ability of DES for biomass by increasing the formation of hydrogen bonds between the DES and components of the biomass.

Lignin is extracted from various natural sources using several methods, each yielding lignin with its unique structure and physicochemical properties. Therefore, one of the most challenging and critical processes in biological refining is lignin extraction from lignocellulosic materials. Currently, the most common lignin are sulphate lignin, soda lignin, and kraft lignin [13]. However, the high sulphur and ash content of sulphate lignin render it unsuitable for further processing and usage. Although lignin-derived alkali pulping does not contain sulphur, the extraction method has many disadvantages, including a low-extraction yield, excessive alkali consumption and environmental contamination [14, 15]. Furthermore, reaction parameters, such as reaction time, temperature, solvent concentration and biomass/solvent ratio, substantially affect the extraction yield and structural characteristics of lignin produced by organic solvent-based extraction.

Lignin extracted using DES treatments was discovered to have a high yield, high purity and low molecular weight, which would be advantageous for biomass valorisation [9]. It is known to have unique structural properties; however, these properties have not been studied or addressed. Therefore, the fundamental properties of lignin must be examined to establish its potential as a carbon precursor. The Oak Ridge National Laboratory (ORNL) established a set of criteria to assess the viability of lignin as a carbon fibre precursor, as shown in Table 1 [16].

Table 1. Lignin specification as carbon fibre precursor [13]

Criteria	Value (wt.%)
Lignin Purity	99%
Ash Content	<0.1
Volatile Matter	<5.0
Particulate Matter	100% removal for matter >1μm in diameter

Materials and Methods

Synthesis of DES

The DESs were prepared by mixing ChCl and glycerol in a 1:3 molar ratio and heating to 100 °C with constant stirring. In our previous study, DES with a molar ratio of 1:3 produced the highest lignin yield from OPF. Heating and stirring were repeated until a clear, homogeneous and stable liquid were obtained. The DESs were then cooled and stored at room temperature for 24 h. DES synthesis was successful if the solution was colourless and remained liquid after 24 h.

Preparation of OPF

The biomass was dried overnight at 45 °C before being cooled to room temperature. 500g of the samples were ground and sieved to sizes between 250–500 μm. Solid-liquid extraction with 3L ethanol was used to remove extractives from the samples. The extracted samples were collected after 6 h and washed with ethanol before being oven-dried overnight at 45 °C.

Experimental works

The OPF was mixed with DESs at a solid loading ratio of 1:10 and subjected to various reaction times and temperatures in a 100-mL batch reactor. The reaction parameters used in these experiments are listed in Table 2. The mixture was immediately immersed in an ice bath after completion of the reaction to quench the reaction. The solution fraction (SF) and solid residue (SR) fractions were separated by centrifugation at 4000 rpm for 15 min. SR was washed with 95% ethanol until the liquid was clear. Subsequently, the SF was combined with an ethanol-washing liquid to form SF1. Deionised water was added to SF1 in a 1:2 volume ratio of ethanol to water to precipitate lignin. After 15-min centrifugation at 4000 rpm, the precipitated lignin was successfully separated from the SF1. The lignin precipitate was washed twice with deionised water to remove solvent impurities and obtain extracted lignin. Lignin was then dried for 24 h at 40 °C.

Table 2. Reaction parameter for experimental work

Abbreviation	Reaction Time (hours)	Reaction Temperature (°C)
DESL-01	3	130
DESL-02		150
DESL-03		170
DESL-04	4	130
DESL-05		150
DESL-06		170
DESL-07	5	130
DESL-08		150
DESL-09		170
DESL-10	6	130
DESL-11		150
DESL-12		170

Particulate matter content analysis

The particulate matter content was determined using the method described by Luo [17]. Approximately 0.25 g of DES-L was dissolved in 100 mL of a 5% NaOH solution. The flask was then immersed in a water bath at 100 °C for 60 min. The sample was filtered to separate insoluble particles. The percentage of insoluble matter was calculated using Equation 1 based on the residual solid mass and mass of the original sample.

$$\text{Particulate Matter} = \left(\frac{m_2}{M_1}\right) \times 100\% \quad (1)$$

where m_2 is the mass of residual solid (g) and M_1 is the mass of the lignin sample (g).

Ash content analysis

The ash content was determined using TAPPI Standard Test Method T 413 om-93. Approximately 0.05 g of DES-L was combusted at 900 °C in a muffle furnace. As shown in Equation 2, the ash content was calculated by dividing the weight fraction of residual ash by the initial weight of the sample.

$$\text{Ash Content} = \left(\frac{m_2}{M_1}\right) \times 100\% \quad (2)$$

where m_2 is the mass of residual ash (g) and M_1 is the mass of the lignin sample (g).

Volatile matter content analysis

The volatile matter content of the DES-L was determined according to the method outlined by Luo [17]. Approximately 0.25 g of DES-L was heated for 6 h at 250 °C in a muffle furnace. The volatile matter content was calculated based on the weight loss of the DES-L relative to the weight of the initial sample (Equation 3).

$$\text{Ash Content} = \left(\frac{M_1 - m_2}{M_1}\right) \times 100\% \quad (3)$$

where m_2 is the mass of the residual lignin sample (g) and M_1 is the mass of the lignin sample (g).

Carbon content analysis

The carbon content of the DES-L was determined using a CHNS/O analyser.

Results and Discussion

Carbon content

The carbon content of the precursor is essential. The low carbon content in the precursor indicated a high content of non-carbon elements in the sample, which resulted in higher weight losses during carbonisation and higher production costs [18]. High-quality carbon fibre requires a carbon content of at least 92 wt% after carbonisations.

The carbon content of lignin extracted at different temperatures (130 °C–170 °C) and reaction times (3–6 h) are shown in Figure 1. The highest carbon content

was 54.1% at 150 °C for 3 h. In contrast, the lowest carbon content attained was 31.5% at 130 °C for 3 h. The carbon content varies with reaction temperature and time, with no discernible trend. The ORNL does not specify the carbon content requirements for lignin as a carbon fibre precursor. However, it is widely accepted that the carbon content of the extracted lignin must be >50% to produce significant carbon fibre yields [19]. As a result, it was concluded that the reaction time and temperature affect the carbon content of the extracted lignin.

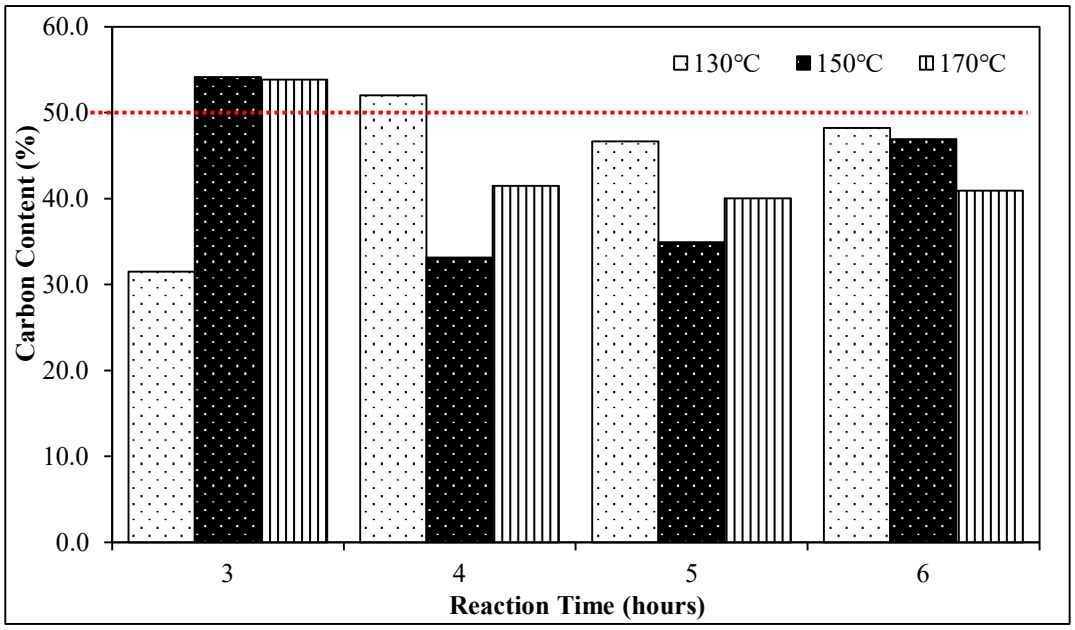

Figure 1. Carbon content (%) at different temperatures (130 °C–170 °C) and reaction times (3–6 h) and a solid loading ratio of 1:10

In this study, only the DESL-02 (150 °C and 3 h), DESL-03 (170 °C and 3 h), and DES-L04 (130 °C and 4 h) samples yielded lignin with a carbon content of >50%. The obtained lignin had a lower carbon content than the previously reported lignin at various reaction temperatures and times. For example, coniferyl alcohol, a common precursor of lignin in softwood, contains approximately 72% carbon.

While sinapyl alcohol, a common lignin monomer found in hardwood, contains 63% carbon, PAN, the most important precursor material used in the industrial production of carbon fibre, contains 68% carbon [17]. The required carbon content differed according to different studies. Previous studies showed that the required carbon content varies. For example, Souto et al. [19] suggested that the carbon content must be >50%, whereas Bengtsson et al. [3] concluded that the carbon content of extracted lignin must be >60% to produce carbon fibres with a high yield after conversion. According to Nunes and Pardini [20], the carbon content of lignin varies depending on the type of biomass, with kraft and sugarcane lignin containing 62% and 58% carbon, respectively.

Alvarez-Vasco et al. [9] demonstrated that lignin extraction with DES results from breaking ether bonds in the lignin carbohydrate complex (LCC), thereby improving lignin solubility in DES. It has been proposed that the breakage of ether bonds and the solvent properties of DES significantly influence the depolymerisation of lignin, facilitating its separation from lignocellulosic biomass. Lignin is more soluble in DES because of the increased cleavage of β-O-4 linkages.

The glycerol-based DES used in this study has a moderate acid-base catalysis mechanism that is advantageous for cleaving labile ether bonds, thus improving lignin solubility in DES. The effectiveness of acid-based DES for lignin extraction has been investigated, and the enhanced hydrogen bond interaction between acidic DES and LCC has been shown to facilitate lignin extraction [21]. However, the increased lignin solubility in DES results in more carbon loss to the liquid fraction and a faster depolymerisation rate at higher temperatures [22]. The carbon content of the recovered lignin decreased as the temperature increased because of the increase in the lignin carbon loss to the liquid fraction.

Nevertheless, recognising that the reaction time significantly affects the carbon content of the extracted lignin is critical. The reaction temperature determined the effect of reaction time on the carbon content. In this study, a shorter reaction time of 3 h and a moderate reaction temperature of 150 °C were optimal for extracting lignin from OPF with higher carbon content. According to Zhang et al. [23], the higher the carbon content of lignin, the more aromatic the structures in the lignin monomers. However, the structure of lignin is extremely complex, with heterogeneous molecular weights, numerous functional groups and varying amounts of monolignols (p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol) linked by various interunit chemical bonds. As a result, the reduced aromatic structure of the extracted lignin accounts for the lower carbon content observed in this study.

Our previous study found that the presence of phenolic compounds in extracted lignin was lower (0.07–0.15 g/mmol) than previously reported in the literature. Consequently, the extracted lignin had less aromatic compounds and reactivity. Lignin is extracted using DES by ether connection cleavage, specifically β-O-4 bonds, which are the weakest links in the lignin unit. However, in this study, DES treatment produced lignin with reduced aromatic structures, resulting in a carbon content of 31.5%–54.1% at different reaction temperatures and times.

Ash content

Ash is the residue left over by high-temperature combustion at 900 °C. Lignin must have low inorganic content as a carbon fibre precursor. The ash content should be <0.1 wt% to ensure that the carbon fibre has minimal defects and imperfections. The lignin source and extraction method heavily influenced the ash content of the extracted lignin. Figure 2 illustrates the effect of temperature (130 °C–170 °C) and reaction time (3–6 h) on ash content.

In this study, the lignin ash content was 9.1%–15.7% with increased reaction times (3–6 h) and temperatures (130 °C–170°C), producing higher lignin ash content. As a result, lignin with low ash content can be produced at a lower reaction temperature (130 °C) and in a shorter reaction time (3 h). The increased condensation of ash caused the high ash content with other by-products as the reaction time and temperature increased.

The ash content determined in this study did not meet the ORNL standard of <0.1%, which makes it a suitable precursor for carbon fibre production [16]. The ash content must be low to avoid a negative impact on the tensile qualities of the manufactured carbon fibre, which is detrimental to the mechanical properties of the carbon fibre produced [3].

The biomass source and extraction method determine the ash content of the extracted lignin. Herbaceous biomass contains significantly more ash than wood, typically containing <1% ash. Calcium, potassium and magnesium are the most abundant elements in wood ash, whereas sodium and silicon are in smaller quantities. However, the source and quantity of minerals in the extracted lignin were significantly more dependent on the extraction method than on plant species. Alkaline pulping processes, such as kraft, produce lignin with high ash content (43.6%), whereas autohydrolysis (1.2%) and organosolv (0.1%) produce lignin with low ash content [24].

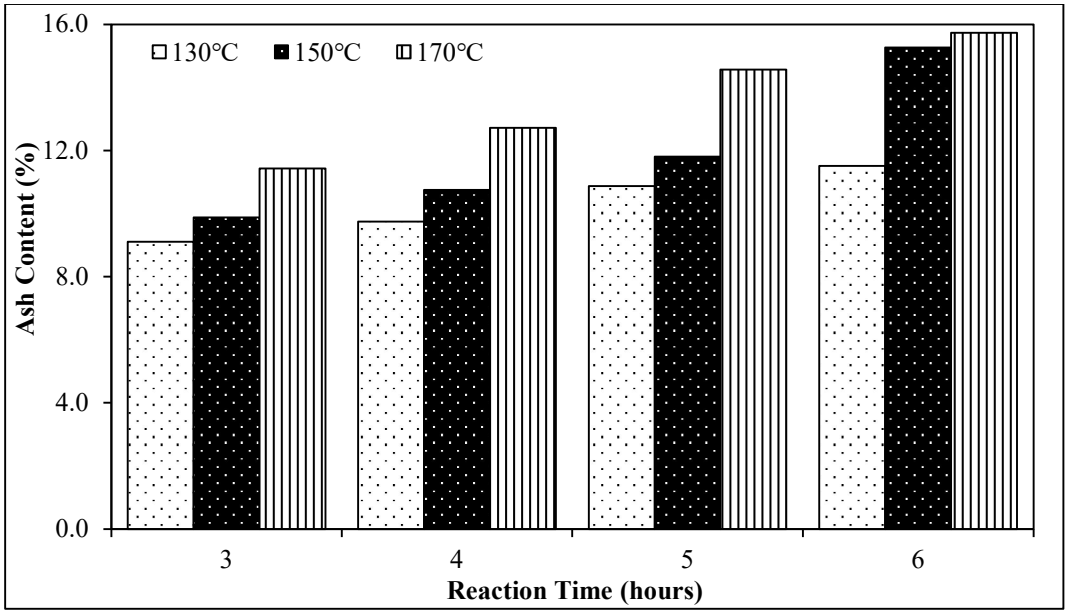

Figure 2. Ash content (%) at different temperatures (130–170 °C), reaction times (3–6 h) and a solid loading ratio of 1:10

Volatile matter content

Volatile matter refers to the portion of a sample that can readily volatilise at high temperatures under typical conditions. This volatile substance typically consists of combustible and non-combustible gases. The volatile matter content of the extracted lignin must be evaluated because it can alter the carbon fibre structures through evaporation, especially during carbonisation at high heating rates. Carbonisation significantly modifies the surface and porosity of carbon fibres by releasing volatile components, resulting in surface flaws and defects. Therefore, low volatile matter content is desired to reduce the flaws in manufactured carbon fibre [25].

As demonstrated in Table 1, the volatile matter content must be <5% for a precursor to be viable for carbon fibre production. Figure 3 depicts the volatile matter content of lignin extracted at various reaction temperatures (130 °C–170 °C) and reaction times (3–6 h). The volatile matter content of lignin ranged was 3.4%–9.4%.

The volatile matter content increased with reaction time (3–6 h) at all temperatures. For example, at 130 °C, the volatile matter content increased linearly from 3.4% to 4.7% between 3 h and 6 h. Additionally, at 150 °C, the volatile matter content varied between 5.3% and 8.8%. Higher reaction temperatures produce lignin with larger amounts of volatile compounds. The increase in volatile matter content with increasing temperature is attributable to the decreased bond strength of lignin at higher temperatures, which produces volatile macromolecules [26]. Low temperatures and shorter reaction times made lignin more thermally resistant to volatilisation, as evidenced by its lower volatile matter content at 130 °C and 3 h.

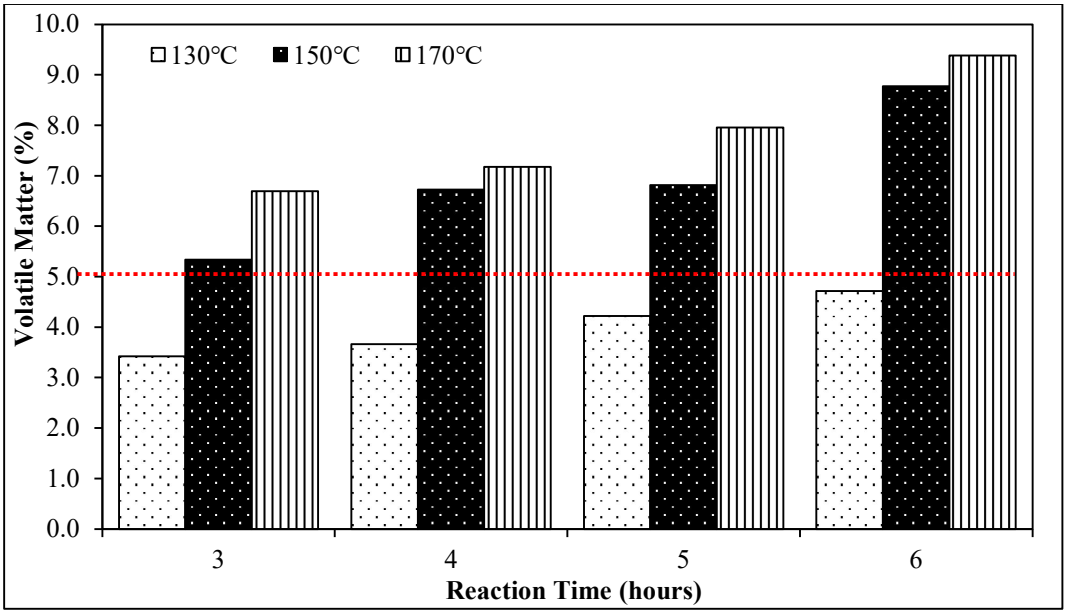

Figure 3. Volatile matter content (%) at different temperatures (130–170 °C), reaction times (3–6 h) and a solid loading ratio of 1:10

In addition, the volatile matter content of lignin extracted at 130 °C for all reaction times (3–6 h) met the ORNL requirement that it should contain <5% volatile matter to be suitable as a carbon fibre precursor. Higher temperatures (150 °C–170 °C) produce lignin with a volatile matter content of >5% [16]. Thus, we can conclude that temperature is important in determining the amount of volatile matter in lignin extracted using DES.

Furthermore, the volatile matter content reported in this study was significantly lower than those reported in previous studies [24,27]. The extraction conditions, solvent type and biomass source, affected the volatile matter content of lignin. According to Omar et al. [25] and Atnaw et al. [28], OPF has high volatile matter contents of 82.4% and 85.1%, respectively. The high volatile matter content of the OPF is attributable to the higher volatile matter content of the lignin recovered in this study.

It is possible that the high inorganic content of lignin, as reflected by its high ash content, could have influenced the volatile matter content. As a result of their catalytic effect on lignin decomposition, the inorganic matter may promote the formation of volatile matter [29]. As depicted in Figure 2, the volatile matter and ash contents exhibited a similar trend, which explains the results obtained for the volatile matter content.

Particulate matter content

As a precursor to carbon fibre, lignin must be devoid of solid particles of >1 µm in size. Particulate matter is the amount of solid particles entrapped in lignin. Natural particles, such as sand, clay and cellulose, are the most prevalent causes of structural defects in carbon fibre. The mechanical properties of carbon fibres, such as modulus and tensile strength, are reduced by high particulate matter content, increasing the breaking point of the fibre [16]. Figure 4 shows the effect of temperature (130 °C–170 °C) and reaction time (3–6 h) on the particulate matter content of DES-L.

Particulate matter content decreased with increasing temperature and reaction time. The highest particulate matter content of 15.5% was obtained after 3 h at 130 °C, whereas the lowest particulate matter content (4.5%) was obtained at 6 h and 170 °C. These findings exceed the ORNL's requirement of 100% removal of particulate matter of >1 µm in diameter.

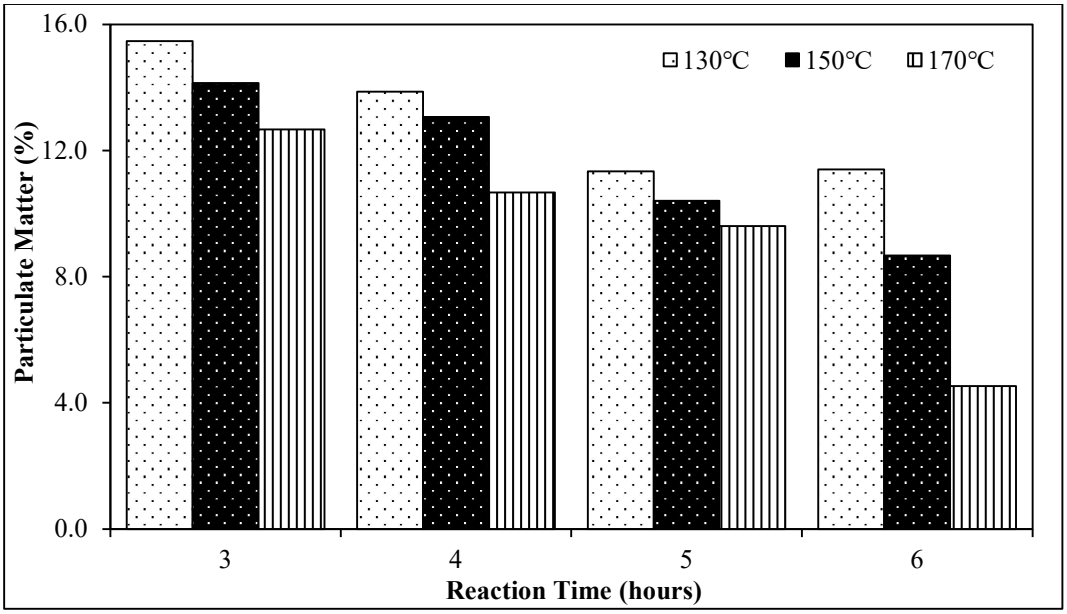

Figure 4. Particulate matter content (%) at different temperatures (130–170 °C), reaction times (3–6 h) and a solid loading ratio of 1:10

The incomplete breakdown of cellulose increases the number of high-molecular-weight compounds in the SR, which explains why lignin extracted using the DES system has a high particulate matter content. Furthermore, owing to the partial breakdown of cellulose, particles and pollutants increased the amount of particulate matter in the lignin. The incomplete removal of extractives during OPF solid-liquid extraction may also contribute to the high particle matter content. The results show that low particulate matter lignin can be obtained at higher temperatures and longer reaction times.

Conclusion

Investigating the fundamental properties of lignin extracted from OPF using DES is critical to assess its viability as a carbon fibre precursor. This study found that reaction temperature and time affect the properties of lignin. The particulate matter content was low at high temperatures (170 °C) and long reaction times (6 h). However, a lower temperature and shorter reaction time are appropriate for lignin extraction with a low ash and volatile matter content. The highest carbon content (54.1%) was obtained at 150 °C for 3 h. The low carbon content of lignin obtained in this study was attributable to the enhanced cleavage of ether linkages by glycerol-based DES, which improved lignin solubility in the solvent and, thus, increased carbon loss into the liquid fraction. Thus, this study establishes the viability of using DES as solvents for effective lignin cleavage and efficient lignin separation from LCC linkages. The viability of the extracted lignin as a carbon fibre precursor should also be examined further by determining other fundamental properties, such as purity, molecular weight and glass transition temperature.

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