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LIGNIN FROM OIL PALM FROND UNDER SUBCRITICAL PHENOL CONDITIONS AS A PRECURSOR FOR CARBON FIBER PRODUCTION

(Lignin daripada Pelepah Kelapa Sawit dibawah keadaan Subgenting Fenol sebagai Produk Perantaraan bagi Penghasilan Serat Karbon)

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Abstract

The market price of carbon fiber which is considerably high, has limited its application as a value-added material. Lignin, a natural source that can be obtained from oil palm frond (OPF) is a promising precursor for carbon fiber production. This study aims to determine the feasibility of OPF lignin extracted under subcritical phenol conditions as a precursor for carbon fiber. The focus of this study is to determine the fundamental properties (ash content and volatile content) of the produced lignophenol produced based on the effect of reaction parameters such as temperature (260–300 °C), reaction time (5–30 minutes), and solid loading (6 and 10 g). The results indicate that the lowest ash content and volatile content of 9.87% and 6.45% was obtained at 260 °C, 5 minutes, and 6 g solid loading respectively. It can be further concluded that low reaction temperature as well as time and higher solid loading produced lignophenol with low ash and volatile content under subcritical phenol conditions.

Keywords: lignin, carbon fiber, subcritical fluid, oil palm frond, lignophenol

Abstrak

Harga pasaran serat karbon yang tinggi telah menghadkan penggunaannya sebagai bahan nilai tambahan. Lignin merupakan sumber asli yang boleh dihasilkan daripada pelepah kelapa sawit dan mempunyai potensi sebagai bahan pengantaraan untuk penghasilan serat karbon. Tujuan kajian ini dijalankan adalah untuk menentukan kebolehgunaan lignin yang diekstrak daripada pelepah kelapa sawit dibawah keadaan subgenting fenol sebagai bahan pengantaraan untuk serat karbon. Tumpuan kajian ini adalah untuk menentukan sifat-sifat asas (kandungan abu dan kandungan meruap) lignophenol yang dihasilkan berdasarkan kesan parameter tindak balas seperti suhu (260–300 °C), masa (5–30 minit) dan kandungan pepejal (6 dan 10 g). Hasil kajian menunjukkan bahawa kandungan abu dan kandungan meruap terendah sebanyak 9.87% dan 6.45% didapati pada suhu 260 °C, 5 minit dan 6 g kandungan pepejal. Kesimpulan dari kajian ini mendapati bahawa suhu tindak balas, masa, dan muatan pepejal yang sederhana mampu menghasilkan lignophenol dengan kandungan abu and kandungan meruap yang rendah dibawah keadaan subgenting fenol.

Kata kunci: lignin, serat karbon, cecair subgenting, pelepah kelapa sawit, lignofenol

Introduction

Carbon fiber is a corrosion-resistant material consisting of at least 92% carbon content, with applications in various industries such as aviation, construction, automobiles, and sporting goods. Unfortunately, the utilization of carbon fiber is restricted by its high purchasing price due to the high cost of feedstock and manufacturing. Polyacrylonitrile (PAN) and pitch are the conventional feedstock for carbon fiber production. Currently, about 96% of carbon fiber's precursors in the market is dominated by PAN due to its effectiveness, and the quality of the fiber produced [1]. However, PAN and pitch are derived from fossil fuels, a known non-renewable resource. Thus, there is a great concern to find sustainable and environmentally friendly alternative resources. Biomass can be an alternative and can be used and as a substitution to fossil fuels as raw material to produce carbon fiber due to its availability, renewability, and sustainability. There are several types of biomass, including animal and plant waste. Cellulose, hemicellulose, and lignin are the major polymeric compounds present in lignocellulosic biomass. These compounds can be depolymerized and decomposed into lower molecular weight compounds, which are the platform chemicals used to produce numerous intermediates and end chemicals for various industries and applications.

The exponential growth of palm oil production over the past few decades has resulted in the expansion of the oil palm plantation area especially in Indonesia and Malaysia since both countries possess optimum conditions for oil palm growth and production such as humid tropical climate, sufficient sunlight, and uniformly distributed annual rainfall. In 2015, the Malaysian Palm Oil Board (MPOB) highlighted that about 5.64 million hectares of plantation areas are dedicated to palm oil which is equivalent to about 23% of Malaysia's total land area [2]. However, the increasing demand for palm oil globally resulted in copious amount of oil palm waste. Oil palm biomass is divided into two types, namely solid and liquid biomass. Solid biomass consists of empty fruit bunch (EFB), oil palm frond (OPF), oil palm trunk (OPT), mesocarp fiber (MF), and palm kernel shells (PKS).

Meanwhile, palm oil mill effluents (POME) are the only liquid biomass produced by the oil palm plantation. Severe environmental problems are often associated with oil palm biomass. The slow decomposition rate of the biomass causes the breeding of mouse and mosquitoes, which may lead to epidemics. Meanwhile, burning the waste to produce steam for energy in the oil palm plantation releases CO_2, which is harmful to the environment. It is estimated that about 231.5 kg dry weight of oil palm biomass are produced yearly, of which 70% is OPF, 10% EFB, and 5% OPT [3]. Therefore, the oil palm industry must be ready to take advantage of these circumstances and exploit these abundant resources in the best possible way. The massive annual generation of OPF has attracted researchers' interest to study its potential as a bio-based chemical and material. All lignocellulosic biomass, such as OPF, consists of three important natural polymers, i.e., cellulose, hemicellulose, and lignin. Lignin has the potential to be a feasible precursor for carbon fiber production.

Lignin is a three-dimensional complex biopolymer, that is amorphous and cross-linked consisting primarily of three monolignols as the building blocks, i.e., *p*-coumaryl (H), coniferyl (G), and sinapyl (S) alcohol. Lignin is categorized as softwood, hardwood, or grass lignin based on the relative amounts of its monolignols where softwood lignin is mainly coniferyl (about 90%), hardwood lignin consists of coniferyl and sinapyl, while grass lignin contains *p*-coumaryl monolignols [4]. Lignin contains numerous functional groups such as phenolic compounds, hydroxyl, carbonyl groups, ether, and ester bonds. Due to the numerous functional groups, it can be used to produce various bio-based chemicals, including as a precursor for carbon fiber [5]. However, the biggest concern of lignin as a precursor for carbon fiber is yielding an equal or better precursor that possesses properties similar to the conventional carbon fiber precursors available in the market. To produce lignin as a commercial precursor for carbon fiber, the presence of contaminants in the lignin should be minimal as contaminants may decrease the quality of carbon fiber [6]. The Oak Ridge National Laboratory (ORNL) has actively investigated the potential of lignin

as carbon fiber precursor and introduced a set of specifications as reference for lignin suitability as a carbon fiber precursor (Table 1) [7].

The decomposition of lignin into low molecular weight compounds are divided into three fractions: liquid product (primarily phenolic compounds) [8, 9], gaseous product mainly CO_2, CO, H_2, CH_4, and trace amounts of C_2 and C_3 hydrocarbons [10] and solid residue (condensed and unconverted lignin) [11]. This study aims to determine the feasibility of OPF lignin extracted under subcritical phenol conditions as a precursor for carbon fiber. The separation of lignin from other biomass constituents (cellulose, hemicellulose, and ash) is the primary focus in this study, which aims to obtain high purity and low contaminants (ash and volatile content). Being an essential part of the plant fiber cell wall, the separation of lignin cannot be done without any significant alterations to its native structural properties. Unfortunately, the alteration may affect the quality and purity of the lignin [12]. This problem was a challenge and prevented the application of lignin as a carbon fiber precursor in large-scale applications. Therefore, finding a new method that permits the extraction of high-purity lignin from biomass with minimal chemical modifications may provide a breakthrough pathway for the high value propositions of lignin.

The focus on biomass conversion using sub and supercritical fluids has increased due to its varying fluid properties as a result of manipulating the temperature and pressure. Solvents such as water, methanol, and ethanol at ambient conditions possess hydrogen-bonded structures that change with the increase in temperature. This condition causes a decrease in polarity and low dielectric permittivity, which subsequently facilitates the dissolution and breakage of the linkages of non-polar substances such as cellulose, hemicellulose, and lignin [13].

Extraction of lignin using sub and supercritical water have been extensively studied previously due to its clean reaction [14, 15]. Unfortunately, several studies reported that subcritical water caused repolymerization of monomers, producing char (an undesirable solid product), which decreased the potential of lignin as a precursor for carbon fiber. Therefore, this study proposes a new method using phenol under its subcritical condition (421.1 °C and 6.13 MPa). Few studies have shown the ability of sub and supercritical phenol in reducing the formation of char [16, 17]. Subcritical phenol functioned as a capping agent to cap active sites, preventing reactions with the decomposing lignin fragments; hence, it suppressed char formation. Hence, this study will focus on the effect of temperature (260–300°C), time (5–30 min) and solid loading (6–10 g) toward lignin properties (ash and volatile content) to determine its suitability as a precursor of carbon fiber production.

Table 1. Lignin specification as carbon fiber precursor

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

Materials and Methods

Raw material and chemicals

OPF was obtained from the Federal Land Development Authority (FELDA) plantation in Negeri Sembilan, Malaysia. Sample preparation followed standard procedures [18]. The samples were ground and sieved to obtain particles in the size range of 210–500 µm. Subsequently, the samples were subjected to an extraction process using methanol and a Soxhlet extractor to remove any oil residues and extractives. After 6 hours, the extracted samples were washed with water and dried in the oven for 48 hours at 45 °C. The chemical composition of OPF was determined based on the standard methods by the Technical Association of the Pulp and Paper Industry (TAPPI). The ultimate analysis of OPF was determined using CHNS/O elemental Analyzer, Perkin Elmer, Series II 2400, USA.

Experimental procedure

The reaction was conducted in an autoclave batch reactor with a working volume of 100 mL. Weighed OPF (6 or 10 g) and 70 mL of phenol were mixed and loaded into the autoclave reactor and subjected to various experimental conditions (temperature, reaction time and solid loading). The amount of phenol was chosen with the aim of maintaining the reaction pressure under subcritical phenol conditions (6.13 MPa). The reaction time was recorded once the temperature inside the vessel reached the target temperature. When the reaction was completed, the reactor was immersed in a water bath to quench the reaction. The solid residue was separated from the liquid residue using vacuum filtration. Subsequently, the solid residue was washed with methanol until the refractive index (RI) reached 1.33141 to ensure the removal of phenol. The solid residue was subsequently dried in an oven at 70 °C for 12 hours. The oven-dry weight (ODW) of the recovered solid residue was measured. The experimental conditions are shown in Table 2.

Table 2. Experimental conditions

Condition	Experimental Range
Reaction temperature (°C)	260, 280, and 300
Reaction time (min)	5, 10, and 30
Solid loading (g)	6 and 10

Lignin recovery and purification

Lignin recovery and purification were conducted according to National Renewable Energy Laboratory (NREL) specifications (determination of structural carbohydrates and lignin in biomass) [19]. An amount 3 mL of 72% sulfuric acid was added in a 50 mL test tube loaded with 300 mg of solid residue. The sample was incubated for 60 ±5 minutes inside a water batch shaker at 30 ± 3 °C. The sample was transferred to a 250 mL volumetric flask, and the acid was diluted to 4% concentration by adding 84.00 ± 0.04 mL deionized water. The sample was subsequently autoclaved at 121°C for another 60 ± 5 minutes. Upon completion, the purified lignin sample, known as an acid-insoluble residue (AIR), was collected by filtering the sample from the aliquot using Whatman™ filter paper with a pore size of 11µm. The AIR was washed with hot water and dried in an oven at 105 °C for 12 hours.

Analysis

Ash content

Ash content was determined according to the TAPPI Standard Test Method T 413 om-93 [20]. The AIR sample was combusted in a muffle furnace at 900 °C. The ash content percentage was calculated by dividing

the weight fraction of residual ash to the weight of the original sample, as shown in equation 1.

Volatile content

The volatile content in the recovered lignin sample was determined by following the standard proposed by ORNL and Luo (2010) [21]. The AIR sample was heated in the muffle furnace at 250 °C for 6 hours. The percentage of volatile content was determined on the basis of the weight loss of the sample to the weight of the original sample (equation 2).

$$\text{Ash content (\%)} = \frac{\text{Weight of the residual ash (g)}}{\text{Weight of the original sample (g)}} \times 100\% \quad (1)$$

$$\text{Volatile Matter Content (\%)} = \frac{\text{Initial weight of the sample (g) - Final weight of the sample (g)}}{\text{Initial weight of the sample (g)}} \times 100 \quad (2)$$

Results and Discussion

Characterization of OPF

The chemical and physical properties of biomass are different due to its origin and types. The high content of ash and extractives present in biomass result in the formation of slag, which reduces the efficiency of the process [22]. Therefore, the characterization of biomass is essential for determining how it may influence the quality of the precursor for carbon fiber production. Generally, biomass consisted of cellulose (30–50 wt.%), hemicellulose (20–35 wt.%), and lignin (15–30 wt.%), respectively [23]. Table 3 shows the chemical composition of OPF used in this study and compares it to other studies.

It can be observed that the lignin content in the OPF is consistent with other reported studies [24–26]. The minor difference in the OPF composition, especially lignin and cellulose, are based on its location, variety and agricultural practice [27–28]. The low amount of ash in OPF is favorable to prevent excessive generation of biochar at high temperatures [24]. Furthermore, the main composition of ash is inorganic salts. The high amount of inorganic salts may result in volatile release and the formation of pores in the fibers due to the catalytic effect of lignin thermal decomposition. Meanwhile, the high content of extractives remaining in carbon fiber resulted in mechanical defects [29]. Although the amount of lignin in OPF is lower than in other oil palm biomass, the high amount of OPF generated annually is certainly an essential consideration in its possibility as a raw material for this study [30–33]. Table 4 shows the analysis of OPF on a dry basis and its comparison with other types of oil palm biomass.

The carbon content (36.2%) of the OPF is lower than other types of oil palm biomass, with trace contents of nitrogen (0.4%) and sulfur (0.2%). Biomass decomposition resulted in the conversion of nitrogen to ammonia and hydrogen cyanide, while sulfur is converted to hydrogen sulfide [24, 36]. Therefore, a minimal amount of both elemental compositions is essential to minimize the formation of hazardous gases.

Ash content

Inorganic residues are commonly referred to as ash. Ash is defined as the residue left after combustion at high temperature (900 °C). Minimum inorganic content matter in lignin is desirable as a precursor for carbon fiber production. The ash content should be <0.1 wt.% to ensure minimal inclusions and defects of the carbon fiber [7, 37].

Figures 1 and 2 show the effect of temperature (260–300 °C), reaction time (5–30 minutes), and solid loading (6 and 10 g) on the ash content in the lignin. From the results, the lowest ash content of 9.87% and 10.10% were obtained at low temperature (260 °C) and short reaction time (5 minutes) for both solid loading. However, as observed in both figures, the ash content increased with higher temperature (280–300 °C) and longer reaction time (10–30 minutes) for both 6 and 10 g solid loading.

Table 3. Chemical composition of OPF (dry basis)

Compounds	This study	Omar et al. [24]	Tan et al. [25]	Kumneadklang et al. [26]
Cellulose	28.4	47.3 ± 1.1	42.8 ± 3.1	41.9
Hemicellulose	39.9	27.3 ± 1.9	14.8 ± 2.5	36.1
Lignin	18.9	20.1 ± 2.4	19.7 ± 2.7	22
Ash	3.6	3.4 ± 0.02	5.8 ± 0.4	NA
Extractives	9.2	NA	20.6 ± 4.1	NA

NA – no data available

Table 4. Ultimate analysis of OPF (dry basis)

Types of Biomass	Ultimate Analysis (wt.%)					Ref.
	C	H	N	S	O	
OPF	36.2	5.9	0.4	0.2	57.3	This study
MF	45.4	10.6	1.3	0. 7	42.0	[34]
OPT	41.6	6.8	0.4	0.9	50.4	[35]

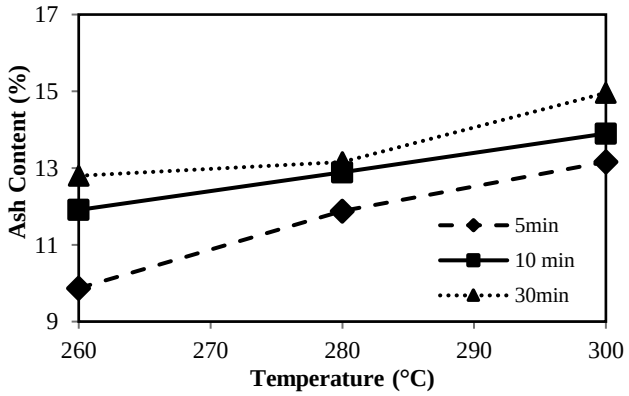

Figure 1. Ash content (%) at various temperatures (260–300 °C), reaction time (5–30 minutes) and 6 g solid loading

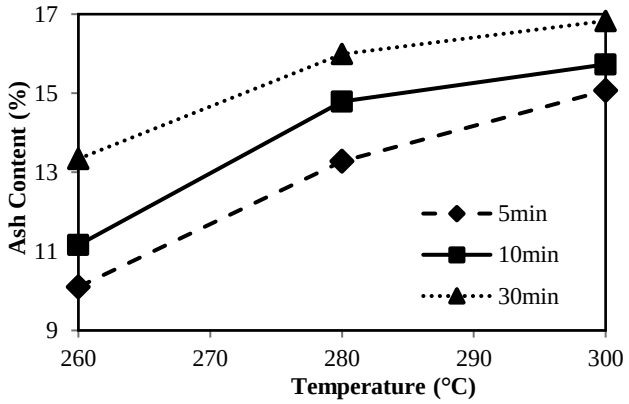

Figure 2. Ash content (%) at various temperatures (260–300 °C), reaction time (5–30 min) and 10 g solid loading

It can be concluded from Figures 1 and 2 that lower temperature and shorter reaction time produced lignin with low ash content under subcritical phenol conditions. Calcium, potassium, and magnesium are the main elements present in wood ash, while sodium and silicon existed relatively in small amounts [38]. The higher amount of ash with the increase in temperature and reaction time could be attributed to the increased condensation rate of the degraded ash with other intermediates. This finding is in line with Mäkelä et al. [40], who reported the increase in ash content from 48% to 67% for hydrothermal carbonization of biomass at 180–260 °C and 1–6.25 hours of reaction time. Shakya et al. [41] observed a similar trend, where they observed the increase in ash content from 6.07% (250 °C) to 43.29% (350 °C) at 60 minutes reaction time. On the other hand, Mäkelä et al. [42] concluded that solid loading is not a significant parameter in the ash content.

Based on the results, the ash content reported in this study did not meet the ORNL specifications (Table 1), which requires it to be less than 0.1% to be considered a suitable precursor for carbon fiber production. This might be due to the presence of sulfur from sulfuric acid in the sample before purification. Sameni et al. [38] obtained a higher ash content of 4.25% for lignin from pine species that had undergone acid hydrolysis compared to samples purified with other methods. Moreover, the incomplete removal of ash and extractives with methanol using Soxhlet extractor in this experimental work may contribute to the high ash content. Furthermore, the removal of ash might decrease due to the recycled solvent. This result is in line with Qu et al. [29].

Volatile content

Volatile content in the extracted lignin needs to be determined since these fragments can cause changes in the carbon fiber structures due to evaporation, especially during carbonization at high heating rate. The volatile content was determined by measuring the change in sample mass before and after heating in an oven at 250 °C for 6 hours. The volatile content must be less than 5% as specified by ORNL for it to be considered a suitable precursor for carbon fiber production (Table 1). The presence of low molecular weight fragments may cause defects in the structure of carbon fiber during lignin carbonization due to the rapid heating rate and evaporation [43]. Figures 3 and 4 show the effect of temperature (260–300 °C), reaction time (5–30 minutes) and solid loading (6 and 10 g) on volatile content.

The lowest volatile content of 6.45% and 8.47% were obtained at 260 °C and 5 minutes at 6 and 10 g solid loading, respectively. The result indicated that the volatile content is minimal at low temperature (260 °C) and reaction time (5 minutes) but increases with an increase in temperature (280–300 °C) and reaction time (10–30 minutes) for both solid loadings. It is also

observed that higher solid loading produced higher volatile content.

The degradation of lignin occurred over a wide range of temperature, between 140–600 °C [44]. The increase in volatile content could be attributed to the reduction of bond strengths in the chemical structure of lignin to form macromolecules volatiles during the reaction and subsequently volatilized. This is in agreement with Zhao et al. [11], who observed higher volatile gas formation at 300–700 °C and 20 minutes. Another study by Zhu et al. [9] shows that the volatile content obtained at 220 °C and 2 minutes is 60.5%. Meanwhile, Nanda et al. [45] obtained 35.5% volatile content at 550°C and 60 minutes with supercritical water. Thus, it can be concluded that lower volatile content can be obtained at low temperature and short reaction time under subcritical phenol conditions.

The results also indicate that the volatile content does not meet the specifications of ORNL (Table 1). One of the drawbacks of biomass is its high volatile content [46,47]; several studies reported that OPF has a high volatile content (82.70–85.10%) [30, 48, 49]. This study was conducted with a batch reactor without agitator. The high amount of solid loading formed a compacted mixture, resulting in a difficulty to mix thoroughly, resulting in challenges to obtaining homogenous reactions. This is in agreement with Meilany et al. [50].

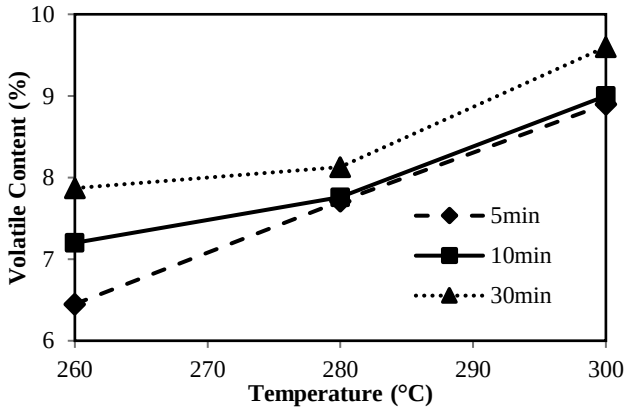

Figure 3. Volatile content (%) at various temperatures (260–300 °C), reaction time (5–30 minutes) and 6 g solid loading

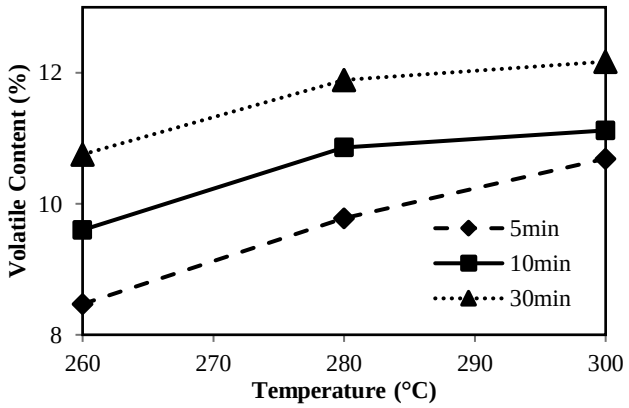

Figure 4. Volatile content (%) at various temperatures (260–300 °C), reaction time (5–30 minutes) and 10 g solid loading

Conclusion

Lignin as a precursor for carbon fiber can be commercially utilized if the impurities are reduced to a minimum. Low ash and volatile content are crucial to producing high-quality carbon fiber. As shown in this study, temperature, reaction time, and solid loading under subcritical phenol conditions have a significant effect on ash and volatile content. Although the results in this study did not meet ORNL specifications, it can be used as a reference for the future development of lignin as a precursor for carbon fiber production. On the other hand, this study has proven the feasibility of obtaining lignin under subcritical phenol conditions as a precursor for carbon fiber production. In this study, the extraction of lignin was focused on solid residues. Further analysis of the liquid residues should be considered as the solubilized lignin may possess the properties needed as a precursor. Additionally, this study could be further expanded by including other parameters such as pressure or pH value. This is because any changes in the reaction condition will alter the properties of the solvent, which would subsequently affect the properties of the lignin.

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