

Enhanced Performance of Lignin Recovery with a Carbon Dioxide Acidification Method

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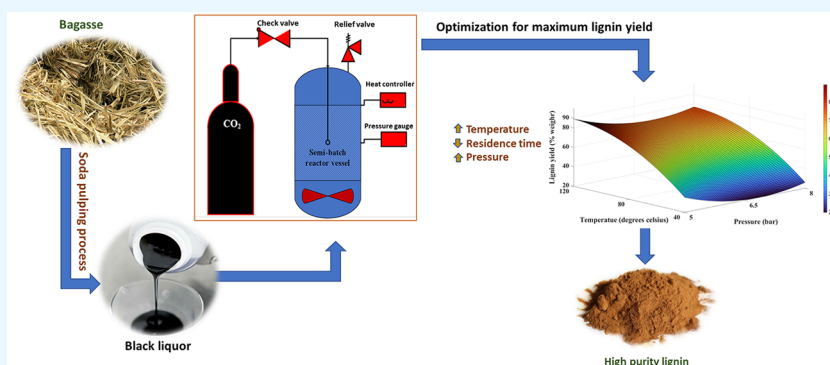
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ABSTRACT: Lignin particles were recovered from the bagasse soda pulping black liquor by acidification with carbon dioxide continuously fed in a semibatch reactor. An experimental model based on the response surface methodology was selected to investigate the effect of parameters and optimize the process for maximizing the lignin yield, and the physicochemical properties of the obtained lignin under the optimum conditions were investigated for further potential applications. A total of 15 experimental runs of three controlled parameters including temperature, pressure, and residence time were carried out based on the Box–Behnken design (BBD). The mathematic model for lignin yield prediction was successfully estimated at 99.7% accuracy. Temperature played a more significant role in lignin yield than pressure and residence time. Higher temperature could facilitate a higher lignin yield. Approximately 85 wt % lignin yield was obtained under the optimum conditions with a purity higher than 90%, high thermal stability, and slightly broad molecular weight distribution. The *p*-hydroxyphenyl–guaiacyl–syringyl (HGS)-type lignin structure and spherical shape were confirmed by Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FE-SEM). These characteristics confirmed that the obtained lignin could be used in high-value products. Moreover, this work indicated that the CO₂ acidification unit for lignin recovery could be efficiently improved for achieving high yield and purity from black liquor by adjustment of the process.

1. INTRODUCTION

Sugarcane is an important crop and one of the main sources of economy in Thailand. As a result, there is a large amount of sugarcane bagasse as a byproduct from the sugar industry left over every year in Thailand.¹ Sugarcane bagasse has become one of the main raw materials in the pulp and paper industry in Thailand. Plant biomass such as sugarcane bagasse is mainly composed of polysaccharides (cellulose and hemicellulose) and aromatic polymers (lignin). Bagasse as a nonwood plant contains about 23–32% of lignin per mass of bagasse,² which is left over in the byproduct from pulp production. It is estimated that 7.5 million tons of lignin is available each year in Thailand from the sugar industry³ and about 100 million tons in the world for utilization.⁴ This is one of the reasons that lignin has considerably gained research attraction in terms of chemical structure characterizations^{5–8} and related properties for different fields of applications in the last decade.^{9–14}

The lignin recovery process from black liquor of the pulping process has been carried out to increase its value instead of burning to produce electricity and to serve the need of product development from lignin since the beginning of the 20th century.¹⁵ Precipitation by acidification is the most current common method for recovering lignin from black liquor. LignoBoost,¹⁶ LignoForce,¹⁷ and Sequential Liquid-Lignin Recovery and Purification (SLRP)¹⁸ are the names of recently commercialized processes for lignin recovery using CO₂ in the

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form of carbonic acid as an acidifying agent. The processes have their differences and advantages. LignoBoost and LignoForce operate at a lower temperature and pressure for CO₂ acidification than those of SLRP.¹⁵ Several articles have reported about the various aspects of each process.^{19–22} Some reports also demonstrated the effect of operation conditions on the lignin properties from mostly kraft pulping black liquor of soft or hardwood.^{23–29} However, there is no statistic study for an optimum process to maximize the lignin yield from soda pulping black liquor of nonwood biomass under various conditions using a CO₂ acidification unit in terms of different temperatures, pressures, and operation times of CO₂ acidification and the properties of the lignin product. In this paper, lignin was separated from bagasse soda pulping black liquor by acidification with CO₂. We investigated the effect of operation temperature (40–120), pressure (5–8 bar), and residence time (30–120 min) of CO₂ acidification on the lignin yield and to maximize the lignin yield from the process using the response surface methodology for saving time and energy. Moreover, physicochemical properties of the obtained lignin from the optimum conditions were studied to indicate the potential use of lignin in various applications.

2. EXPERIMENTAL SECTION

2.1. Materials. Industrial bagasse soda pulping black liquor was obtained from Environment Pulp and Paper Company Limited, Nakhon Sawan, Thailand. Carbon dioxide (CO₂, 99.5%) was purchased from Praxair (Thailand) Co., Ltd. and used in the acidification process. Kraft lignin (alkaline), potassium hydroxide, and para-hydroxybenzoic acid were purchased from Sigma Aldrich. Sulfuric acid (H₂SO₄, 98%) and hydrochloric acid (HCl, 37%) were purchased from Honeywell Fluka.

2.2. Characterization of Black Liquor. The pH of the black liquor was measured with silver/silver chloride (Ag/AgCl) pH electrodes (Seven Easy S20, Thermo Scientific) calibrated for pH 4.0, 7.0, and 10. The dissolved solid content in the black liquor was measured according to the standard method TAPPI T650 om-09.³⁰ Black liquor was dried using an oven at 100 °C until a constant weight of dry black liquor samples was recorded. The Klason lignin (KL), acid-insoluble lignin, content in black liquor was measured by precipitation via acidification using a 72 wt % sulfuric acid solution followed by gravimetric analysis according to TAPPI T222 om-02.³¹ The acid-soluble lignin (ASL) content was determined using an ultraviolet–visible (UV–vis) spectrophotometer (LABDA 650, PerkinElmer) at a wavelength of 280 nm following the TAPPI UM 250 standard method.³²

2.3. Lignin Recovery Process. A 500 mL lab-scale semibatch reactor was designed and constructed to generate an acidification reaction. A total of 400 mL of black liquor was fed in the reactor and then heated to the desired reaction temperature. The black liquor was acidified with carbon dioxide at controlled pressure. Lignin was allowed to precipitate for the designated time; then, the lignin slurry was centrifuged to separate the liquid and precipitated solid. The lignin solid was purified by washing with 2M sulfuric acid followed by deionized water until the pH value was 5 and further dried with a freeze drier (α 1-2 LDplus, Christ) at a temperature of –80 °C.

2.4. Characterization of Lignin. The mass yield was calculated based on the Klason lignin as shown in eq 1

$$\text{lignin yield (\%)} = \frac{\text{WPF} \times \text{AILPF}}{\text{WBL} \times \text{SBL} \times \text{AILSBL}} \times 100 \quad (1)$$

where WPF is the weight of the precipitated fraction, AILPF is the percent of acid-insoluble lignin in the precipitated fraction, WBL is the weight of the black liquor, SBL is the percent solid content of the black liquor, and AILSBL is the percent of acid-insoluble lignin in the solid of the black liquor.

The relative proportions of carbon (C), hydrogen (H), and nitrogen (N) in lignin samples were analyzed according to ASTM with a LECO model CHN682. The samples were first dried in an oven at 105 °C overnight to remove any moisture.

The sodium ion content in the lignin sample was determined using an atomic absorption spectrophotometer (PinAAcle 900F, PerkinElmer). The samples were digested by a microwave digestion method at 200 °C for 20 min prior the measurement.

Functional groups of lignin samples were analyzed by Fourier transform infrared spectroscopy (FTIR). Measurements were performed using a Nicolet 6700 with an attenuated total reflection (ATR) accessory, Thermo Scientific. The spectra were recorded in the transmittance mode in the range of 4,000–400 cm^{–1}, with 32 scans, at a resolution of 4 cm^{–1}.

The carboxylate group and phenolic hydroxyl contents of lignin were calculated using an automatic potentiometric titrator (T50, Mettler Toledo) following a previously reported procedure.³³ Next, 0.03 g of dried lignin was added to 100 mL of deionized water containing 1 mL of 1.2 mol L^{–1} potassium hydroxide. After mixing for 5 min, 4 mL of 0.5 vol % para-hydroxybenzoic acid solution was added as an internal standard, and the solution was titrated with 0.1 mol L^{–1} hydrochloric acid solution.

Thermal stability was studied by thermogravimetric analysis (TGA) on an STA 449 F5 Jupiter from the Netzsch instrument under a N₂ atmosphere. Approximately 1.0 mg of the sample was heated in a porcelain crucible from 30 to 600 °C at a rate of 10 °C min^{–1}.

The relative molecular weight of lignin was determined using a gel permeation chromatography system (GPC) with a standalone HPLC instrument (Waters Breeze) consisting of HPLC 1525 binary pumps with a 2414 refractive index detector and a 2487 dual λ absorbance UV/vis detector operating with a GPC KF-805L column (Shodex) at 40 °C, with tetrahydrofuran as the mobile phase. A total of 100 μ L of sample solution at 1 mg mL^{–1} in THF was injected into the column at a flow rate of 0.5 mL min^{–1}. Molecular weight determinations (M_n and M_w) were based on calibrations with monodisperse polystyrene standards (M_w = 500, 2000, 10,000, 70,000, and 150,000). Prior analysis, the lignin was acetylated with pyridine/acetic chloride (1:1) overnight. After the reaction, the samples were washed to remove the byproduct and impurities with deionized water and dried in a vacuum oven at 40 °C overnight.

2.5. Experimental Design and Optimization Analysis. The experimental design was based on a Box–Behnken design (BBD) of the response surface methodology (RSM) using Minitab software version 19.2020.1 to statistically evaluate the effect of three independent variables, residence time, temperature, and pressure, on the response of the lignin yield to optimize these variables. The values for each level of the experimental factor are shown in Table 1. The design of the experimental models was performed using statistical software, which resulted in 15 experimental runs. To maximize the lignin

Table 1. Experimental Range and Factor Level of the BBD for Three Factors and Three Levels

parameters	range and levels		
	−1	0	1
residence time, X_1 (min)	30	75	120
temperature, X_2 (°C)	40	80	120
pressure, X_3 (bar)	5	6.5	8

yield achieved from bagasse soda black liquor and to study the relationship between process parameters affecting the response, a quadratic polynomial equation was used, which is presented in eq 2

$$Y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_3x_3 + \beta_1x_1^2 + \beta_2x_2^2 + \beta_3x_3^2 + \beta_{12}x_1x_2 + \beta_{13}x_1x_3 + \beta_{23}x_2x_3 \quad (2)$$

where Y is the predicted response, which represents the lignin yield. In the present study, the three parameters residence time (x_1), temperature (x_2), and pressure (x_3) are considered in the BBD for measuring the lignin yield from the black liquor. In the quadratic polynomial equation mentioned above, β_0 indicates the set term; β_1 , β_2 , and β_3 are the terms responsible for the linear affect; and β_{12} , β_{13} , and β_{14} are the interaction terms for the calculation of the lignin yield. The significance of the parameters can be determined from the mathematical model, which explains the relationship between the process variables and response from variance analysis and can be presented by the response surface plot. The significance of the generated model was expressed in terms of the p value and coefficient of determination (R^2) from analysis of variance (ANOVA). For the determination of the optimum conditions for the highest lignin yield, the trial and error were plotted, which is also constructed using Minitab software.

3. RESULTS AND DISCUSSION

3.1. Statistical Analysis of the Experimental Design by a Response Model. An acidification process using carbon dioxide was employed in this study for the recovery of lignin from soda black liquor, a byproduct of cellulose production from bagasse. To receive the maximum lignin yield and improve the efficiency of the process, the parameters in the acidification process were optimized using the response surface methodology with the BBD. The BBD experimental data were employed to develop a full quadratic model equation as shown in eq 3. The experimental conditions for conducting the BBD with Minitab software and the predicted values of the lignin yield which were compared with the experimental data are summarized in Table 2.

$$Y = 172.0 - 0.262(\text{time}) + 2.052(\text{temp}) - 62.52(\text{pressure}) + 0.002(\text{time})^2 - 0.008(\text{temp})^2 + 4.546(\text{pressure})^2 - 0.003(\text{time} \times \text{temp}) + 0.027(\text{time} \times \text{pressure}) - 0.013(\text{temp} \times \text{pressure}) \quad (3)$$

The accuracy and applicability of the regression quadratic polynomial equation were verified by correlating the experimental and predicted data over the factors under consideration through the coefficient of determination (R^2) (Table 3). Generally, the R^2 value between 0.80 and 1 represents a good model. The predicted R^2 value of 0.9872 in

Table 2. Condition Design Using the Response Surface Methodology with the Box–Behnken Design and Experimental/Predicted Data of the Response

run order	variables			lignin yield (%)	
	time (min)	temp (°C)	pressure (bar)	actual	predicted
1	30	80	5	74.01	74.51
2	30	40	6.5	20.82	20.18
3	75	40	8	26.90	27.83
4	120	40	6.5	28.60	28.14
5	75	120	5	79.39	78.43
6	75	40	5	33.39	33.48
7	120	80	8	66.61	66.07
8	75	120	8	69.88	69.76
9	30	80	8	64.01	63.67
10	120	80	5	69.25	69.56
11	75	80	6.5	55.42	54.50
12	75	80	6.5	53.32	54.50
13	30	120	6.5	72.42	72.85
14	75	80	6.5	54.79	54.50
15	120	120	6.5	61.73	62.34

Table 3. Analysis of Variance (ANOVA) for the Estimated Linear and Interaction Effects of the Process Parameters on the Lignin Yield^a

term	lignin yield
p -value of model	0.000
p -value of time	0.165
p -value of temperature	0.000
p -value of pressure	0.000
S	1.102
R -squared (adj)	0.9966
R -squared (pred)	0.9872

^a* p -value less than 0.05 is considered significant.

this study is in reasonable agreement with the adjusted R^2 value of 0.9966 and close to 1, which is an important indicator to determine the accuracy of the model, indicating high prediction ability compared with the actual value. The comparison between the predicted values and the experimental values of the response (lignin yield) is exhibited in Figure 1. The results indicated that the observed values were distributed relatively near to a straight line, and an adequate correlation between these values is observed. The probability value or p value was employed as a tool to identify the significance of each coefficient and indicated the interaction strength between each linear and independent term variable on the response. The p value of the model shows the significance level ($p < 0.05$) (Table 3), indicating that the model fits against the experimental data. The p values for the two factors (temperature and pressure) were less than 0.05. Therefore, the temperature and the pressure significantly influenced lignin recovery. However, the pressure was not significant ($p > 0.05$).

3.2. Effect of Residence Time, Temperature, and Pressure on the Lignin Yield. For the model equation based on eq 3, the terms residence, time, and pressure had a negative coefficient in the equation of lignin yield. This indicated that the obtained lignin yield was increased with a decrease in the residence time and pressure. On the other hand, the term temperature showed significant positive coefficients in the equation, implying that the lignin yield depends mainly on temperature. The effect of the two factors on lignin yield is

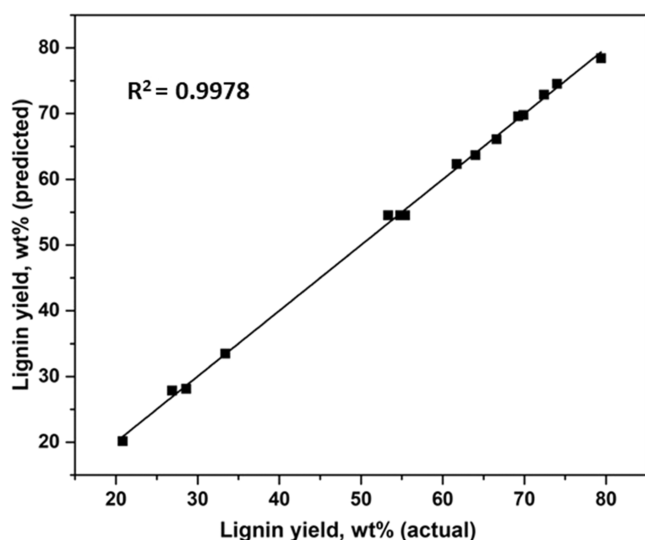


Figure 1. Plots of predicted and experimental (actual) values of lignin yield.

represented by each three-dimensional (3D) response surface plot for determination of a minimum and maximum quantity of lignin when considering two factors at a time (Figure 2). The temperature and pressure interaction presented in Figure 2a shows that at a low level of temperature, a low lignin yield was obtained at any level of pressure. At the temperature level of 40 °C and pressure level of 6.5 bar, the lignin yield exhibited the lowest value (20.82%). However, after increasing the temperature to 80 °C and pressure to 8 bar, the lignin yield increased to 64.01% (Table 2). The interaction between the pressure and residence time indicates that at a low level of pressure and residence time, the maximum lignin yield could be achieved, Figure 2b. The % yield of lignin was achieved at 69.88 when the pressure and residence time were 8 bar and 75 min, respectively. However, by decreasing the pressure and the residence time to 5 bar and 30, respectively, the lignin yield value reached the maximum value of 74.01% (Table 2). The temperature–residence time interaction in Figure 2c shows a similar impact on the lignin yield as the temperature–pressure interaction that at a high level of temperature, a high lignin yield was obtained at any level of residence time. The minimum value of lignin yield (28.60) was presented for the lowest level of temperature (40 °C) and residence time (30 min). The total lignin yield was observed at the maximum value (72.42) at 120 °C and 30 min temperature and residence time, respectively.

In this study, the use of CO₂ as an acidification agent can be effective in reducing the pH of the black liquor to be in the range of 7–10. In principle, when a lower pH is achieved, a higher lignin yield is obtained. There are two pH ranges in which changes in pH had large effects on the lignin yield. One such range is above pH 8, due to the progressive protonation of phenolic hydroxyl groups ($pK_a = 9-10$). The second one is at a pH of about 3 or 4; it is attributed to the protonation of hydroxy carboxylic acid, in which the carboxylic acid is at a carbon adjacent to a C–OH hydroxyl group ($pK_a = 3-4$).³⁴ The observed trend in the lignin yield due to the change in the temperature is a primary factor because temperature is an important factor governing the lignin condensation reaction to larger molecules or depolymerization into smaller phenolic compounds in some period of time.²⁸ The mass yield of lignin

trends increase with increasing temperature, confirmed by the larger M_w of lignin at high temperature. It could be simply explained by the lower solubility of larger molecules due to better protonation and an increase in the condensation of lignin fragments at high temperature.²⁶ However, the M_w decreases with residence time at high temperature ($M_w = 2500 \pm 300$ and 1500 ± 400 g mol⁻¹ at 30 and 120 min, respectively), indicating that an increased time allows a higher depolymerization reaction than the condensation rate of lignin fragments and residue carbohydrate, resulting in a lower M_w under high-temperature conditions. As the lignin degraded into lower MW compounds, the new compounds are not precipitated by the antisolvent (water) and a low- pK_a value unit of lignin fragments remains in the solution; therefore, it results in a lower lignin yield at a longer residence time (61% for 120 min and 72% for 30 min).

3.3. Optimization by the D-Optimality Index. An analysis of the D-optimality index was performed to determine the optimum conditions to maximize the quantity of lignin recovery by CO₂ acidification from soda black liquor. The D-optimality plot for lignin yield for residence time, temperature, and pressure is shown in Figure 3. A D-optimality value of 1.0 (the best index possible) with a maximum lignin yield of 89.26% was predicted at residence time = 30 min, temperature = 120 °C, and pressure = 5 bar. Additionally, to confirm the accuracy of the analysis using the RSM, the predicted values were compared with the experiment data under the optimum conditions. The actual lignin yield was 85.24 ± 4.32 wt %, which corresponded to the response's desirability scores of 0.96. The verification experiments proved that the predicted lignin yield values for the model were satisfactorily achieved within a 95% confidence interval of experimental values, which indicates that the optimum value of the factors was achieved.

The maximum lignin yield result from this study was higher compared to the previous reports of recovery lignin by CO₂ acidification from hardwood soda pulping black liquor by Kumar (59 wt %³⁵ and 50 wt %³⁶), softwood kraft pulping black liquor by Ohman et al. (40–68 wt %³⁷), and by Wallmo et al. (56–59 wt %³⁸). Moreover, our lignin yield result was similar to the lignin recovery with sulfuric acid (91 wt%), which was able to reduce the pH of the liquor to about 2.³⁵ Lauwaert et al.³⁹ investigated a pilot-scale procedure for the mild soda pulping of *Miscanthus x giganteus* chips in which the lignin was recovered by means of acidification, an enzymatic treatment, and subsequent filtration. Interestingly, the lignin recovery conditions studied from this report showed a slightly high lignin yield (91.3 wt %) as our report.

3.4. Black Liquor Characterization. The obtained soda pulping bagasse was characterized and compared with the previous literature (Table 4). As a result of the soda pretreatment, the pH of the black liquor is in the alkaline range (pH 13–14), but it was slightly higher than other reports (pH 11–13). The black liquor consisted of acid-insoluble lignin (Klason lignin) at about 24.6 wt %, which was in the range of the previous studies. A high sodium content (37.5 wt %) was found in the black liquor sample. The total ash was 67.0 wt % after thermal decomposition at 550 °C.

3.5. Lignin Characterization. To further clarify the result, the lignin product from soda pulping bagasse black liquor under the optimum conditions of the CO₂ acidification process was investigated for its physicochemical properties using various techniques. Elemental analysis was employed to show the composition of the carbon, hydrogen, and nitrogen in the

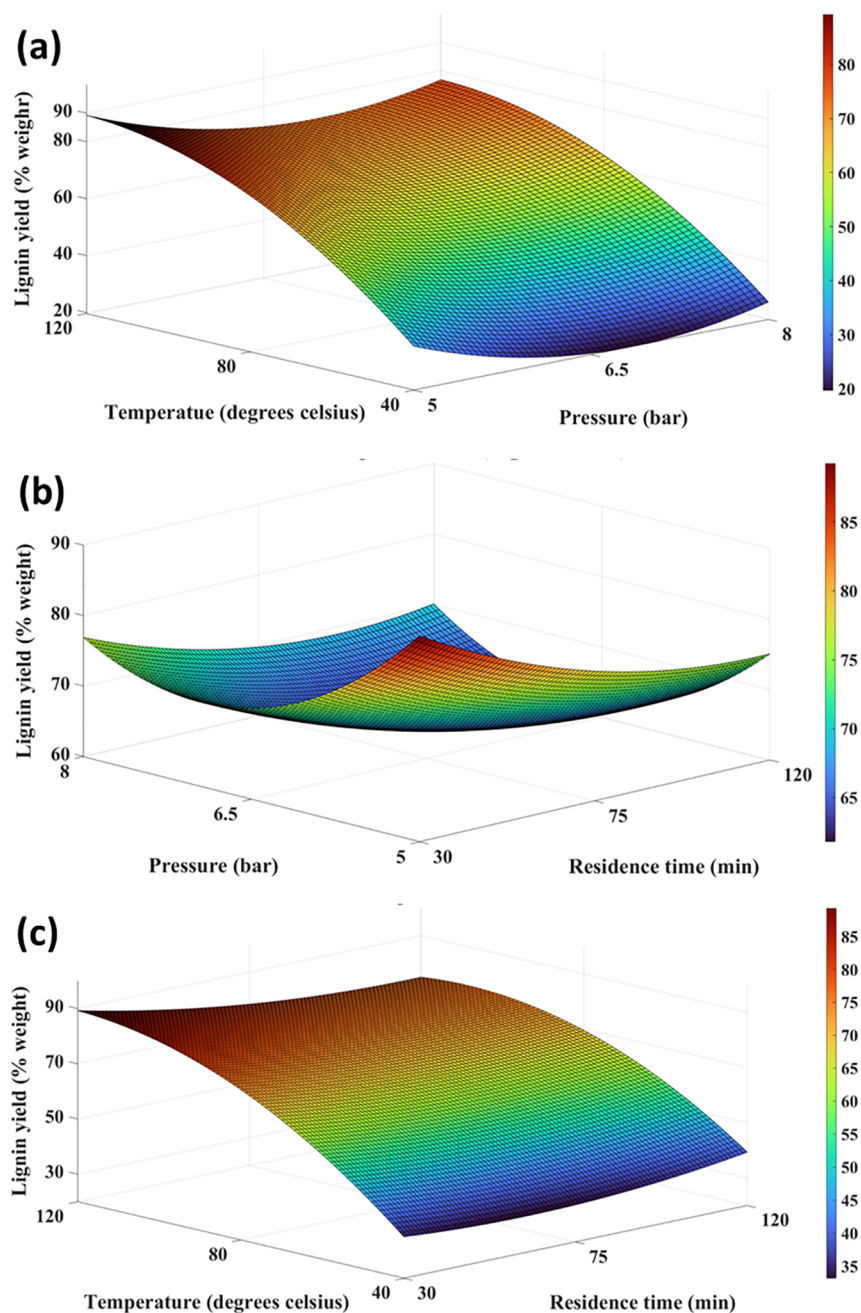


Figure 2. Response surface plot showing the design factors effect on the lignin yield: (a) temperature and pressure for a residence time of 75 min, (b) pressure and residence time for a temperature of 75 °C, and (C) temperature and residence time for a pressure of 6.5 bar.

lignin product based on a percentage of each atom (Table 5). A high carbon ratio in the lignin product was detected due to its six carbon atoms in the benzene ring of its phenylpropane (C9) monomer unit. The nitrogen content was presented at 0.62 wt %, which is potentially due to the formation of protein–lignin complexes in the soda pretreatment process. However, free proteins can be removed easily during the lignin recovery process by acidification because they dissolve well under alkaline conditions.⁴³ The lignin purity in the combination of the Klason lignin and ASL was about 93 wt %. Trace amounts of sodium (0.71%) and ash (5.09%) were also detected in the lignin product. The average molecular weight (M_w) and the number-average molecular weight (M_n) of lignin from sugarcane bagasse were 3000 and 1000 g mol⁻¹, respectively similar to the results of the previous studies as

shown in Table 5 and others reported by Zeng et al.⁴⁴ and Sun et al.⁴⁵ Soda pulping practically causes hydrolytic cleavage of the native lignin into small fragments that are soluble in the strongly alkaline cooking liquor, resulting in lower molecular weight compared to the native lignin or extracted lignin by the organic solvent.^{45,46}

The optimum conditions for recovery of lignin in this study provided 2.97 polydispersity for the lignin products, indicating a broad mass distribution or the nonuniformity of the lignin structure. However, soda-type lignin from different sources such as flax, straws, bagasse, softwood, or hardwood typically provides a polydispersity ranging from 1.5 to 3.5.^{39,44,45,50,51} The total phenolic hydroxyl and carboxyl contents in the lignin from sugarcane bagasse are similar to those reported by Naron et al.⁴⁷ for the soda process and Luo et al.⁵² for the kraft

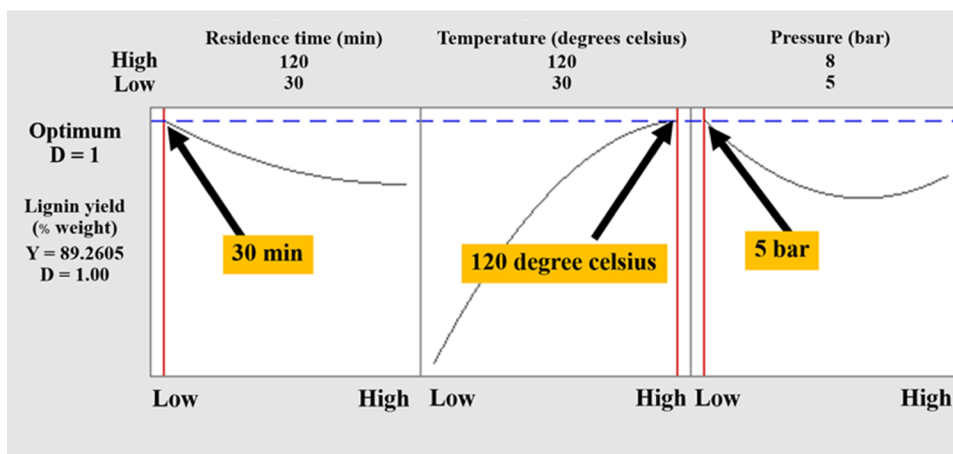


Figure 3. Optimality plot to locate the optimum factor levels for the maximum lignin yield.

Table 4. Soda Pulping Bagasse Black Liquor Characterization and Comparison with Literature Data^a

parameters	this work	refs 404142
pH	13–14	11–13
dry matter (wt %)	37.1	ND
Klason lignin ^b (wt %)	24.6	20.2–30
sodium ^c (wt %)	37.5 ± 1.4	28.5
ash (wt %)	67.0	ND

^aND = not determined. a, b, and c are values in dry matter.

process but lower than those reported by Mousavioun et al.⁴³ and Ghatak et al.⁴¹

In addition, the chemical structure of the lignin product was analyzed by FTIR spectroscopy. The chemical structure of lignin is extremely complex, irregular, and three-dimensional with a highly branched phenolic polymer of three basic phenylpropanoid monomers, *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units connected via the C–O–C ether or C–C bond. The monomers differ only with respect to the degree of methoxy groups substituted on the aromatic ring. Qualitative ATR-FTIR analysis for the confirmation of functional groups such as hydroxyl, carbonyl, methoxyl, and carboxyl and aromatic characteristics was performed in the

range from 4000 to 500 cm⁻¹, as shown in Figure 4. The corresponding assignments and bands for the lignin product

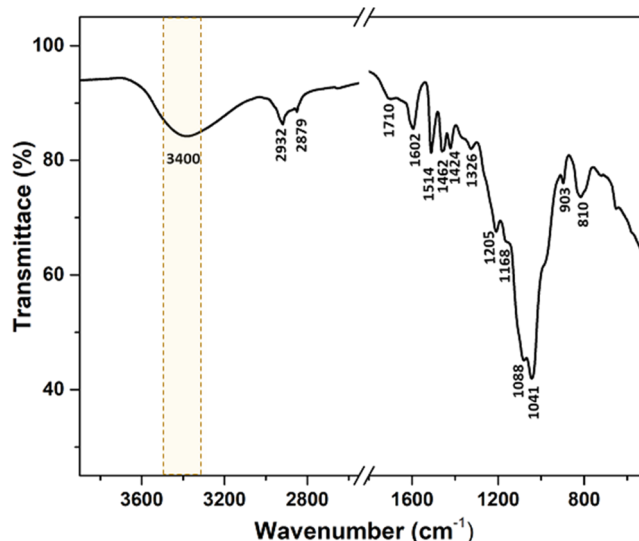


Figure 4. FT-IR spectrum of lignin from soda pulping bagasse black liquor.

Table 5. Characterization of Lignin from Soda Pulping Bagasse Black Liquor and Comparison with Lignin from Bagasse in Literature Data^a

parameters	this work	refs			
		43	47	48	49
elemental analysis (%)					
C	50.92 ± 0.12	63.25	61	63.7	ND
H	5.39 ± 0.12	5.95	5.5	5.3	ND
N	0.62 ± 0.01	0.29	0.2	0.78	ND
Klason lignin (%)	90.10 ± 0.23	96	89	87	90–94
ASL (%)	3.35 ± 0.15	ND	ND	ND	0.89–1.54
ash (%)	5.09 ± 0.12	2	<5	ND	0.29–0.51
sodium (%)	0.71 ± 0.53	ND	0.1	ND	ND
Ph–OH (%)	5.6 ± 0.26	5.1	5.4	ND	ND
Carboxyl (%)	11.8 ± 0.32	13.1	5.3	ND	ND
M _w (g mol ⁻¹)	3000 ± 200	2410	3257	1374	4118–4740
M _n (g mol ⁻¹)	1000 ± 9	2160	1721	785	2484–2660
polydispersity (M _w /M _n)	2.97 ± 0.20	1.12	1.89	1.75	1.53–1.78

^aND = not determined.

based on the assignments given by Faix⁵³ or Erdtman⁵⁴ for three different types of lignin structures, namely G-type, GS-type, and HGS-type, are presented in Table 6. A wide

Table 6. Assignment of Bands in the Infrared Spectra of the Lignin Product^{a,b,c}

band (cm ⁻¹)	vibration	assignment
3400	st O–H	phenolic & aliphatic OH
2932	st C–H	–CH ₂ & –CH ₃
2879	st C–H	–CH ₂ & –CH ₃
1710	st C=O	unconjugated ketone, carbonyl and ester
1600	st C–C	aromatic skeleton
1512	st C–C	aromatic skeleton
1462	C–H deform	asymmetric in –CH ₂ & –CH ₃
1426	st C–C	aromatic skeleton
1326	st C–O, C–C	S ring breathing
1205	st C–C, C–O, C=O	G ring breathing
1168	C=O	ester groups (conjugated)
1088	C–O deform	secondary alcohols & aliphatic ethers
1041	δ_{ip} C–H deform	G & S ring (G > S)
	C–O deform	primary alcohol
	st C=O	unconjugated
903	δ_{op} C–H	Aromatic
810	δ_{op} C–H	G ring

^ast: stretching vibration. ^b δ_{ip} : in-plane deformation vibration. ^c δ_{op} : out-of-plane deformation vibration.

absorption band that appeared at about 3400 cm⁻¹ was assigned to the aromatic and aliphatic O–H groups, while the absorption peaks at 2932 and 2879 were related to the C–H vibration in methyl and methylene groups on the side chain. The band at 1710 cm⁻¹ corresponds to the C=O stretching–unconjugated ketones and carbonyl groups.

The main characteristic of the phenylpropane skeleton was confirmed at 1600, 1512, and 1426 cm⁻¹ corresponding to the stretching vibration of the C–C bond in the aromatic ring. An additional band was located at 1462 cm⁻¹ referring to the C–H deformations (asymmetric) in methyl, methylene, and methoxy groups. The spectral bands lower than 1400 cm⁻¹ are complex due to the combination of various vibration modes. The bands were located at 1326 cm⁻¹ (syringyl ring breathing with C–O and C–C stretching), 1205 cm⁻¹ (guaiacyl ring breathing with C–O, C–C, and C=O stretching), 1088 cm⁻¹ (C–O deformation, secondary alcohols and aliphatic ethers), 1041 cm⁻¹ (aromatic C–H in-plane deformation in G ring plus C–O in primary alcohols and C=O stretching), 903 cm⁻¹ (C–H out-of-plane in aromatics) and 810 cm⁻¹ (C–H out-of-plane in the G ring).

The weak signal at 1168 cm⁻¹ showed the presence of a *p*-coumaric ester group, typical for the HGS type of lignin.⁵⁵ The aromatic C–H deformation at 1041 cm⁻¹ strongly appeared in the spectrum and is associated with a complex vibration associated with the C–O and C–C bonds that usually appears in polysaccharides. This result indicated the presence of polysaccharide impurities, which is the vibration in the spectral region of 1000–1300 cm⁻¹.^{56,57}

Thermal analysis was also performed to evaluate the thermal property of the lignin product. TG curves demonstrate the weight loss of the samples related to the temperature of thermal degradation, while the first derivative of the TG curve (dTG) exhibits the corresponding rate of weight loss. The

peak of the dTG curve is expressed as a maximum thermal decomposition temperature (dTG_{max}) and can be used to express the thermal stability characteristics for any materials. Three degradation stages can be identified in the lignin thermogram shown in Figure 5. The first stage in the

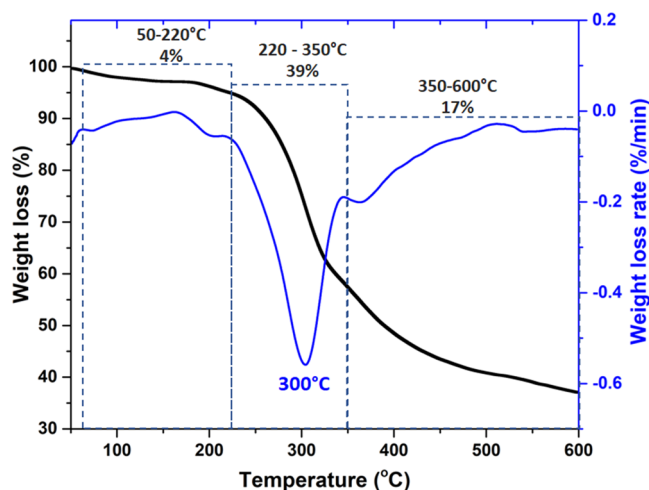


Figure 5. TGA/dTG curve of lignin from soda pulping bagasse black liquor.

temperature ranges from 50 to 220 °C (4 wt % loss), which is associated with the loss of moisture presented in the lignin and some decomposition products with a low molecular weight such as CO, CO₂, and CH₄ due to the cleavage of the lignin side chains.^{48,58} The second degradation stage can be attributed to the main degradation of lignin, which takes place between 220 and 350 °C (39 wt % loss) with dTG_{max} at 300 °C. This degradation process involves fragmentation of interunit linkages of monomers and derivatives of phenol into the vapor phase.⁵⁹ A last degradation stage occurred at the temperature above 350 °C (17 wt % loss), which is related to the decomposition and condensation reactions of aromatic rings. At the end of the test, residue char at 600 °C was 39 wt % due to the condensed structure of the lignin.

The surface morphology of the lignin product analyzed by FE-SEM is presented in Figure 6. A round shape with different sizes was observed. The particles take a spherical form due to

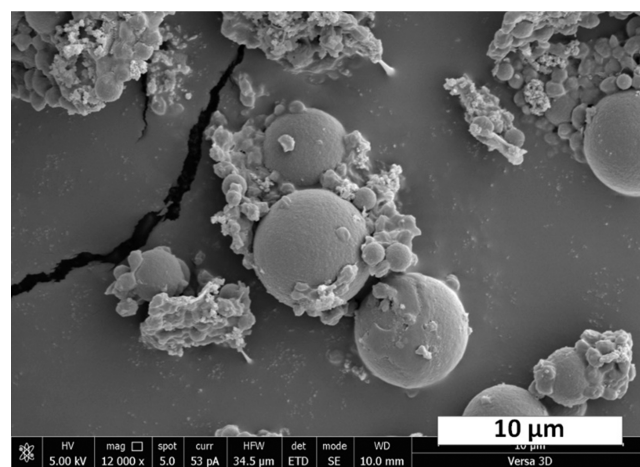


Figure 6. FE-SEM image of the lignin product.

their surface tension, which is thermodynamically stable.⁶⁰ The size of the particles could be divided into two groups, with one group showing approximately 1 μm and the other group having approximately 7 μm .

4. CONCLUSIONS

This study attempted to optimize the parameters in the CO₂ acidification process for recovery of lignin from bagasse soda pulping black liquor, including pressure, temperature, and residence time to obtain the maximum lignin yield. The experiments were designed and analyzed with a response surface methodology with the BBD using Minitab software. The optimal conditions for the maximum lignin yield were estimated to be 5 bar, 120 °C, and 30 min pressure, temperature, and residence time, respectively. The predicted responses based on the maximum lignin yield were 89.26% with the desirability function found to be close to 1. The experiment was carried out under the predicted optimum conditions to confirm that the % yield of lignin was approximately 85.24 \pm 4.32 wt %, close to the result of response surface analysis. High purity and high quality of lignin were achieved from the optimum conditions and confirmed using different techniques. The obtained lignin showed approximately 3000 g/mol average molecular weight with a slightly broad polydispersity and two groups of particles sizes, approximately 1 μm and 7 μm . The CO₂ acidification temperature can be used to control the characteristics of lignin.

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Notes

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■ REFERENCES

- (1) Sriroth, K.; Vanichsriratana, W.; Sunthornvarabhas, J. The Current Status of Sugar Industry and By-Products in Thailand. *Sugar Tech* **2016**, *18*, 576–582.
- (2) Reddy, N.; Yang, Y. Biofibers from Agricultural Byproducts for Industrial Applications. *Trends Biotechnol.* **2005**, *23*, 22–27.
- (3) Sriroth, K.; Sunthornvarabhas, J. Lignin from Sugar Process as Natural Antimicrobial Agent. *Biochem. Pharmacol.: Open Access* **2018**, *7*, No. 239.
- (4) Bajwa, D. S.; Pourhashem, G.; Ullah, A. H.; Bajwa, S. G. A Concise Review of Current Lignin Production, Applications, Products and Their Environmental Impact. *Ind. Crops Prod.* **2019**, *139*, No. 111526.
- (5) José, C.; Lino, A. G.; Colodette, J. L.; Lima, C. F.; Gutiérrez, A.; Martínez, A. T.; Lu, F.; Ralph, J.; Rencoret, J. Differences in the Chemical Structure of the Lignins from Sugarcane Bagasse and Straw. *Biomass Bioenergy* **2015**, *81*, 322–338.
- (6) 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.
- (7) Vermaas, J. V.; Crowley, M. F.; Beckham, G. T. Molecular Lignin Solubility and Structure in Organic Solvents. *ACS Sustainable Chem. Eng.* **2020**, *8*, 17839–17850.
- (8) Li, H.; McDonald, A. G. Fractionation and Characterization of Industrial Lignins. *Ind. Crops Prod.* **2014**, *62*, 67–76.
- (9) Sajjadi, M.; Ahmadpoor, F.; Nasrollahzadeh, M.; Ghafari, H. Lignin-Derived (Nano) Materials for Environmental Pollution Remediation: Current Challenges and Future Perspectives. *Int. J. Biol. Macromol.* **2021**, *178*, 394–423.
- (10) Espinoza-Acosta, J. L.; Torres-Chávez, P. I.; Ramírez-Wong, B.; López-Saiz, C. M.; Montañaño-Leyva, B. Antioxidant, Antimicrobial, and Antimutagenic Properties of Technical Lignins and Their Applications. *BioResources* **2016**, *11*, 5452–5481.
- (11) Li, H.; Wang, H.; Miao, Q.; Du, J.; Li, C.; Fang, J. High-Efficiency Adsorbent for Biobutanol Separation Developed from Lignin by Solvents Fractionation. *Ind. Eng. Chem. Res.* **2020**, *59*, 17483–17494.
- (12) Meng, Y.; Lu, J.; Cheng, Y.; Li, Q.; Wang, H. Lignin-Based Hydrogels: A Review of Preparation, Properties, and Application. *Int. J. Biol. Macromol.* **2019**, *135*, 1006–1019.
- (13) Gao, W.; Fatehi, P. Lignin for Polymer and Nanoparticle Production: Current Status and Challenges. *Can. J. Chem. Eng.* **2019**, *97*, 2827–2842.
- (14) Glasser, W. G. About Making Lignin Great Again—Some Lessons from the Past. *Front. Chem.* **2019**, *7*, No. 565.
- (15) Kienberger, M.; Maitz, S.; Pichler, T.; Demmelmayr, P. Systematic Review on Isolation Processes for Technical Lignin. *Processes* **2021**, *9*, No. 804.
- (16) Alvira, P.; Tomás-Pejó, E.; Ballesteros, M.; Negro, M. J. Pretreatment Technologies for an Efficient Bioethanol Production Process Based on Enzymatic Hydrolysis: A Review. *Bioresour. Technol.* **2010**, *101*, 4851–4861.
- (17) Kouisni, L.; Holt-Hindle, P.; Maki, K.; Paleologou, M. The Ligninforce System: A New Process for the Production of High-

- Quality Lignin from Black Liquor. *J. Sci. Technol. For. Prod. Processes* **2012**, *2*, 6–10.
- (18) Lake, M. A.; Blackburn, J. C. SLRP-an Innovative Lignin-Recovery Technology. *Cellul. Chem. Technol.* **2014**, *48*, 799–804.
- (19) Kihlman, J. The Sequential Liquid-Lignin Recovery and Purification Process: Analysis of Integration Aspects for a Kraft Pulp Mill. *Nord. Pulp Pap. Res. J.* **2016**, *31*, 573–582.
- (20) Kouisni, L.; Gagné, A.; Maki, K.; Holt-Hindle, P.; Paleologou, M. LignoForce System for the Recovery of Lignin from Black Liquor: Feedstock Options, Odor Profile, and Product Characterization. *ACS Sustainable Chem. Eng.* **2016**, *4*, 5152–5159.
- (21) Vancaessele, S.; Wearing, J.; Foan, J. Kraft Lignin Production: A Lignoforce (Tm) Perspective. *J. Sci. Technol. For. Prod. Processes* **2020**, *7*, 26–35.
- (22) Wallmo, H.; Lindholm, K.; Christiansen, G.; Karlsson, H.; Littorin, A. The Next-Generation Lignoboost-Tailor-Made Lignin Production for Different Lignin Bioproduct Markets. *J. Sci. Technol. For. Prod. Processes* **2018**, *7*, 6–10.
- (23) Suota, M. J.; da Silva, T. A.; Zawadzki, S. F.; Sasaki, G. L.; Hansel, F. A.; Paleologou, M.; Ramos, L. P. Chemical and Structural Characterization of Hardwood and Softwood LignoForce Lignins. *Ind. Crops Prod.* **2021**, *173*, No. 114138.
- (24) Zhu, W.; Westman, G.; Theliander, H. Investigation and Characterization of Lignin Precipitation in the Lignoboost Process. *J. Wood Chem. Technol.* **2014**, *34*, 77–97.
- (25) Zhu, W.; Westman, G.; Theliander, H. The Molecular Properties and Carbohydrate Content of Lignins Precipitated from Black Liquor. *Holzforchung* **2015**, *69*, 143–152.
- (26) Ela, R. C. A.; Spahn, L.; Safaie, N.; Ferrier, R. C., Jr; Ong, R. G. Understanding the Effect of Precipitation Process Variables on Hardwood Lignin Characteristics and Recovery from Black Liquor. *ACS Sustainable Chem. Eng.* **2020**, *8*, 13997–14005.
- (27) Velez, J.; Thies, M. C. Liquid Lignin from the SLRPTM Process: The Effect of Processing Conditions and Black-Liquor Properties. *J. Wood Chem. Technol.* **2016**, *36*, 27–41.
- (28) Velez, J.; Thies, M. C. Temperature Effects on the Molecular Properties of Liquid Lignin Recovered from Kraft Black Liquor. *ACS Sustainable Chem. Eng.* **2015**, *3*, 1032–1038.
- (29) Pichler, T.; Maitz, S.; Kienberger, M. Influence of Long-Term Heat Treatment of Kraft Black Liquor on Lignin Precipitation and Material Properties. *Holzforchung* **2020**, *74*, 286–292.
- (30) Leite, B. S.; Andreuccetti, M. T.; Leite, S. A. F.; d'Angelo, J. V. H. TG and DSC Analyses of Eucalyptus Black Liquor as Alternative Methods to Estimate Solids Content. *J. Therm. Anal. Calorim.* **2013**, *112*, 1539–1544.
- (31) Tappi Test Method T222 om-98. *Acid-insoluble Lignin in Wood and Pulp* Tappi Press: Atlanta, 1998.
- (32) TAPPI, UM 250. *Acid-Soluble Lignin in Wood and Pulp*, TAPPI Useful Methods; TAPPI Standard Method: Atlanta, 1991.
- (33) Kong, F.; Wang, S.; Gao, W.; Fatehi, P. Novel Pathway to Produce High Molecular Weight Kraft Lignin–Acrylic Acid Polymers in Acidic Suspension Systems. *RSC Adv.* **2018**, *8*, 12322–12336.
- (34) Hubbe, M. A.; Alén, R.; Paleologou, M.; Kannangara, M.; Kihlman, J. Lignin Recovery from Spent Alkaline Pulping Liquors Using Acidification, Membrane Separation, and Related Processing Steps: A Review. *BioResources* **2019**, *14*, 2300–2351.
- (35) Kumar, H.; Alén, R. Partial Recovery of Aliphatic Carboxylic Acids and Sodium Hydroxide from Hardwood Black Liquor by Electrodialysis. *Ind. Eng. Chem. Res.* **2014**, *53*, 9464–9470.
- (36) Kumar, H.; Alén, R.; Sahoo, G. Characterization of Hardwood Soda-AQ Lignins Precipitated from Black Liquor through Selective Acidification. *BioResources* **2016**, *11*, 9869–9879.
- (37) Ohman, F.; Theliander, H. Filtration Properties of Lignin Precipitated from Black Liquor. *Tappi J.* **2001**, *6*, 3–9.
- (38) Wallmo, H.; Richards, T.; Theliander, H. An Investigation of Process Parameters during Lignin Precipitation from Kraft Black Liquors: A Step towards an Optimised Precipitation Operation. *Chem. Pulping* **2009**, *24*, 158–164.
- (39) Lauwaert, J.; Stals, I.; Lancefield, C. S.; Deschaumes, W.; Depuydt, D.; Vanlerberghe, B.; Devlamynck, T.; Bruijninx, P. C. A.; Verberckmoes, A. Pilot Scale Recovery of Lignin from Black Liquor and Advanced Characterization of the Final Product. *Sep. Purif. Technol.* **2019**, *221*, 226–235.
- (40) Lei, Y.; Liu, S.; Li, J.; Sun, R. Effect of Hot-Water Extraction on Alkaline Pulping of Bagasse. *Biotechnol. Adv.* **2010**, *28*, 609–612.
- (41) Ghatak, H. R.; Kundu, P. P.; Kumar, S. Thermochemical Comparison of Lignin Separated by Electrolysis and Acid Precipitation from Soda Black Liquor of Agricultural Residues. *Thermochim. Acta* **2010**, *502*, 85–89.
- (42) Yue, F.; Chen, K.-L.; Lu, F. Low Temperature Soda-Oxygen Pulping of Bagasse. *Molecules* **2016**, *21*, No. 85.
- (43) Mousavioun, P.; Doherty, W. O. S. Chemical and Thermal Properties of Fractionated Bagasse Soda Lignin. *Ind. Crops Prod.* **2010**, *31*, 52–58.
- (44) Zeng, J.; Tong, Z.; Wang, L.; Zhu, J. Y.; Ingram, L. Isolation and Structural Characterization of Sugarcane Bagasse Lignin after Dilute Phosphoric Acid plus Steam Explosion Pretreatment and Its Effect on Cellulose Hydrolysis. *Bioresour. Technol.* **2014**, *154*, 274–281.
- (45) Sun, J.-X.; Sun, X.-F.; Sun, R.-C.; Fowler, P.; Baird, M. S. Inhomogeneities in the Chemical Structure of Sugarcane Bagasse Lignin. *J. Agric. Food Chem.* **2003**, *51*, 6719–6725.
- (46) Windeisen, E.; Wegener, G. Lignin as Building Unit for Polymers. In *Polymer Science: A Comprehensive Reference*; Matyjaszewski, K.; Möller, M. B. T.-P. S. A. C. R., Eds.; Elsevier: Amsterdam, 2012; pp 255–265.
- (47) Naron, D. R.; Collard, F.-X.; Tyhoda, L.; Görgens, J. F. Characterisation of Lignins from Different Sources by Appropriate Analytical Methods: Introducing Thermogravimetric Analysis-Thermal Desorption-Gas Chromatography–Mass Spectroscopy. *Ind. Crops Prod.* **2017**, *101*, 61–74.
- (48) Imman, S.; Khongchamnan, P.; Wanmolee, W.; Laosiripojana, N.; Kreetachat, T.; Sakulthaew, C.; Chokeyaroenrat, C.; Suriyachai, N. Fractionation and Characterization of Lignin from Sugarcane Bagasse Using a Sulfuric Acid Catalyzed Solvothermal Process. *RSC Adv.* **2021**, *11*, 26773–26784.
- (49) Pongchaiphol, S.; Chotirotukon, C.; Raita, M.; Champreda, V.; Laosiripojana, N. Two-Stage Fractionation of Sugarcane Bagasse by a Flow-through Hydrothermal/Ethanosolv Process. *Ind. Eng. Chem. Res.* **2021**, *60*, 12629–12639.
- (50) Vishtal, A.; Kraslawski, A. Challenges in Industrial Applications of Technical Lignins. *BioResources* **2011**, *6*, 3547–3568.
- (51) L'udmila, H.; Michal, J.; Andrea, S.; Ales, H. Lignin, Potential Products and Their Market Value. *Wood Res.* **2015**, *60*, 973–986.
- (52) Luo, B.; Jia, Z.; Jiang, H.; Wang, S.; Min, D. Improving the Reactivity of Sugarcane Bagasse Kraft Lignin by a Combination of Fractionation and Phenolation for Phenol–Formaldehyde Adhesive Applications. *Polymers* **2020**, *12*, No. 1825.
- (53) Faix, O. *Fourier Transform Infrared Spectroscopy BT - Methods in Lignin Chemistry*; Lin, S. Y.; Dence, C. W. Eds.; Springer: Berlin, Heidelberg, 1992; pp 233–241.
- (54) Erdtman, H. Lignins: Occurrence, Formation, Structure and Reactions. *J. Polym. Sci., Part B: Polym. Lett.* **1972**, *10*, 228–230.
- (55) Galkin, S.; Ämmälähti, E.; Kilpeläinen, I.; Brunow, G.; Hatakka, A. Characterisation of Milled Wood Lignin from Reed Canary Grass (*Phalaris Arundinacea*). *Holzforchung* **1997**, *51*, 130–134.
- (56) Boeriu, C. G.; Bravo, D.; Gosselink, R. J. A.; van Dam, J. E. G. Characterisation of Structure-Dependent Functional Properties of Lignin with Infrared Spectroscopy. *Ind. Crops Prod.* **2004**, *20*, 205–218.
- (57) García, A.; Toledano, A.; Serrano, L.; Egiés, I.; González, M.; Marín, F.; Labidi, J. Characterization of Lignins Obtained by Selective Precipitation. *Sep. Purif. Technol.* **2009**, *68*, 193–198.
- (58) Dagnino, E. P.; Chiappero, L. R.; Nicolau, V. V.; Chamorro, E. R. Separation Process Optimisation and Characterisation of Lignin from Black Carob Tree Sawdust into a Biorefinery. *Chem. Eng. Res. Des.* **2020**, *155*, 66–79.

(59) Dávila, I.; Gullón, P.; Andrés, M. A.; Labidi, J. Coproduction of Lignin and Glucose from Vine Shoots by Eco-Friendly Strategies: Toward the Development of an Integrated Biorefinery. *Bioresour. Technol.* **2017**, *244*, 328–337.

(60) Fierro, V.; Torné-Fernández, V.; Celzard, A. Kraft Lignin as a Precursor for Microporous Activated Carbons Prepared by Impregnation with Ortho-Phosphoric Acid: Synthesis and Textural Characterisation. *Microporous Mesoporous Mater.* **2006**, *92*, 243–250.