Reactivity Enhancement of Lignin Extracted from Preconditioning Refiner Chemical-Recycle Bleached Mechanized Pulp (PRC-RBMP) Black Liquor by Phenolation

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ABSTRACT

Despite black liquor's (BL) renown as a difficult-to-manage contaminant in the pulp and paper industry, BL has been found as a viable alternative material for adhesive formulation due to its high lignin content. Nevertheless, modification is required to enhance lignin's reactivity, and there is currently a lack of study focusing on this aspect for BL-lignin. This study aims to increase the phenolic hydroxyl content of BL-lignin by phenolation. After being phenolated at lignin to phenol ratio of 1:1, at a temperature of 100°C for 110 minutes, and with the addition of 8% sulfuric acid (H_2SO_4) as a catalyst, the phenolic hydroxyl content improved by 51.5%. The results of Fourier transform infrared spectroscopy (FTIR), UV/Vis spectrophotometry, proton nuclear magnetic resonance (^{1}H-NMR), thermogravimetry-differential scanning calorimetry (TG-DSC), and its differential curve showed that the structural change in phenolated lignin

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opened up more active sites, implying that this lignin could be a good substitute for phenol in phenol-formaldehyde resin manufacturing.

Keywords: Adhesive, black liquor, lignin, modification, phenolation, phenol-formaldehyde resin, pulp and paper, sustainability

INTRODUCTION

Other than solely focusing on pulp and paper products, many pulp and paper companies are driven to diversify their products to contribute to sustainability. With modern technology, most pulp and paper mills could improve the utilization of available renewable resources, such as black liquor (BL). Conventionally, BL was discharged to waterways as a disposal method or directed to a recovery boiler to recover chemicals and generate bioenergy (Lora & Glasser, 2002). Nevertheless, lignin, the major constituent of BL, can be utilized for various bioproducts development due to its variable functional groups (Ibrahim et al., 2011). Numerous researchers agreed that the abundant industrial lignin produced from pulp and paper mills could be an alternative material to replace some petrochemical feedstocks in the future (Kazzaz et al., 2019; Luo et al., 2020; Podschun, Saake, et al., 2015; Yang & Fang, 2014).

Nonetheless, studies have found that the pulping or processing conditions used to make paper, primarily sulfite, and kraft, can cause the lignin fraction in BL to have large impurities, limiting its use (Sammons et al., 2013). There are numerous different types of pulping and extraction procedures, and each one produces lignin with different purity and chemical properties depending on the feedstock. The structural variations in lignin caused by processing conditions are obstacles that must be overcome for lignin to be employed in a wide range of applications (Hidayati et al., 2020). Depending on the feedstock and pretreatment employed in the pulping process, a variety of lignin preparations with varied chemical structures and physical properties can be created and used in new applications, such as in the phenol-formaldehyde formulation, which was often used for wood adhesive, owing to its high phenolic content (Hussin et al., 2019; Ibrahim et al., 2013).

Nevertheless, lignin has complex and random cross-linked structures, and it is made up of three units of a phenolic core or also known as monolignols, which are p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) (Hussin et al., 2019). The existence of these monolignols in the structure of lignin enables it to undergo many modifications. However, due to lignin structural complexity and poor chemical reactivity, there are broad chemical differences depending on the source, processability, and depolymerization reaction, which remains a challenge (Gan & Pan, 2019; Chung & Washburn, 2012). Numerous researches have been carried out to enhance lignin reactivity, and one of them is through chemical modification to overcome this challenge (Hu et al., 2011; Kazzaz et al., 2019; Mansouri & Salvadó, 2006; Wang et al., 2017; Zhang et al., 2019).

Lignin modification through phenolation is one of the effective modification methods that can reduce the relative molecular mass and methoxy content of lignin and increase the phenolic hydroxyl group on the lignin structural unit with the application of catalyst and heating (Podschun, Saake, et al., 2015; Taleb et al., 2020; Thébault et al., 2020). The reaction process is simple, and the number of lignin active points can be increased to an extent that gives a positive performance (Hu et al., 2011; Yang et al., 2014). In terms of the positive performance of reactivity, Ghaffar and Fan (2013) discovered that the phenolic hydroxyl group is significantly affecting the physical and chemical properties of lignin, which is influenced by the modification process of lignin that plays a significant role in the lignin-formaldehyde reaction for adhesive production.

It was also supported by Laurichesse & Avérous (2014), who discovered that through phenolation, the resulting material could react rapidly with formaldehyde due to phenolation with free ortho and para units. Besides that, to support the results of modification, brominable substance content is also an auxiliary factor that could reflect the effectiveness of phenolation and reactivity of lignin (Jin et al., 2010; Qiao et al., 2016). According to China National Standard GB/T 14074, it can be determined by the percentage of the mass of phenol converted from the mass of brominable active groups to the total mass of the sample during the reaction. Phenolation reaction has triggered phenol to increase the reactive sites of lignin maximally. It explains that the lower the amount of brominable substance, which indicates the lesser the free phenol in the reaction, the higher the effectiveness of phenolation (Qiao et al., 2016).

Regarding this matter, phenolation can be considered a promising and practical method to modify lignin. Unlike primary sources of biomass such as fiber, wood logs, woodchips, bark, and sawdust, there is still a lack of reports on the phenolation of lignin extracted from a secondary source of biomass such as an empty fruit bunch-black liquor (EFB-BL). Due to the differences in the composition, structure, and functional group content of EFB-Lignin and other lignins, the reaction conditions of phenolation are also different. Verification tests are needed to set reasonable reaction conditions. Much research literature showed that it is known that the conditions affecting the phenolation effect of lignin are: the ratio of lignin/phenol, reaction temperature, reaction time, and catalyst dosage (Hu et al., 2011; Jiang et al., 2018; Yang et al., 2014; Zhang et al., 2019).

Preconditioning Refiner Chemical-Recycle Bleached Mechanized Pulp (PRC-RBMP) is a hybrid process that involves using steam for a short time, low concentration of the alkaline solution, and extrusion to produce EFB pulps. The processing eliminates oil and light contaminants, and the thermally treated fiber was further stretched and torn to the desired condition. Black liquor was collected and used in this study, henceforward referred to as EFB-BL. Unlike kraft and soda pulping, which relies on chemical treatment, the PRC-RBMP applies mechanical, thermal, and chemical treatments to disintegrate lignin,

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hemicelluloses, and cellulose to enhance the pulp's quality sustainably. The process does not create any hazardous chemicals, and it is cost-, energy- and time-efficient as well as practical to be applied on an industrial scale.

This study hence attempts to modify the lignin extracted from EFB-BL, which has undergone an integrated pulping and extraction method which, are PRC-RBMP and Lignoboost, by exploring the effect of four modification parameters on the phenolic hydroxyl content and brominable substances, which are the ratio of lignin to phenol (L/P ratio), reaction temperature, reaction time, and dosage of catalyst acid. The phenolated EFB-Lignin was subjected to UV/Vis spectrometry, Fourier transforms infrared (FTIR) spectroscopy, ^{1}H NMR, and thermogravimetric (TG) analyses to determine its properties and its potential for partial incorporation into phenolic resins such as phenol-formaldehyde resin.

MATERIALS AND METHODS

Lignin Extraction

Lignin was extracted from the black liquor (BL) of oil palm empty fruit bunch (EFB), and the pulping residues were collected from Nextgreen Pulp & Paper Sdn. Bhd. (Pekan, Pahang, Malaysia). Chemicals: H_2SO_4 (98% v/v,) which acts as a catalyst, phenol reagent, KBrO3 (99.99% w/v), and KBr (99% w/v) were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China) and used as received. Black liquor (BL), which has undergone a Preconditioning Refiner Chemical-Recycle Bleached Mechanised Pulp (PRC-RBMP) treatment, a patented technology developed by Nextgreen Global Berhad (Grant no.: MY172437A, MY144559A), was then subjected to "LignoBoost" treatment to solely extract lignin (modified from Ma et al., 2007; Zhang & Lei, 2010; Zhu, 2013). Lignin was precipitated from 10 mL of EFB-BL through the acidification process, performed at pH 3, for 1 h, and at 60°C. Sulphuric acid (80 wt%) was slowly added into the sample until the desired pH was achieved, and the mixture was then left to allow lignin precipitation to occur. The sample was then vacuum-filtered prior to phenolation.

Lignin Modification by Phenolation

The optimum condition of lignin phenolation was identified by phenolate of the extracted lignin at certain conditions of lignin/phenol (L/P) ratio, reaction temperature, reaction time, and catalyst dosage (H_2SO_4), as shown in Table 1. These four evaluation factors were selected based on a few studies which affect the phenolation (Hidayati et al., 2020; Jiang et al., 2018; Podschun, Saake et al., 2015). Each range of the independent variables was selected based on a few studies which gave positive outcomes (Podschun, Stucker et al., 2015; Thébault et al., 2020; Yang et al., 2014). Approximately 2 g of lignin, a prescribed amount of phenol, and 98% concentrated H_2SO_4 were mixed in a flask equipped

with a condenser and a mechanical stirrer. The mixture was then heated to a set reaction temperature and time in a temperature-controlled water bath. The effect of variables' conditions on the content of brominable substances and phenolic hydroxyl group were then determined.

Table 1
Prescribed composition of L/P ratio, reaction temperature, reaction time, and catalyst dosage for phenolation

Experiment	A	B	C	D
Evaluation factor	**L/P ratio**	**Reaction temperature**	**Reaction time**	**Catalyst dosage**
L/P ratio	1:2, 1:1.5, 1:1, 1.5:1, 2:1	1:2	1:2	1:2
Reaction temperature (°C)	100	80, 90, 100, 110, 120	100	100
Reaction time (min)	90	90	30, 50, 70, 90, 110	90
Catalyst dosage (%)	4	4	4	2, 4, 6, 8, 10

Determination of Phenolated Hydroxyl Content of Lignin Sample

The phenolic hydroxyl content of lignin was determined, referring to a method by Lai et al. (2007). Approximately 10 mL of dried lignin was dissolved in 100 mL distilled water. The solution was stirred, and NaOH was slowly dropped until the dried lignin was completely dissolved. Approximately 1 mL of dissolved lignin was transferred to a 50 mL volumetric flask. Then, 3 mL Folinol reagent and 30 mL distilled water were added into the dissolved lignin, followed by 10 mL of 20% Na_2CO_3 after 5–8 min. Distilled water was added until it reached 50 mL. The mixture was stirred for 2 h at room temperature prior to UV/Vis spectrometry analysis. The absorbance at 760 nm was measured with a sample having a phenol concentration of 0 as a blank. The measured absorbance was compared with the concentration-absorbance value standard curve to obtain the content of phenolic hydroxyl groups in the lignin sample.

Determination of Content of Brominable Substance of Lignin Sample

The content of the brominable substance was determined according to China National Standard GB/T 14074/2017. A solution was prepared by mixing 2.8 g potassium bromate with 10 g potassium bromide and 1000 ml distilled water. Separately, 0.5 g of lignin was diluted with 500 mL distilled water, then 50 mL of this diluted lignin was added with 25 mL potassium bromate-potassium bromide solution and 5mL hydrochloric acid (analytical reagent). The solution was then quickly stirred until it was homogeneously mixed and placed in the dark for 15 min. After 15 min, 1.8 g potassium iodide was added to the solution and kept in the dark for another 5 min.

Titration was then conducted using 0.1 mol/L $Na_2S_2O_3$ solution as a standard. It was slowly added until the color of the solution turns to pale yellow. Titration was continued by adding 3 mL starch indication until the blue color disappeared. A blank test was performed by substituting samples with 50 mL of distilled water. The calculation to determine the brominable substance content is as in Equation 1:

$$B = \frac{(V1 - V2) \times C \times 0.01568 \times 500}{(m \times 50) \times 100\%} \qquad (1)$$

Where,

$V1$: the volume of the $Na_2S_2O_3$ standard solution consumed by the blank test, in units of mL;

$V2$: the volume of the $Na_2S_2O_3$ standard solution consumed by the titration sample, in units of mL;

C: $Na_2S_2O_3$ standard solution concentration, the unit is mL;

0.01568 - the concentration of C $(Na_2S_2O_3)$ = 0.167mol / L sodium thiosulfate standard solution corresponding to the molar mass of phenol, the unit is g / mmol;

m: The mass of the sample, the unit, is g.

UV/Vis Spectrometry Analysis

UV/Vis spectrophotometry (Lambda 25 UV/VIS, Perkin Elmer, Waltham USA) was used to determine the lignin content on the phenolated EFB-Lignin. Absorbance within a 200 to 400 nm spectral range was measured at 1 nm spectral resolution at a scan speed of 250 nm/min. The non-phenolated EFB-Lignin was used to reference the phenolated EFB-Lignin (Skulcova et al., 2017).

Fourier-Transform Infrared Spectroscopy

The functional group of both phenolated and non-phenolated EFB-Lignin was analyzed by Fourier-transform infrared spectroscopy (FTIR) using KBr pellets containing 1% finely ground samples. Each spectrum was recorded at a range of 500 – 4000 cm^{-1} using an infrared spectrometer (Vertex70, Bruker, Massachusetts, USA) (Y. Zhang et al., 2020).

^{1}H NMR Analysis

The chemical structure of phenolated and non-phenolated EFB-Lignin was determined by ^{1}H NMR spectroscopy (German Bruker 400MHz nuclear magnetic resonance (NMR) spectrometer, specification model: ADVANCEIII 400MHz.) About 1 mg of samples were dissolved in 0.5 mL of deuterated chloroform $(CDCl_3)$. The NMR spectrum was recorded at 400 MHz, at a probe temperature of 25°C, and chemical shifts are given in ppm.

Thermogravimetric Analysis

Thermal stability of phenolated and non-phenolated EFB-Lignin was determined by subjecting approximately 10 mg of samples to the thermogravimetry-differential scanning calorimetry (TG-DSC) thermal analyzer (STA449F3-1053-M, Netzsch, Selb Germany). The samples were heated from 30 to 800°C at 10°C min^{-1} under constant nitrogen (H. Zhang et al., 2020).

Statistical Analysis

The brominable substances and phenolic hydroxyl content of different tested conditions were statistically analyzed using a one-way analysis of variance (ANOVA) in a general linear model using Statistical Analysis Software (SAS) Ver. 9.5. The mean for each measured parameter was separated statistically using Duncan Multiple Range Test (DMRT) at $p < 0.05$.

RESULTS AND DISCUSSION

Effects of Lignin/Phenol Ratio on the Content of Phenolic Hydroxyl and Brominable Substance

The effectiveness of phenolation was measured by determining the phenolic hydroxyl content and brominable substances of the phenolated EFB-Lignin. In order to determine the optimum L/P ratio that can produce the highest content of phenolic hydroxyl, several variables were set constantly, which were reaction temperature (100°C), reaction time (90 min), and catalyst dosage (4%). The objectives are to achieve maximum phenol incorporation and lignin fragmentation with the optimum L/P ratio (Podschun, Saake et al., 2015). It can be observed from Figure 1 that there is a significant difference in phenolic hydroxyl content produced from different L/P ratios. Nevertheless, among all L/P ratios, the L/P = 1:1 yielded the highest phenolic hydroxyl content at 8.12 mol.g^{-1}.

It shows that an equal ratio of phenol to lignin allows better phenolation than those with a higher ratio of phenol to lignin, allowing maximum production of phenolic hydroxyl content. It was also proven by Gan & Pan (2019), where the yield of phenolic hydroxyl content decreased significantly with the increase of phenol to lignin ratio. The same author also reported that applying a low mass ratio of L/P (1:1) has reduced the molecular weight from 14,400 to 6,000 g/mol, which indicates that lignin has been depolymerized during phenolation. Despite a similar L-to-P ratio, it revealed enough acid to hydrolyze and phenolate the lignin (Jiang et al., 2018).

Besides the content of phenolic hydroxyl, an efficient phenolation process is also reflected by the content of brominable substances. Qiao et al. (2016) agreed that the lesser the content of brominable substances in a sample, the more complete the phenolation

process, as it contains a lesser amount of free phenol in the reaction. This study shows that an L/P ratio 1:1 can produce a relatively low amount of brominable substances compared to the second high L/P ratio (indicated L/P ratio of 2:1 in Figure 1). It could also support the idea that using more lignin in the L/P ratio to produce high phenolic hydroxyl content was unnecessary since it could obstruct phenolation and alter other parameters as lignin may polymerize. In this study, a higher phenol (1:2) in the L:P ratio does not result in a higher phenolic hydroxyl content, as excessive phenol may accelerate lignin re-polymerization (Gan & Pan, 2019).

In comparison to other studies stated in Table 2, which used a higher phenol-to-lignin ratio to produce high phenolic hydroxyl content, this study discovered that a 1:1 L/P ratio is sufficient, as it produces the maximum phenolic hydroxyl content when compared to other L/P ratio compositions. It was also revealed that at similar L/P ratios, different feedstocks and pulping procedures yielded varied phenolic hydroxyl content yields. It is supported by Sammons et al. (2013) theory that the phenolation process was influenced directly by the feedstock and pulping process.
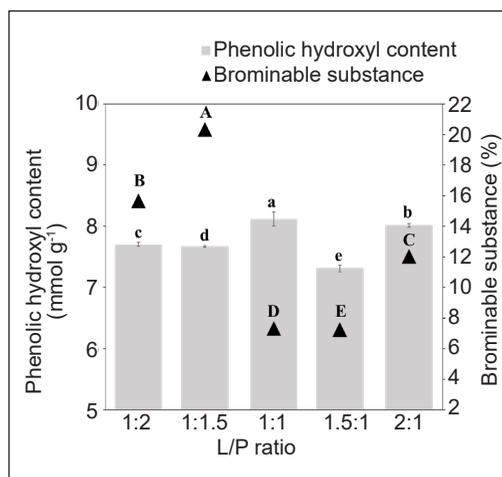

Figure 1. The effect of the L/P ratio on the content of phenolic hydroxyl and brominable substances. All data are means of 3 replicates ± SD. Capital letters indicate a significant difference ($p < 0.05$) of brominable substance, while small letters indicate a significant difference ($p < 0.05$) in phenolic hydroxyl content among different L/P ratio samples

Effects of Reaction Temperature on the Content of Phenolic Hydroxyl and Brominable Substance

Further analysis was then carried out to determine the effect of phenolation temperature on the phenolic hydroxyl content, with 3 different temperatures ranging from 80 to 120°C. This study's constant variables were the L/P ratio, set at 1:2, the reaction time at 90 minutes, and the catalyst dosage at 4%. Figure 2 shows that the phenolic hydroxyl content increased by increasing the reaction temperature from 80 to 100°C by 14.7%. It indicates that the phenolation reaction progresses completely at 100°C after gradually increasing the phenolic hydroxyl content. Jiang et al. (2018) found a similar pattern of results, concluding that increasing the reaction temperature can produce more phenolic hydroxyl content. Alonso et al. (2005) also discovered that phenol conversion is greater at high temperatures. Meanwhile, a rapid drop in phenolic hydroxyl content at 120°C may be attributed to re-condensation, which occurs when the phenolation temperature exceeds 100°C, lowering the phenolic hydroxyl content. According to Podschun, Saake et al. (2015), and Jiang et

al. (2018), such conditions could be due to extreme degradation caused by the reaction conditions, or they could be related to the solubility of lignin in phenol.

As the reaction temperature rises, so does the amount of brominable substance. The amount of brominable substances increased dramatically from 2.62 % (at 80°C) to 11.52 % (at 90°C), reaching a maximum increment at 100°C. It indicates that increasing the temperature impacts the concentration of brominable substances. Nonetheless, when the temperature increased to 120°C, a drop in brominable substances was observed. Although the phenolation reaction increases as the temperature rises, the release of free phenol also increases, weakening the overall reaction effect. It is also supported by Qiao

Figure 2. The effect of reaction temperature on the content of phenolic hydroxyl and brominable substances. All data are means of 3 replicates ± SD. Capital letters indicate a significant difference ($p < 0.05$) in brominable substance, while small letters indicate a significant difference ($p < 0.05$) in phenolic hydroxyl content among different temperature samples

et al. (2016). Theoretically, the amount of derived brominable substance indicates the free phenol in the reaction, reflecting the phenolation process's efficiency. Phenolation is assumed to occur efficiently if the amount of brominable substance is low, as the reaction reduces free phenols from the sample. A similar graph pattern can also be observed on the phenolic hydroxyl content, as when the temperature is set to 100°C, the phenolic hydroxyl content reaches its maximum. For this study, a reaction temperature of 100°C was chosen for phenolation by considering a thorough reaction, experimental goal, energy consumption, and applicability on a commercial scale.

Effects of Reaction Time on the Content of Phenolic Hydroxyl and Brominable Substance

The reaction time, in addition to the L/P ratio and reaction temperature, may impact the phenolic hydroxyl content. As a result, the samples were subjected to 5 different reaction times ranging from 30 to 110 minutes at 100°C, with a constant L/P ratio of 1:2 and a catalyst dosage of 4 %. When the reaction time was increased from 30 to 110 min, the phenolic hydroxyl content increased (Figure 3). It could be due to the irreversible polymerization of degraded lignin during long-term high-temperature reactions. It then explains that sufficient reaction time was necessary for the desired depolymerization to enhance the phenolation process. However, re-polymerization of lignin may occur if the reaction is extended, supported by Gan and Pan (2019). Compared to the L/P ratio, reaction temperature, and
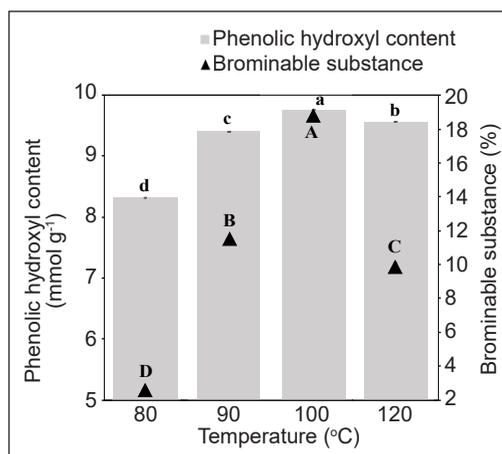
acid concentration, Podschun, Saake, et al. (2015) also found that reaction duration has little effect on the degree of phenolation. Meanwhile, the content of brominable substances fluctuated throughout short and long durations, eventually reaching a minimum after 110 min of treatment. As a result, 110 min is the best duration for a complete phenolation reaction when both phenolic hydroxyl contents and brominable substances are considered.

Figure 3. The effect of reaction time on the content of phenolic hydroxyl and brominable substances. All data are means of 3 replicates ± SD. Capital letters indicate a significant difference ($p < 0.05$) of brominable substance, while small letters indicate a significant difference ($p < 0.05$) in phenolic hydroxyl content among different time samples

Effects of Catalyst Dosage on the Content of Phenolic Hydroxyl and Brominable Substance

In this study, a catalyst (H_2SO_4) was also added to speed up the phenolation reaction to the samples. In order to determine the optimum dosage of catalyst needed to produce a high amount of phenolic hydroxyl content, a different dosage of catalyst in a range of 2%–10% was added. The L/P ratio, reaction temperature, and reaction time were fixed at 1:2 = L/P, 100°C, and 90 min. Meanwhile, several catalyst dosages were tested, which were 2%, 4%, 6%, 8%, and 10%. The analysis was conducted at 100°C for 90 min and at a constant L/P ratio=1:2. Figure 4 shows an increase in phenolic hydroxyl content by increasing the catalyst dosage from 2% to 8%. The phenolic hydroxyl dosage notably achieved a maximum increment after 8% catalyst was added into the sample, which was 8.7 mmol g^{-1}. It shows that a high catalyst dosage may help complete the phenolation reaction and indirectly influence the production of phenolic hydroxyl.

A similar result was also reported by Zhang et al. (2019), where a significant increment of phenolic hydroxyl content was seen in samples added with a high percentage of H_2SO_4 which acts as a catalyst. It shows that a high percentage of catalysts may facilitate the phenol incorporation, lignin fragmentation, and hydrolysis of the polysaccharides. The author also agreed that the catalyst (H_2SO_4) might be diluted when more phenol is added, as phenol can act as a reactant and solvent. Meanwhile, the H_2SO_4 charge was based on the weight of lignin alone. However, a reduction in phenolic hydroxyl content was observed after adding 10% catalyst. It was due to the re-condensation of phenolated lignin, which affected the reaction's production of phenolic hydroxyl and free phenol. It is also possible that over a period at a specified temperature, this EFB-Lignin is still not phenolated in acid conditions. This factor may also explain the pattern of reaction temperature results
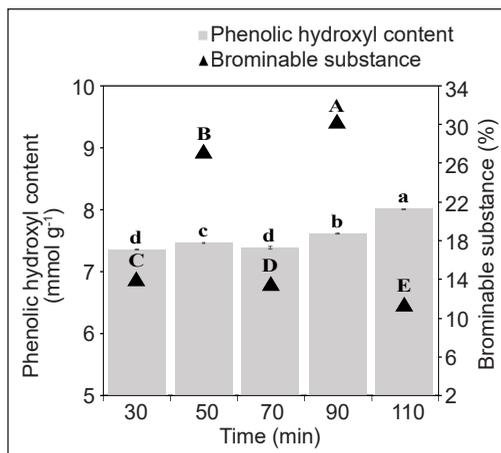
(Figure 2). It is speculated that concentrated sulfuric acid might not be the most suitable acid catalyst for EFB-Lignin from PRC-RBMP pulping. However, this study also proves the ability of H_2SO_4 to catalyze the phenolation reaction at a moderate temperature, as reported by other studies as tabulated in Table 2.

Meanwhile, results also revealed that the content of brominable substances reduced tremendously after 6%–10% catalysts were added, with a minimum amount (11.52%) recorded when 8% catalyst was added. Similar to other variables, the catalyst dosage also created a direct relationship between brominable substances and the amount of phenolic hydroxyl. In this study, adding an 8% catalyst was the most effective

Figure 4. The effect of catalyst dosage on the content of phenolic hydroxyl and brominable substances. All data are means of 3 replicates ± SD. Capital letters indicate a significant difference ($p < 0.05$) in brominable substance, while small letters indicate a significant difference ($p < 0.05$) in phenolic hydroxyl content among different catalyst dosage samples

in producing the highest phenolic hydroxyl contents and the lowest amount of brominable substances. The dosage of the catalyst was in a similar range to other studies. Podschun, Saake et al. (2015) discovered that phenolic hydroxyl content was noticeably increased in samples with a 6.7%–7.5% catalyst. Similarly, Jiang et al. (2018) also reported that samples containing 4%–8% catalysts produced higher phenolic hydroxyl content compared to samples with the addition of 10%–15% catalyst.

Hence, considering the experimental objectives, energy-saving, cost-effectiveness as well as practicability to be applied on a commercial scale, the overall findings discovered that the optimum phenolation greatly occurred at a condition of L/P ratio = 1:1 at a temperature of 100°C for 100 min, and with the addition of 8% catalyst. In addition, the phenolic hydroxyl content of phenolated EFB-Lignin was improved by 51.5% after phenolation, which is 7.896 mmol g^{-1}.

Table 2 compares the phenolic hydroxyl content and the best phenolation conditions for various raw materials. Despite using a secondary biomass source in the form of EFB-BL, this study was able to yield the highest phenolic hydroxyl content when compared to other types of biomasses, including those primary sources of biomass such as poplar wood, corn cob, bamboo, wheat straw, and many more. It could be owing to PRC-RBMP and LignoBoost's efficient integrated process during pulping and lignin extraction. It demonstrates that EFB-BL has a similar and comparable potential to be used as the primary feedstock for lignin extraction and, ultimately, adhesive production.
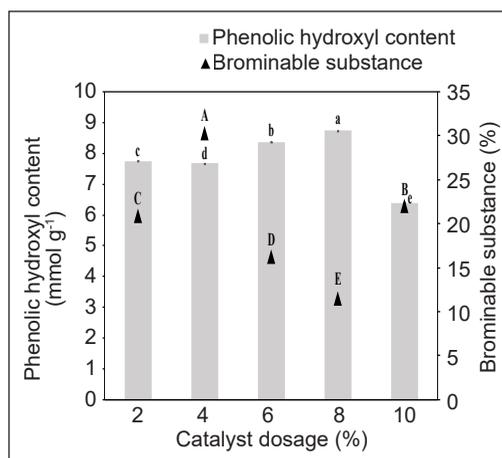
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Table 2
Comparison of phenolation conditions between different raw materials

Raw Materials	Lignin extraction	Phenolation (Acid/Alkali)	The ratio of lignin to phenol	Temperature (°C)	Time (minute)	Catalyst	Catalyst concentration (%)	Phenolic hydroxyl content (mmol g^{-1})	Reference
Lignin									
EFB Lignin from black liquor	PRC-RBMP and LignoBoost	Acid	1:1	100	110	H$_2$SO$_4$	8	7.9	This Study
Pine kraft lignin	LignoBoost	Acid	3:5	90	120	H$_2$SO$_4$	5	4.47	Jiang et al., (2018)
Spruce industrial kraft lignin	-	Acid	1:10	25	60	H$_2$SO$_4$	40	5.81	Zhang et al., (2021)
Alkali Lignin	-	Acid	1:4	110	120	H$_2$SO$_4$	5	5.66	Zhen et al. (2021)
Kraft lignin	-	Alkali	1:3	160	120	NaOH	50	4.52	Gan & Pan, (2019)
Sugarcane bagasse kraft lignin	Precipitated	Alkali	1:4	110	150	NaOH	30	6.63	Luo et al. (2020)
Black Liquor									
Kraft black liquor	Precipitated (acidifying)	Alkali	1:1	80	240	NaOH	10	-	Abdelwahab & Nassar (2011)
Kraft black liquor	-	Alkali	1:1	95	60	NaOH	30	2.20	Yang et al., (2014)
Fibers									
Air-dried wood	Ethanol-benzene	Acid	-	100	60	H$_2$SO$_4$	3	1.5	Funaoka et al., (1995)
Beech wood	Ethanol water pulping	Acid	1:2	110	20	H$_2$SO$_4$	19.8	4.1	Podschun, Stucker et al. (2015)
Poplar wood	Hydrothermal	Alkali	1:1	95	60	NaOH	30	2.23	Yang et al., (2014)
Poplar wood	Ethanol water pulping	Acid	1:2	110	20	H$_2$SO$_4$	19.8	3.5	Podschun, Stucker et al. (2015)

Table 2 *(continue)*

Raw Materials	Lignin extraction	Phenolation (Acid/Alkali)	The ratio of lignin to phenol	Temperature (°C)	Time (minute)	Catalyst	Catalyst concentration (%)	Phenolic hydroxyl content (mmol g^{-1})	Reference
Pinewood	Ethanol water pulping	Acid	1:2	110	20	H_2SO_4	19.8	2	Podschun, Stucker et al., (2015)
Beechwood chips	Ethanol water pulping	Acid	1-2:0.3-2	110	20	H_2SO_4	6.7	6.2	Podschun, Saake et al., (2015)
Corn cob	Hydrothermal and chemical	Alkali	1:1	95	60	NaOH	30	3.14	Yang et al., (2014)
Bamboo	Precipitated (acidifying)	Alkali	1:1	90	60	NaOH	30	2.15	Pang et al., (2017)
Bamboo	Organosolv pulping a process with acetic acid	Alkali	1:1	90	60	NaOH	30	1.75	Pang et al., (2017)
Wheat straw	Ethanol water pulping	Acid	1:2	110	20	H_2SO_4	19.8	1.9	Podschun, Stucker et al., (2015)
Wheat straw	Autohydrolysis followed by mechanical refining and enzymatic hydrolysis	Acid	1:3	120	120	H_2SO_4	10	2.67	Zhang et al (2019)
Wheat straw	Hydrothermal and chemical	Alkali	1:1	95	60	NaOH	30	3.17	Yang et al (2014)
EFB	Hydrothermal and chemical	Acid	1:3	130	60	H_2SO_4	5	6.5	Ahmadzadeh et al., (2009)

Unlike most of the other studies listed in Table 2 that rely on the catalyst with an average of 22%, this study only uses 8% H_2SO_4 to speed up the phenolation reaction and at a low L/P ratio (1:1). It demonstrates that a higher phenolic hydroxyl content can be produced by adjusting low catalyst dosage with L/P ratio, temperature, and phenolation time. It is beneficial as the usage of phenol and catalyst can be minimized. It can also be assumed that phenolation occurs effectively under mild phenolation conditions for lignin extracted from EFB-BL, compared to those extracted lignins from a primary source of biomass. The low L/P ratio, reaction temperature, reaction time, and catalyst quantity used in this modification are all examples of mild phenolation conditions.

Properties of Phenolated and Non-Phenolated EFB-Lignin

The properties of the optimized phenolated EFB-Lignin were compared to those of the non-phenolated EFB-Lignin. The UV/Vis analysis determines any changes in conjugated phenolics of the phenolated EFB-Lignin. Maximum absorption peaks of lignin at 250, 300, and 350 to 360 nm can be observed, as shown in Figure 5. The two absorption peaks at 250 nm and 300 nm are caused by the chromophoric shift of the benzene ring absorption band in the lignin structure, and the third absorption peak is composed of the a-carbonyl group-containing phenol structure. It was also observed that the phenolated EFB-Lignin has a stronger absorption band near 205 to 220 nm than the non-phenolated EFB-Lignin, which might be due to the ionization of the phenolic hydroxyl group during phenolation. It indicates that selective and effective phenolation at reactive sites in the side chains leads to the disappearance of conjugated systems (Funaoka et al., 1995).
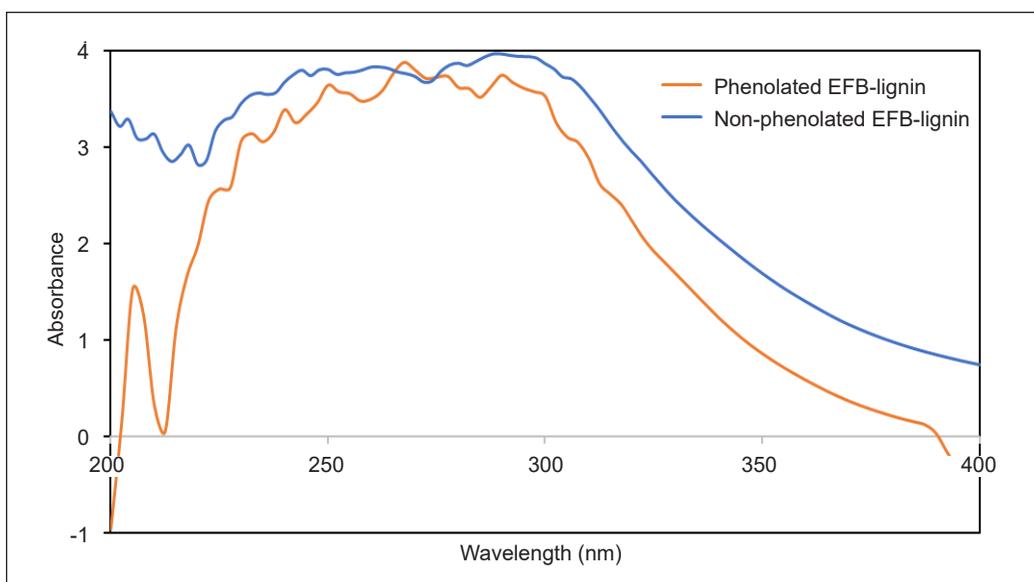

Figure 5. UV spectra of non-phenolated and phenolated EFB-lignin

Similar to the UV/Vis spectra, spectral differences in the FTIR peaks were observed between the non-phenolated and phenolated EFB-Lignins (Figure 6). The absorption peaks of the infrared spectrum of EFB-Lignin before and after phenolation are similar, and the intensity has somehow changed. A similar trend was also observed on peaks around $3000 – 3500$ cm^{-1}, which denotes the hydroxyl group (O-H). It was observed that the non-phenolated EFB-Lignin has intense peaks at around $640–1820$ cm^{-1} and $2800–3800$ cm^{-1}, and it indicates the complex crosslinking in the lignin structure (Inwood, 2014). Figure 6 shows a new band at the peak of 755 cm^{-1} for the phenolated EFB-Lignin. This band arises from the reaction between phenol in ortho or para-position and a-hydroxyl groups in the side chain of lignin (Alonso et al., 2005). It was also noticeable that peaks around $1043–1200$ cm^{-1} which indicate the presence of –CH$_2$ and syringyl and guaiacyl units, have disappeared after phenolation. It shows that phenolation has caused CH deformation from the CH$_2$ group (Inwood et al., 2018). Meanwhile, 1120 cm^{-1} is the stretching vibration peak of the methoxy group (O–C), and it can be observed here that the absorption peak of the phenolated EFB-Lignin is weakening, indicating that part of the methoxy group of the phenolated EFB-Lignin is shed due to groups cleavage (Alonso et al., 2005). It is also to note that there is an enhanced absorption peak at 1230 cm^{-1}, which belongs to the phenolic hydroxyl group on the spectrum of phenolated EFB-Lignin, and this indicates a successful phenolation for the phenolated EFB-Lignin (Inwood, 2014; Luo et al., 2020).

Meanwhile, a peak at 1394 cm^{-1}, which belongs to the C-H stretch in methyl groups, significantly reduced in the phenolated lignin. It is also mirrored by the peak of 837 cm^{-1}, which was attributed to the aromatic C-H bending (Rashid et al., 2016). The aromatic skeletal or benzene ring skeleton vibrations, which can be observed around $1400–1600$ cm^{-1} on the non-phenolated EFB-Lignin, were seen to be reduced after phenolation, as shown by the spectra of phenolated EFB-Lignin.
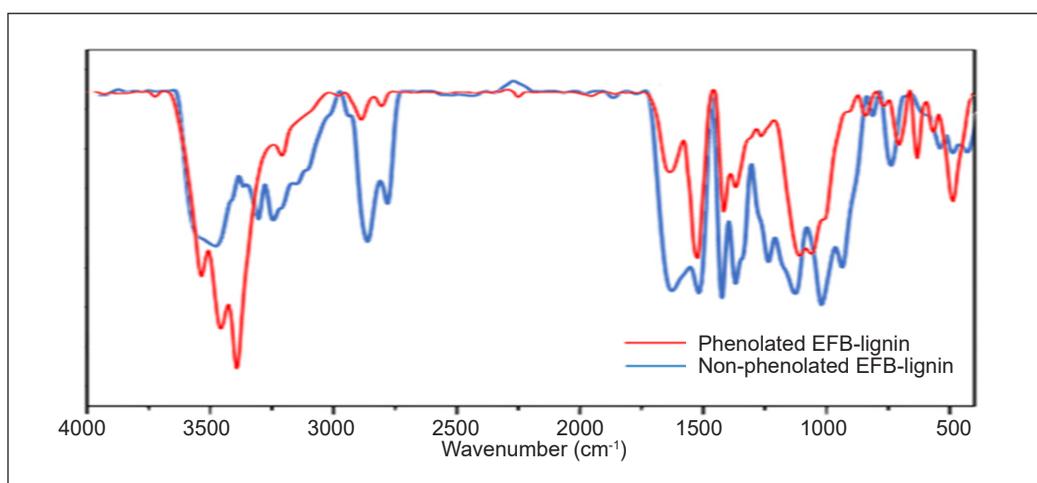

Figure 6. FTIR spectrum of non-phenolated and phenolated EFB-lignin

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The ^{1}H-NMR spectrum was integrated to evaluate the change in the content of the compound (Gao et al., 2021). In this study, ^{1}H NMR was used to evaluate the change of the compound in lignin after phenolation. ^{1}H NMR spectrum of phenolated and non-phenolated EFB-Lignin is shown in Figure 7. For this study, tetramethylsilane (TMS) was used as an internal standard, and for further quantitative analysis, deuterated chloroform (d-chloroform) was used as an internal standard. D-chloroform is a good solvent for many resins as it produces only small proton impurity peaks compared to other deuterated solvents (Garrigues, 2019). Meanwhile, TMS was used as it is good as the internal reference standard of ^{1}H NMR (Makulski & Jackowski, 2020).

A peak at 7.29 ppm in Figure 7 refers to the internal standard of d-chloroform (Pretsch et al., 2020). Compared to the non-phenolated EFB-Lignin, the phenolated EFB-Lignin shows an intense peak from 6.84 to 7.26 ppm. This range of points represents the aromatic
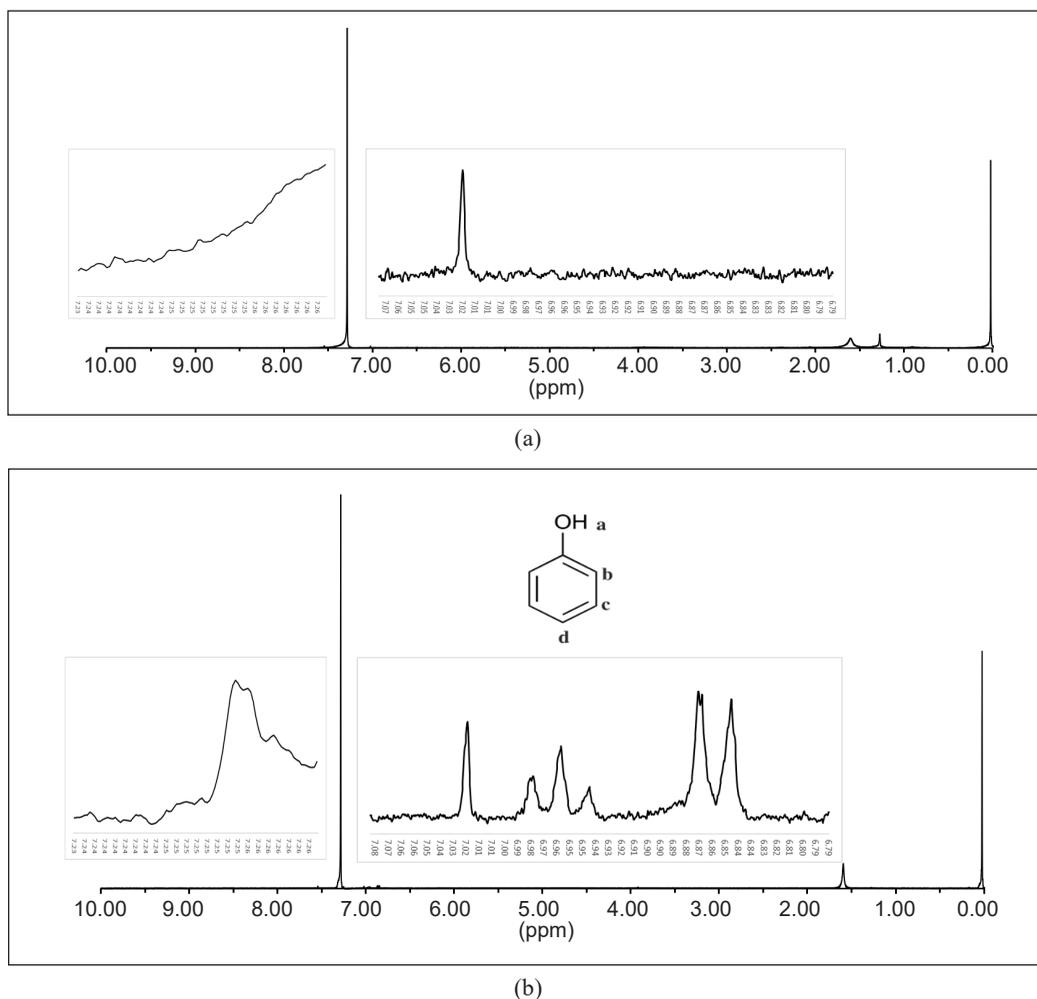

(a)

(b)

Figure 7. ^{1}H NMR of non-phenolated (a) and phenolated EFB-lignin (b)

compound. According to Pretsch et al. (2020), by using d-chloroform as an internal standard, the appearance of peaks that represent an aromatic structure can be observed, and it was depicted in Figure 7(b) as peaks at 6.84–6.87 ppm, 6.94–6.98 ppm and 7.24–7.26 ppm that represent the aromatic structure of b, d, and c, were respectively observed. Meanwhile, Figure 7(a) shows no peak from 6.84 to 7.26 ppm. It shows that the aromatic structure was not there prior to phenolation.

The non-phenolated EFB-Lignin sample exhibits no peak at point 4.69 ppm. However, the phenolated EFB-Lignin sample shows an intense peak at this point. According to the literature, this point represents the OH component (a) in the aromatic structure observed in peak 6.84 to 7.26 ppm. As seen in Figure 7(b), this peak demonstrates that the phenolation EFB-Lignin has a phenolic structure. It then proves that the phenolation of lignin was successful. According to Ibrahim et al. (2011), the phenolic compound in the phenolated EFB-Lignin is contributed by the cleaving of alkyl–aryl ether linkages during lignin modification, which led to the formation of new phenolic groups in the phenolated EFB-Lignin. It also leads to the higher existence of reactive sites, allowing the phenolated EFB-Lignin to be more reactive to combine with other materials, such as formaldehyde.

The thermal stability of non-phenolated and phenolated EFB-Lignin was evaluated based on the decomposition temperature at 5% weight loss ($T_{d5\%}$), 10% weight loss ($T_{d10\%}$), and 30% weight loss ($T_{d30\%}$) of the samples. The TG thermogram, as shown in Figure 8, indicates the weight loss percentage, while the first DTG curves indicate the corresponding rate of weight loss (Hussin et al., 2018). It can be observed from the TG graph of phenolated and non-phenolated EFB-Lignin, that the pyrolysis of lignin occurred in phases. First, as the temperature reaches 25°C–160°C, a little amount of water in the lignin begins to evaporate. The quality of lignin will deteriorate to some level at this time, but not rapidly. It primarily disintegrates glycan chains, some low molecular weight, and easily decomposable lignin groups. In the temperature range of 180°C–300°C, the C-chain of lignin begins to break, and the lignin macromolecules begin to degrade in the temperature range of 300°C–600°C (Gerassimidou et al., 2020). After phenolation, the lignin is mainly p-hydroxyphenyl lignin, as shown in the ^{1}H NMR, and the pyrolysis product produces a large amount of phenol, which also proves that the phenolation reaction can condense both phenol and lignin.

Nevertheless, the phenolated EFB-Lignin degraded earlier at $T_{d10\%}$, at 165°C, than the non-phenolated EFB-Lignin, which degraded at 192°C. A similar trend was also recorded for $T_{d30\%}$, as phenolated EFB-Lignin started to degrade earlier at 243°C, compared to non-phenolated EFB-Lignin, which started to degrade at 324°C. It was implied that the main lignin degradation starts at this stage. This stage of degradation implies the breakdown of weak chemical bonds in phenolated EFB-Lignin, such as hydroxyl bond, carbon bond in the alkyl side chain, and alkyl ether bond (Taleb et al., 2020). In addition, the breakage of methylene and methine bridges in the molecular chain of phenolated EFB-Lignin and
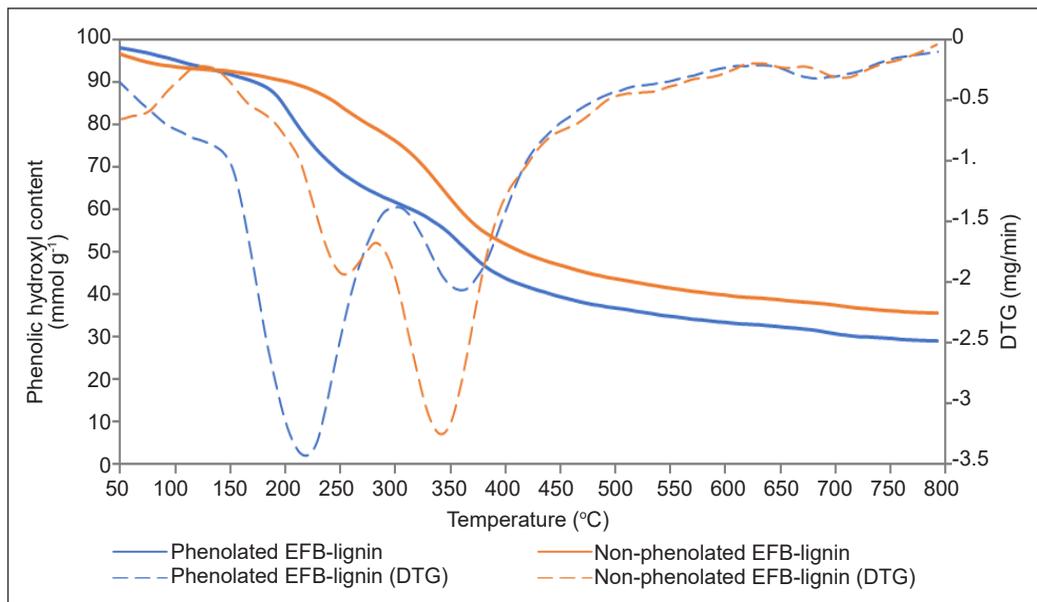
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Figure 8. TG and DTG thermograms of non-phenolated and phenolated EFB-lignin

the pyrolysis of aromatic rings led to rapid degradation (H. Zhang et al., 2020). It also confirms the findings of ^{1}H NMR, as it indicates the presence of aromatic rings following the phenolation process.

Observation on phenolated and non-phenolated lignins also discovered a high rate of weight loss in the temperature range of 350°C to 600°C, but the trend is gradually slowing down. It is mainly due to combining lignin macromolecules with air and oxidative degradation into volatile small molecules (Gerassimidou et al., 2020). After 600°C, the inorganic matter in the lignin is decomposed. When the temperature reaches 800°C, the weight loss tends to balance, and the residual rate is higher, indicating that the ash impurity content in the EFB lignin is relatively small.

Ház et al. (2019) reported that lignin with a higher proportion of guaiacyl units has higher activation energy and thermal stability, which is reflected in this study. From the FTIR spectrum (Figure 6), peaks related to guaiacyl units have disappeared in the phenolated EFB-Lignin, which explains its low thermal stability. The lower thermal stability also may be due to the higher hydroxyl content in phenolated EFB-Lignin, which volatilizes at a relatively low temperature at 202.9°C and 366.0°C (Jiang et al., 2018). The non-phenolated lignin did not undergo additional modification. Therefore, the aromatic structure of lignin was largely retained, which attributed to the higher thermal stability. It was also supported by Wang et al. (2019), that discovered in their study that the non-phenolated EFB-Lignin has stronger chemical linkages and carbohydrates in the lignin fractions, which helps to delay the thermal degradation.

At the final stage of degradation, both phenolated and non-phenolated EFB-Lignin did not record a remarkable difference in the percentage of char residues, as phenolated EFB-Lignin had 30% char residues and non-phenolated EFB-Lignin had 34% char residues. It can be inferred that the thermal stability of EFB-Lignin was affected much by phenolation (difference <5%), which has changed its structure. Hence, a deep understanding of the changes in EFB-Lignin structure from different modification conditions can reflect its functionality in its subsequent application. The low thermal stability of phenolated EFB-Lignin might also indicate its ability to react with other ingredients to produce adhesive.

CONCLUSION

This study explored the possibility of EFB-Lignin, derived from EFB-BL subjected to the PRC-RBMP and Lignoboost processes, to be used in a resin. It was phenolated to increase its phenolic hydroxyl content, and this study found that the best conditions for extracting lignin from the EFB-BL were at a 1:1 L/P ratio, a temperature of 100°C for 110 min, and the addition of 8% H_2SO_4 as a catalyst. This phenolation provided a high phenolic hydroxyl content of 7.9 mmol g^{-1} despite mild phenolation conditions. The parameters found in this study increased reactivity, as shown from the data of UV/vis, FTIR, ^{1}H NMR, and TG/DTG, indicating that more active sites in lignin are available to react with formaldehyde in a resin. Characterization of phenolated EFB-Lignin determined in this study could provide useful information for its future use in resin adhesives.

ACKNOWLEDGEMENTS

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