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Isolation and Characterization of Soda Lignin from OPEFB and Evaluation of its Performance as Wood Adhesive

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Abstract

The purpose of this study was to explore the mechanical properties of plywood panels that had been bound with lignin-phenol-formaldehyde (LPF) adhesive. LPF, composed of lignin that was extracted from Oil Palm Empty Fruit Bunch (OPEFB) fiber by soda pulping method and characterized by Fourier Transform Infrared (FT-IR), Nuclear Magnetic Resonance (HNMR), and Thermal Gravimetric Analyzer (TGA) analysis. Then, various compositions of soda lignin (10-50 wt %) were used as a phenol substitute in LPF synthesis. The characteristics of the synthesized adhesive were compared to the properties of phenol formaldehyde (PF) adhesive. Plywood was fabricated with LPF and its mechanical properties were studied and evaluated using industrial standards. The result indicates that the increase of phenol substitution with soda lignin, up to 40%, improves the mechanical properties of plywood. This research demonstrated the use of lignin as a renewable replacement of phenol in PF adhesive formulation.

[copyright information to be updated in production process]

Keywords:Lignin; Empty Fruit Bunch; Wood Adhesive; Formaldehyde Resin; Black Liquor

1. Introduction

Since the turn of the century, phenolic adhesives have been extensively employed in the wood industry. For the manufacturing of specific wood-based composites, such as plywood, laminated veneer lumber, glue laminated timber, fibreboard, and particleboard, phenol-formaldehyde (PF) adhesives are widely employed [1]. Additionally, they are commonly utilized as binders in manufacturing impregnated paper and thermal goods derived from mineral fibers [2]. In order to prepare phenolic resins, which are based on petroleum, phenol and formaldehyde are utilized as raw materials [3]. These are from non-renewable sources [4] and are connected with environmental concerns and health difficulties. Consequently, replacing these petroleum-based reagents with bio-based components is a motivating alternative to environmental, economic, and health perceptions [5]. Lignin can be used as a bio-based material to partially substitute the phenol in the phenolic adhesive due to its similar structure to phenol.

Coniferyl, sinapyl, and p-coumaryl alcohols are three phenylpropanoid monomers that combine to form the highly branching, three-dimensional, amorphous, polyphenolic biopolymer known as lignin [6]. Several inter-unit bonds link these structures, such as ethers of different sorts (α-O-4, β-O-4, and 4-O-5) and carbon-carbon connections. As a by-product of the pulping process, lignin (also known as soda lignin, Kraft lignin, and organosolv lignin) can have a variety of chemical compositions depending on the pulping material and conditions [7]. Among all the pretreatment techniques (Soda, kraft, organosolv) for developing bio-based adhesives, the soda pulping procedure appears to be

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extremely promising [8,9]. For non-woody materials, the soda pulping technique is regarded as a prospective pulping method [10]. The application of soda pulping for non-woody base materials, such as empty fruit bunch fiber, is growing in popularity [11,12]. Due to chain polymerization and the formation of additional phenolic groups, lignin isolation using the alkaline procedure has attracted much attention [13]. A lignin macromolecule is deteriorated by breaking alkyl ether linkages during alkaline pulping, increasing the number of aromatic hydroxyl groups in the lignin [14]. Because of all these reasons, it is possible to prepare wood adhesives using soda lignin as a co-monomer. Compared to petro-chemically produced phenol adhesive, lignin is less toxic to the environment and may offer significant economic benefits. In contrast to phenol, lignin's reactivity with formaldehyde during adhesive formation is moderate. For this reason, when lignin is used as a phenol substitute in the adhesive synthesis, the desired properties do not meet. Nevertheless, it is possible to overcome these limitations by enhancing lignin's reactivity through chemical modification (phenolation) and producing a new form of resin. Thus, this work aimed to isolate lignin by soda pulping and investigate whether soda lignin could replace phenol in a phenol-formaldehyde (PF) adhesive. The physical and mechanical characteristics of lignin-phenol-formaldehyde (LPF) adhesive were examined by varying the weight percent of lignin incorporation. Adhesive was characterized using FTIR, also mechanical properties such as shear strength, modulus of elasticity, modulus of rupture, and formaldehyde emission were investigated.

2. Experimental Methods

2.1 Extraction of Lignin

At first, 20 g of Oil Palm Empty Fruit Bunch (OPEFB) fiber was soaked in hot water at 80 °C for 1.5 h. After the treatment, the solid part was separated and washed with water. The fiber was then dried in an oven at 50 °C for 24 hours. Then the fiber was cut into small pieces, ground, and sieved using a 2-5 mm sieve tray. The lignin was then extracted from treated OPEFB fiber by the soda pulping process. This process was carried out in a rotary digester. For soda lignin extraction, the fiber was treated with an aqueous alkaline solution (15% NaOH; w/v), the fiber-to-solvent ratio was 1:8 (w/v), and all components were placed in a rotary digester. The treatment was conducted for 2 hours at 110 °C under continuous rotation. The motor-driven rotation stirred the contents of the digester. After completing the treatment, the delignified liquid was filtered as black liquor. Following that, the soda lignin was extracted from the black liquor. Black liquor was filtered with filter paper to separate the insoluble materials from the liquor. The pH level of the black liquor was 11.5. 5N sulfuric acid was added to the concentrated black liquor to precipitate the soda lignin until the pH reached 2 with continuous stirring. The precipitated soda lignin was then filtered, rinsed with distilled water, and dried in a vacuum oven at 45 °C for 48 hours. The yield of lignin was determined using the formula shown in Equation 1. This extracted soda lignin was further characterized and used to prepare LPF adhesive.

$$\%\, Yield\ of\ soda\ lignin = \frac{weight\ of\ the\ extracted\ soda\ lignin}{weight\ of\ OPEFB\ fiber\ used\ in\ extraction} \times 100 \qquad \textit{Equation 1}$$

2.2 Lignin Characterization

The ash content of soda lignin from OPEFB was determined based on the method proposed by [15]. The crucible was dried first at 105 ℃, nearly 500 mg of lignin samples were weighed into the crucible and calcined at 900 ℃ for four hours. The ash content was determined by calculating the percentage of lignin in the crucible after the burning process had finished. The carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) content was analyzed using a CHNS analyzer. The percentage of oxygen (O) was calculated by subtracting the C, H, N and S contents from 100% [16].

Using a Fourier Transform Infrared (FTIR) Spectrophotometer, functional groups analysis of lignin was performed (model: THERMO). The solid sample was put in the FTIR test area and analyzed with the help of OMNIC software. Each spectrum was recorded with 40 scans in the frequency range from 4000 cm^{-1} with resolution of 4 cm^{-1}. Bands indicative of lignin were compared with data from the literature.

The proton nuclear magnetic resonance (HNMR) spectroscopy was also employed to characterize the lignin. A Bruker AVANCE 400 NMR spectrometer was used to measure the one-dimensional (1D) HNMR spectra at room temperature and 500 MHz of operating frequency. DMSO-d_6 was used to dissolve the samples. The ^1H chemical shifts were calculated in parts per million. The thermogravimetric analyzer, (TGA) (TA instrument, TGA Q500) was used to determine the decomposition and oxidation of lignin. Each specimen was evaluated at a scanning temperature range of 25-600 °C and a heating rate of 20 °C/min with a weight of approximately 5.2 mg. The sample was placed in a platinum crucible under a nitrogen environment with a 40 ml/min flow rate.

2.3 Preparation of Adhesive

All the adhesives samples were prepared in a reaction fitted with an electric stirrer, heating mantle, thermometer, and condenser. In a typical synthesis, phenol and formaldehyde were reacted in a molar ratio (P/F) of 1:1.5, where the total formaldehyde was divided into two parts adding to the synthesis. The flask was filled with a mixture of phenol and 5N NaOH, and it was heated to 50 °C for 20 minutes while being agitated. Then formaldehyde (80% of the total amount) was poured into the flask and reacted at 60 °C for an hour. After that, the temperature was raised to 90 °C, and formaldehyde was added (20% remaining). The reaction was stopped when the viscosity (regularly checked at 25 °C with a viscometer (Brookfield) reached 400 to 600 cp. Once the adhesive cooled down, it was stored at 4 °C. After that, the adhesive was characterized in terms of viscosity, pH, solids content, and gel time following the ASTM D 4426-01 method. For the preparation of the LPF adhesive, the same technique was followed, only 10 to 50% of the phenol was substituted with soda lignin.

2.4 Plywood Manufacture and Testing

Red-Meranti veneer measuring 300 mm × 300 mm × 3.3 mm (width×length×thickness) was used to fabricate the plywood sample. An equal amount of wood adhesive was applied to ensure consistency during plywood production. The adhesive was put on both sides of a core veneer using a glue spreader. The plywood was allowed to dry at room temperature for at least 5 minutes prior to cold-pressed for 20 minutes at 9 kg/cm^2 pressure. After 20 minutes, the plywood sample was withdrawn from the cold press and allowed to rest for 5 minutes prior transferred to the hot press device. During the hot pressing process, the pressure was maintained at 9 kg/cm^2, and the temperature was maintained at 120 °C for 240 seconds. Following the completion of the hot press, the plywood product was allowed to cool at room temperature before further testing. The mechanical characteristics commonly evaluated in plywood panel applications were studied. Plywood panels' modulus of elasticity (MOE), modulus of rupture (MOR), and tensile strength values were calculated using the standards established by EN 314 (1993) and EN 310 (1993).

2.5 Formaldehyde Emission Test

The plywood panel's formaldehyde emissions was tested using the desiccator method. A crystallizing dish with a diameter of 120 mm and a height of 60 mm was positioned in the middle of the desiccator (inner capacity 9-11 liters). About 300 ml of distilled water was filled in the crystallizing dish. After 24 hours, 25 ml of distilled water was taken to measure the formaldehyde concentration because it absorbed the formaldehyde released from test pieces. In brief, a conical flask with a co-ground cap was filled with 25 ml of sample solution. A conical flask was poured with 25 ml of acetyl-acetone ammonium acetate solution. The co-ground stopper of the conical flask was heated to 65 °C for 10 minutes. A UV-Vis spectrophotometer was used to measure the absorbance of the solution at a wavelength of 412 nm.

The formaldehyde concentration of the sample solution can be calculated by using Equation 2.

$$C = F \times (A_d - A_b) \qquad \textit{Equation 2}$$

Where,

C=Formaldehyde concentration of test pieces (mg/L);
A_d=Absorbance of a sample solution;
A_b=Absorbance of the blank test (freshly distilled water);
F=Inclination of the calibration curve (mg/L).

3. Results and Discussion

3.1 Yield of Soda Lignin

The yield of dried soda lignin extracted from OPEFB fiber was 15 wt%. The yield percentages were determined on a dry-weight basis. The ash content and elemental composition of soda lignin are presented in Table 1. The table shows that the ash content in the soda lignin was 0.93% (<1%). Low ash content indicates that the lignin obtained has low inorganic compounds and dirt residue from the raw fibers [17]. Elemental analysis of hardwood lignin shows 59.8% C, 6.4% H and 33.7% O [18]. Table 1 reveals that the soda lignin contains 46.67% C, 3.85% H, 0.48% N, 0.21% S and 48.79% O. Compared to Khan and Ashraf [18], the lower C and higher O may be due to the existence of

a higher number of syringyl units or saccharides in soda lignin [18]. The percentage of nitrogen in the soda lignin suggests that the nitrogen was bound tightly to lignin molecules as a protein-lignin complex and cannot be separated during lignin isolation [17]. Thus, less nitrogen content (0.48%) in lignin indicates a high-purity product. On the other hand, the sulfur content in soda lignin was also very low (0.21%). These values are similar to those reported in the literature [19,20].

Table 1. Physical properties of extracted lignin from OPEFB fiber via the soda pulping method.

Property	Soda Lignin
Ash content	0.93
Carbon	46.67
Hydrogen	3.85
Nitrogen	0.48
Sulfur	0.21
Oxygen	48.79

3.2 Characterization of Lignin

The functional group and chemical structure of soda lignin were determined using FT-IR spectra. Figure 1 shows the FTIR spectra of soda lignin. Band designations are provided based on a review of the relevant literature [21]. Several functional groups were detected by the FTIR spectrum, including hydroxyl groups O-H, aromatic skeletal vibrations from the syringyl group, carbonyl stretching from the unconjugated ketone and carbonyl groups. The Infrared spectrum of soda lignin (Figure1) is distinguished by a large peak at 3418cm^{-1}, which corresponds to -OH hydrogen bonds, which indirectly confirm the existence of phenolic groups in the soda lignin. The reactivity of soda lignin is essentially influenced by the number of phenolic hydroxyl [22]. Therefore, when lignin is utilized to produce phenolic resin, the presence of this group tends to increase lignin's reactivity toward formaldehyde. So, the activity of soda lignin is higher, which is suitable for utilization in the preparation of phenol formaldehyde wood adhesive. A sharp peak at 2937cm^{-1} can be assigned to C-H stretching in methyl, methylene and methoxyl groups. Carbonyl stretching unconjugated ketones and carbonyl groups are responsible for the tiny peak at 1635cm^{-1}. At 1519cm^{-1}, a sharp peak reveals aromatic skeletal vibrations. Secondary alcohol peaks at 1119cm^{-1} have been attributed to syringyl and guaiacyl type ring breathing with C-O stretching. The presence of guaiacyl-type (G) confirms that soda lignin from OPEFB possesses a potential active site for polymerization. The presence of a G-type unit revealed that soda lignin could react with formaldehyde and crosslink with formaldehyde in the same way as in the phenol-formaldehyde condensation reaction [23].

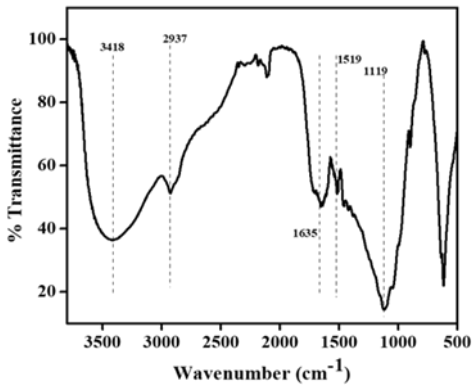

Figure 1. FTIR spectrum of soda lignin

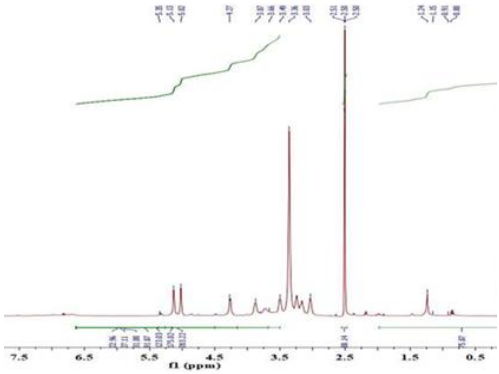

Figure 2. HNMR of soda lignin

Further information for the structure of the extracted soda lignin was obtained by HNMR spectroscopy. Figure 2 presents the HNMR spectra of soda lignin. Protons in DMSO were indicated by a signal about 2.5 ppm. The broad signal at 5.35 ppm (Figure 2) corresponds to H-α of β-5′ structures. H-β, and OH in β-O-4′ were responsible for the signals at 4.27 ppm and 5.13 ppm, respectively. The aliphatic moiety may be responsible for signals between 0.8 and 1.5 ppm [24]. As a result of its connection to the ratio of G and S units, the proton of methoxyl gives a strong signal at 3.87 ppm, which is consistent with the FTIR analysis (Fig 1).

Figure 3 shows the TGA curve of soda lignin. Soda lignin was degraded across a wide temperature spectrum, from around 200 to 800 °C. The graph shows that there are three stages to weight loss. Water and other solvents, such as formaldehyde and alcohols, volatilize at temperatures between 20 and 100 °C, causing the first weight-loss phase to occur [25]. The adjacent hydroxyl reaction reduced moisture during the second stage (200-350 °C), followed by creating an ether bond and the subsequent degradation of lignin. The TGA fraction significantly dropped during the second stage, reaching 35%. Lignin was degraded at temperatures higher than 350 °C. High temperatures caused the structure to deteriorate [26]. Notably, at 800 °C, about 25% of the non-volatile solid residue had not been completely burned. This result demonstrates that soda lignin is stable at high temperatures and can be related to the high degree of branching and development of a highly condensed aromatic structure in soda lignin. The thermogravimetric analysis shows that these lignin are not damaged at 200 °C.

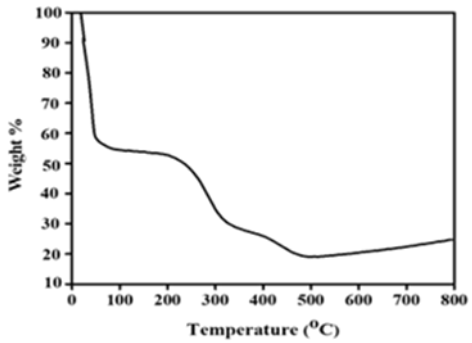

Figure 3. TGA of soda lignin

3.3 Lignin Valorization

For the production of wood adhesive, soda lignin from OPEFB fiber was chosen and employed. The dry tensile strength, MOE and MOR values of plywood bonded with adhesive made with various weight ratios of lignin/phenol (0/100, 10/90, 20/80, 30/70, 40/60, and 50/50) were tested at 160 °C and 150 seconds of press time (a hot press machine)

Figure 4 illustrates a typical FTIR spectrum of PF and LPF adhesive (40% LPF). This measurement aimed to examine the impact of reacting between PF and soda lignin on the adhesive's functional group. The spectral variance between PF and LPF adhesive was detected at 1006 cm^{-1}, attributed to the presence of C-O stretching vibration of aliphatic C-OH, aliphatic C-O (Ar) and methylol C-OH [27]. Due to the existence of additional species, the peaks at 1006 cm^{-1} of the LPF adhesive were broader than those of the PF adhesive (not only methylol-OH but also alphatic-OH in LPF). The PF adhesive's bond at 1223 cm^{-1} was larger than the LPF adhesive's, indicating that the phenolic -OH groups in PF had undergone more C-O stretching.

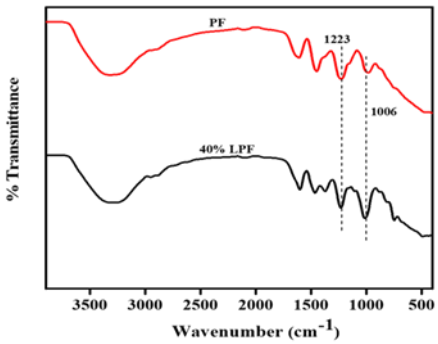

Figure 4. FTIR spectra of phenol formaldehyde (PF) and 40% lignin-phenol-formaldehyde (LPF) adhesives

Table 2 illustrates the mechanical and physical properties of the plywood test panels prepared using PF and LPF adhesives. There was a statistically significant difference between PF and 40% LPF adhesive. Compared to PF adhesive, replacing up to 40% lignin (40%LPF) enhanced the mechanical properties. The strength of PF adhesive was 2.1 MPa, whereas the strength of 40% LPF was 2.6 MPa. The result suggests that soda lignin containing LPF adhesive had better bond strength under the current experimental conditions. It appears that lignin copolymerizes with PF, resulting in improved bond strength in LPF. The higher tensile strength of 40% LPF can be explained by the increased incorporation of lignin, crosslinking between the polymer chains increases, providing better bonding in wood composites [28]. A decrease in tensile strength was noticed on 50 wt% loading of soda lignin in LPF. Due to the excess lignin in the adhesive, tensile strength has been reduced [29].

Table 2. Mechanical properties of plywood panels prepared with phenol-formaldehyde (PF) and lignin-phenol-formaldehyde (LPF) adhesives.

Adhesive type	Composition lignin/phenol (w/w)	Dry tensile strength (MPa)	Modulus of Elasticity (MPa)	Modulus of Rupture (MPa)	Formaldehyde emission (mg/L)
PF	0/100	2.1	3475	42	1.73
10% LPF	10/90	1.9	3240	44	1.58
20% LPF	20/80	2.3	3350	49	1.51
30% LPF	30/70	2.4	3680	52	1.37
40% LPF	40/60	2.6	3810	56	1.08
50% LPF	50/50	1.9	3140	38	1.48

The values of MOE and MOR were found as 3475 MPa and 42 MPa for the plywood panels prepared with PF adhesive. The values for the plywood samples made with 40% LPF were 3810 MPa and 56 MPa, respectively. It can be explained by the fact that better crosslinking of lignin with formaldehyde in LPF adhesive, which makes the panel stronger [30]. From Table 2, it is shown that 40% of LPF-adhesive-treated plywood panels emit significantly less formaldehyde than PF-adhesive-treated plywood panels. Due to the penetration of PF adhesive into the wood and the substitution of lignin for PF adhesive, plywood panels' formaldehyde emission has been reduced [31]. As the percentage rises above 50%, a noticeable increase in formaldehyde emission is seen. A similar finding was reported by Reh et al. [32] and they explained that this increase is typically caused by inadequate PF wood penetration [32].

4. Conclusion

The soda pulping method was used to extract lignin from OPEFB fiber, and its composition and physicochemical characteristics were reported. FTIR, HNMR, and TGA were done for soda lignin characterization. Due to its greater number of activated free ring locations and higher thermal decomposition temperature, soda lignin is considered a better alternative in the synthesis of LPF resins, according to its structural and thermal properties. Increasing the

substitute amount of soda lignin up to 40 wt% in PF adhesive enhanced the mechanical strength and reduced the formaldehyde emission of the plywood panels.

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References

[1] Zhang R, Jin X, Wen X, Chen Q, Qin D. Alumina nanoparticle modified phenol-formaldehyde resin as a wood adhesive. Int. J. Adhes. Adhes. 2018;81:79–82. doi: 10.1016/j.ijadhadh.2017.11.013.

[2] Kumar A, Jyske T, Petrič M. Delignified wood from understanding the hierarchically aligned cellulosic structures to creating novel functional materials: A review. Adv. Sustain. Syst. 2021;5(5):1-45. doi: 10.1002/adsu.202000251.

[3] Sarika PR, Nancarrow P, Khansaheb A, Ibrahim T. Bio-based alternatives to phenol and formaldehyde for the production of resins. Polymers (Basel). 2020;12(10): 1–24. doi: 10.3390/polym12102237.

[4] Hussin MH, Samad NA, Latif NHA, Rozuli NA, Yusoff SB, Gambier F, Brosse N. Production of oil palm (Elaeis guineensis) fronds lignin-derived non-toxic aldehyde for eco-friendly wood adhesive. Int. J. Biol. Macromol. 2018;113:1266–1272. doi: 10.1016/j.ijbiomac.2018.03.048.

[5] Dubé MA, Gabriel VA, Pakdel AS, Zhang Y. Sustainable polymer reaction engineering: Are we there yet? Can. J. Chem. Eng. 2021;99(1):31-60. doi: 10.1002/cjce.23865.

[6] Liao JJ, Latif NHA, Trache D, Brosse N, Hussin MH. Current advancement on the isolation, characterization and application of lignin. Int. J. Biol. Macromol. 2020;162: 985–1024. doi: 10.1016/j.ijbiomac.2020.06.168.

[7] Yang W, Rallini M, Natali M, Kenny J, Ma P, Dong W, Torre L, Puglia D. Preparation and properties of adhesives based on phenolic resin containing lignin micro and nanoparticles: A comparative study. Mater. Des. 2019;161:55-63. doi: 10.1016/j.matdes.2018.11.032.

[8] Verma S, Hashmi SAR, Mili M, Hada V, Prashant N, Naik A, Rathore SKS, Srivastava AK. Extraction and applications of lignin from bamboo: A critical review. Eur. J. Wood Wood Prod. 2021;79(6):1341–1357. doi: 10.1007/s00107-021-01743-w.

[9] Carvajal JC, Gómez A, Cardona CA. Comparison of lignin extraction processes: Economic and environmental assessment. Bioresour. Technol.2016;214: 468–476. doi: 10.1016/j.biortech.2016.04.103.

[10] Liu Z, Wang H, Hui L. Pulping and papermaking of non-wood fibers. In: Kazi SN, editor. Pulp and Paper Processing. 2018; 3–32. doi: 10.5772/intechopen.79017.

[11] Ferrer A, Vega A, Ligero P, Rodríguez A. Pulping of empty fruit bunches (EFB) from the palm oil industry by formic acid. BioResources. 2011;6(4):4282–4301.

[12] Wan Rosli WD, Law KN, Zainuddin Z, Asro R. Effect of pulping variables on the characteristics of oil-palm frond-fiber. Bioresour. Technol. 2004;93(3): 233–240. doi: 10.1016/j.biortech.2003.11.016.

[13] Schutyser W, Renders T, Van Den Bosch S, Koelewijn SF, Beckham GT, Sels BF. Chemicals from lignin: An interplay of lignocellulose fractionation, depolymerisation, and upgrading. Chem. Soc. Rev.2018;47(3): 852–908. doi: 10.1039/c7cs00566k.

[14] Santos JI, Fillat U, Martin-Sampedro R, Eugenio ME, Negro MJ, Ballesteros I, Rodriguez A, Ibarra D. Evaluation of lignins from side-streams generated in an olive tree pruning-based biorefinery: Bioethanol production and alkaline pulping. Int. J. Biol. Macromol. 2017;105(1): 238–251. doi: 10.1016/j.ijbiomac.2017.07.030.

[15] Ibrahim MnM, Zakaria N, Sipaut CS, Sulaiman O, Hashim R. Chemical and thermal properties of lignins from oil palm biomass as a substitute for phenol in a phenol formaldehyde resin production. Carbohydr. Polym. 2011;86(1):112–119. doi: 10.1016/j.carbpol.2011.04.018.

[16] Hussin MH, Rahim AA, Ibrahim MNM, Brosse N. Physicochemical characterization of alkaline and ethanol organosolv lignins from oil palm (Elaeis guineensis) fronds as phenol substitutes for green material applications. Ind. Crops Prod. 2013;49:23–32. doi: 10.1016/j.indcrop.2013.04.030.

[17] Risanto L, Hermiati E, Sudiyani Y. Properties of lignin from oil palm empty fruit bunch and its application

for plywood adhesive. Makara J. Technol. 2014;18(2):67-75.doi: 10.7454/mst.v18i2.2944.
[18] Khan MA, Ashraf SM. Development and characterization of a lignin-phenol-formaldehyde wood adhesive using coffee bean shell. J. Adhes. Sci. Technol. 2005;19(6): 493–509. doi: 10.1163/1568561054352577.
[19] Xue Y, Li Y, Liu Z, Hou Y. Structural changes of lignin in soda delignification process and associations with pollution load. BioResources. 2019;14(4):7869–7885. doi: 10.15376/biores.14.4.7869-7885.
[20] Borrero-López AM, Blanquez A, Valencia C, Hernandez M, Arias ME, Eugenio ME, Fillat U, Franco JM. Valorization of soda lignin from wheat straw solid-state fermentation: Production of oleogels. ACS Sustain. Chem. Eng. 2018;6(4): 5198–5205. doi: 10.1021/acssuschemeng.7b04846.
[21] Ibrahim MNM, Iqbal A, Shen CC, Bhawani SA, Adam F. Synthesis of lignin based composites of TiO2 for potential application as radical scavengers in sunscreen formulation. BMC Chem., 2019;13(3):1–15. doi: 10.1186/s13065-019-0537-3.
[22] El Mansouri NE, Salvadó J. Structural characterization of technical lignins for the production of adhesives: Application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins. Ind. Crops Prod. 2006;24(1): 8–16. doi: 10.1016/j.indcrop.2005.10.002.
[23] Moubarik A, Grimi N, Boussetta N, Pizzi A. Isolation and characterization of lignin from Moroccan sugar cane bagasse: Production of lignin-phenol-formaldehyde wood adhesive. Ind. Crops Prod. 2013;45:296–302. doi: 10.1016/j.indcrop.2012.12.040.
[24] Aziz NA, Latip AFA, Peng LC, Latif NHA, Brosse N, Hashim R, Hussin MH. Reinforced lignin-phenol-glyoxal (LPG) wood adhesives from coconut husk. Int. J. Biol. Macromol. 2019;141:185–196. doi: 10.1016/j.ijbiomac.2019.08.255.
[25] Ovejero-Pérez A, Rigual V, Domínguez JC, Alonso MV, Oliet M, Rodriguez F. Acidic depolymerization vs ionic liquid solubilization in lignin extraction from eucalyptus wood using the protic ionic liquid 1-methylimidazolium chloride. Int. J. Biol. Macromol. 2020;157: 461–469. doi: 10.1016/j.ijbiomac.2020.04.194.
[26] Sabaruddin FA, Paridah MT, Sapuan SM, IIyas RA, Lee SH, Abdan K, Mazlan N, Roseley ASM, Khalill HPSA.The effects of unbleached and bleached nanocellulose on the thermal and flammability of polypropylene-reinforced kenaf core hybrid polymer bionanocomposites. Polymers (Basel). 2021;13:(1): 1–19, 2021, doi: 10.3390/polym13010116.
[27] Yuan Q, Nour-Eddine EM, Huang F. Preparation and characterization of phenol-formaldehyde resins Modified with Alkaline Rice Straw Lignin. BioResources,/ 2018;13(4): 8061–8075, 2018, doi: 10.15376/biores.13.4.8061-8075.
[28] Zhao M, Jing J, Zhu Y, Yang X, Wang X, Wang Z.. Preparation and performance of lignin-phenol-formaldehyde adhesives. Int. J. Adhes. Adhes. 2016;64: 163–167, doi: 10.1016/j.ijadhadh.2015.10.010.
[29] Gadhave RV, Srivastava S,, Mahanwar PA, Gadekar PT. Lignin: renewable raw material for adhesive. Open J. Polym. Chem. 2019;9(2):27-38. doi: 10.4236/ojpchem.2019.92003.
[30] Cavdar AD, Kalaycioglu H, Hiziroglu S. Some of the properties of oriented strandboard manufactured using kraft lignin phenolic resin. J. Mater. Process. Technol.2 008;202(1-3): 559–563. doi:10.1016/j.jmatprotec.2007.10.039.
[31] Benhamou AA, Boussetta A, Kassan Z, Nadifiyine M, Salim MH, Grimi N, ElAchaby M, Moubarik A. Investigating the characteristics of cactus seeds by-product and their use as a new filler in phenol formaldehyde wood adhesive. Int. J. Adhes. Adhes. 2021;110:102940. doi: 10.1016/j.ijadhadh.2021.102940.
[32] Réh R, Kristak L, Sedliacik J, Bekhta P., Bozikova M, Kunecova D, Vozarova V, Tudor EM, Antov P, Savov V. Utilization of birch bark as an eco-friendly filler in urea-formaldehyde adhesives for plywood manufacturing. Polymers (Basel). 2021;13(4) 1–21. doi: 10.3390/polym13040511.