

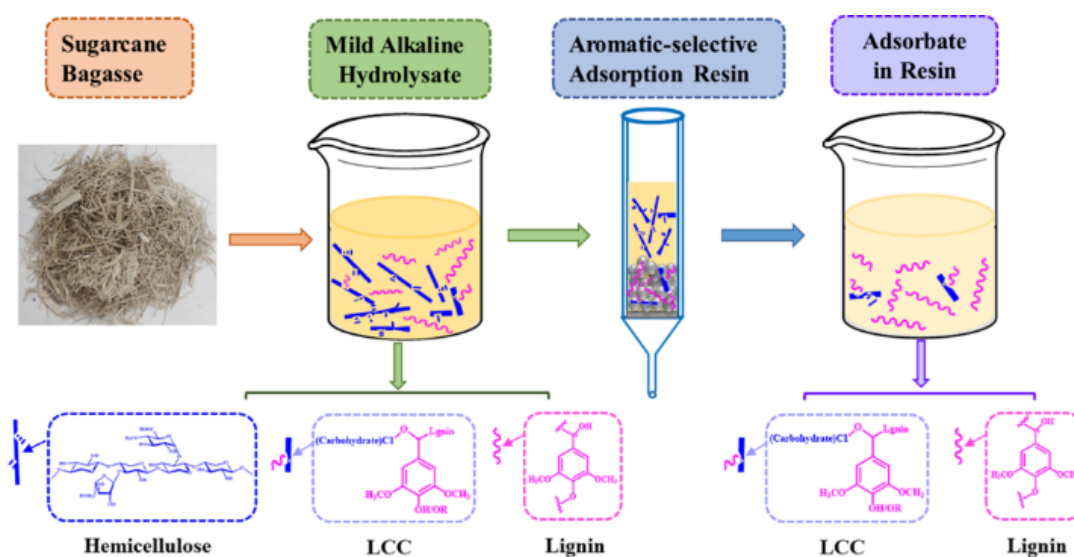
Efficient Separation of Lignin from Mild Alkaline Hydrolysate of Bagasse by Selective Adsorbent Resin

Juan Du,^{a,b} Chen Liang,^c Song Bai,^{a,b} Jiayan Ge,^d Shuangquan Yao,^c and Liping Xu^{a,b,*}

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GRAPHICAL ABSTRACT



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Amongst industrial lignins, such as alkaline and kraft lignins, lignin from hemicellulose pre-treatment liquor is gaining considerable interest because of its various properties. To explore application potential, a lignin sample that was selectively adsorbed by XAD-16N resin from mild alkaline extracts of sugarcane bagasse waste was identified by structural analysis. Trace amounts of hemicellulose were found in the adsorbates that exhibited lignin carbohydrate complexes (LCCs) structure. Prominent NMR signals indicated β -O-4', β -5', β - β' , and β -1' structures in the side chain, and aromatic signals corresponded to major bagasse lignin units: *p*-coumarate and ferulate. The quantity of benzyl ether (BE) was 3.33 per 100 Ar-units, which was considerably higher than that of hydrolysate obtained from hydrothermal pretreatments. The content of various hydroxyl groups of mild alkaline lignin obtained by resin adsorption was higher than that of lignin isolated by other methods. Moreover, the adsorbed lignin was relatively pure, and its thermal stability was superior to that of the centrifuged lignin. These results revealed new characteristics of lignin and LCC structures obtained *via* mild alkaline pretreatment and resin adsorption.

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Keywords: Sugarcane bagasse; Lignin; Aromatic-selective adsorbent resin; Mild alkaline extracts

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INTRODUCTION

Lignocellulosic biomass is an abundant renewable resource utilized, to produce bio-energy and bio-products through an environmentally friendly method (Costa *et al.* 2020; Lu *et al.* 2021). In the lignocellulosic biofuel industry, the overall economic benefits of biofuel production process can be improved by the development of valuable co-products (Cheng *et al.* 2020). Lignin is considered to be a low value by-product of the papermaking and biofuel industries (Li *et al.* 2020; Gomes *et al.* 2025). The efficient and clean separation of lignocellulosic components allows for their effective use (Xu *et al.* 2022; Sunar *et al.* 2024). Typically, the total amount of dissolved lignin after pretreatment is back-calculated using both biomass weight loss and diminution in lignin content. (Arni 2018; Geng *et al.* 2019). This quantitative method helps to quantitatively describe the degree of lignin removal, but it cannot describe the chemical and molecular properties of the soluble lignin (Narron *et al.* 2017). Therefore, the understanding of the molecular and chemical properties of the soluble lignin obtained through pretreatment is usually incomplete.

Sugarcane bagasse, as one of the most abundant agricultural residues, is considered a promising renewable lignocellulosic raw material due to the fact that its main components (cellulose, hemicellulose, and lignin) can be separated and converted into various value-added products (Sukhbaatar *et al.* 2014). Traditionally, sugarcane bagasse was used for composting and incineration, which might be detrimental to its further value-added transformation or lead to secondary environmental pollution, *etc* (Wang *et al.* 2019). In the concept of biomass biorefining, due to the vast market of the global sugar alcohol industry, sugarcane bagasse is regarded as an important raw material for producing cellulose ethanol and the paper industry (Miyamoto *et al.* 2018). Sugarcane bagasse can be extracted from hemicellulose through various pretreatment methods, such as alkaline pretreatment, organic solvent pretreatment, and hydrothermal pretreatment, which typically involve the dissolution and degradation of a large amount of lignin (Sun *et al.* 2013; Yao *et al.* 2017; Đorđević and Antov 2018). In fact, the extraction of hemicellulose is usually accompanied by the dissolution and degradation of lignin (Chen *et al.* 2019; Giummarella *et al.* 2019). Additionally, pseudo-lignin is formed by self-polymerization on the surface of hemicellulose, which can also result in lignin carbohydrate complexes (LCCs) forming with hemicellulose (Nicola *et al.* 2017; You *et al.* 2019; Jin *et al.* 2019).

High-purity hemicellulose is obtained mainly through ethanol precipitation and ultrafiltration purification (UF) of hemicellulose in different extracts, but there is still some lignin that have not been separated (Egüés *et al.* 2011; Yao *et al.* 2015). However, hemicellulose separation and purification are influenced by the existence of lignin. Currently, lignin is removed by aromatic adsorbents. Narron *et al.* (2017) studied aromatic adsorption resin that could selectively adsorb the bagasse hydrolysate. Results from their study indicated that 90% of soluble lignin was recovered from the hydrolysate of pretreated maple and bagasse (Narron *et al.* 2017). Resins were also employed to selectively adsorb lignin from pine/eucalyptus hydrolysate (Koivula *et al.* 2013). Additionally, xylo-oligosaccharides and lignosulfonates were effectively adsorbed from sweet gum tree hydrolysate *via* resin adsorption (Huang *et al.* 2016). Lignin was also separated from monosaccharide hydrolysates by a similar method (Heinonen *et al.* 2017) with a recovery of 80%.

In this study, sugarcane bagasse underwent mild alkaline pretreatment, and the subsequent lignin separation was achieved by XAD-16N resin adsorption. The extracted components of lignin were studied by ^{31}P , ^1H , ^{13}C , and 2D-nuclear magnetic resonance (NMR) spectroscopies. Additionally, lignin thermostability was analyzed by thermogravimetric analysis (TGA), ultraviolet spectrophotometry (UV) and the hemicellulose content was investigated by ion chromatography (IC).

MATERIALS AND METHODS

Materials

The sugarcane bagasse was obtained from a sugar factory in Guangxi, China. After air-drying, it was placed in sealed bags to balance the moisture content and then stored for later use. The selective adsorption resin, XAD-16N macroporous resin, was obtained from Sigma (Shanghai).

Weak Alkaline Extraction

The bagasse raw material was subjected to mild alkaline extraction. The bagasse (1.0 kg) was dispersed in an 8% NaOH solution at 90 °C for 60 min. The mild alkaline extracts were collected, pH values were adjusted to 5.5 to 6.0, centrifuged, and the supernatant fluid was collected.

Macroporous Resin Adsorption Protocol

About 3 g of macroporous resin was added to 50 mL of the centrifuged supernatant, and the resultant solution was placed into a constant temperature shaker (Narron *et al.* 2017). The adsorbed resin was collected by filtration and rinsed with deionized water to dislodge residual solution, and 150 mL of methanol solution was then added. After subsequent shaking, the methanol filtrate and adsorbed resin were separated by filtration, and the methanol was removed through rotary evaporation. The resultant powder was collected for analysis.

Lignin Content Analysis

The content of lignin sample was determined by UV spectrophotometry (You *et al.*, 2019). The absorbance of the lignin sample was detected at 205 nm using a UV spectrophotometer (SPECORD 50, Germany), and the lignin concentration was calculated. The formula is as follows,

$$X = \frac{A \times n \times m_0}{89.222 \times V} \times 100 \quad (1)$$

where X is lignin content in %, A is UV absorbance, n is the dilution multiple, m_0 is hemicellulose quality, and V is solution volume. The value of 89.222 was calculated according to the standard curve.

Analysis of Sugar Content in Lignin Adsorbate

The sugar content was determined by ion chromatography (ICS-5000+SP, Thermo Scientific, USA). Five monosaccharide standard solutions (xylose, arabinose, glucose, galactose, and mannose) were prepared, and the corresponding standard curve of the concentration-peak area was plotted. The glycan in the samples was determined according to the National Renewable Energy Laboratory standard method, which was NREL/TP-510-42623 (2008).

Nuclear Magnetic Analysis

Structural features of the adsorbate were studied by NMR spectroscopy (Zeng *et al.* 2013). The adsorbate sample (20 mg) was dissolved in 0.5 mL of dimethyl sulfoxide- d_6 (99.9%). The ^1H , ^{13}C , and 2D-NMR experiments were conducted using a AVANCE III HD500 (Germany) NMR spectrometer. ^1H NMR measurement was conducted using D_2O as the internal standard with a chemical shift at δ 4.7 ppm, a sampling time of 3.9 s, and a relaxation time of 1.0 s. ^{13}C NMR measurement was performed at 25 °C with 10,000 scans, a pulse width of 16.8 μs , a pulse angle of 60°, and a scan delay time of 1.10 s. The t_1 and t_2 relaxation effects on 2D HSQC sampling data were obtained as $t_1 \times t_2 = 1024 \times 256$.

Functional Group Analysis

The functional groups of the analyte were determined by NMR analysis (Zeng *et al.* 2013). The adsorbed and centrifuged samples of lignin were first dried in a vacuum oven. To the adsorbates (20 mg) in a 2-mL vial was added 400 μL of a mixture of pyridine

and CDCl_3 (1.6:1, v/v). Cyclohexanol solution (13.94 mg/mL) and chromium acetylacetonate solution (5.39 mg/mL) were then added. Vigorous stirring completely dissolved the lignin sample, after which 100 μL of TMDP (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane) was added and the solution was placed in a 5 mm NMR tube to be analyzed using ^{31}P NMR.

Thermal Stability Analysis

The thermal stability of the adsorbed and centrifuged lignin samples was analyzed by TGA (STA 449 F5, NETZSCH, Germany) after they were dried under vacuum. The lignin samples (8 to 10 mg) were heated from 30 to 800 $^{\circ}\text{C}$ under a nitrogen atmosphere and the heating rate used was 10 $^{\circ}\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Lignin Content Analysis

The alkaline extract of sugarcane bagasse was treated with acid, which brought about precipitation. There was a comparison of lignin content in the supernatant before and after adsorption. The alkaline extracts of sugarcane bagasse after acid precipitation still contained lignin. The lignin concentration in the extract after adsorption was significantly reduced by using XAD-16N resin for adsorption (Fig. 1), indicating that the XAD-16N resin can effectively separate lignin. There was still some lignin in the supernatant, which may be due to a decrease in the amount of lignin that is easily adsorbed after the resin dosage reaches a certain level.

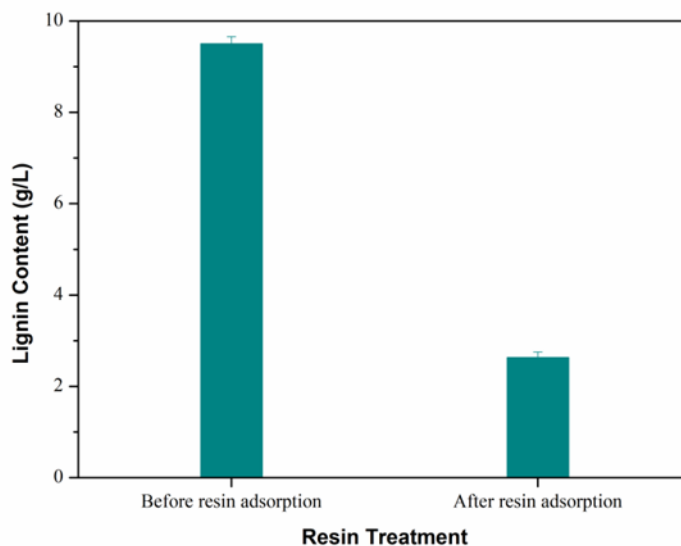


Fig. 1. Comparison of lignin content in the supernatant before and after adsorption

Component Analysis of Adsorbates

The IC analysis (Fig. 2) showed that adsorbates consisted of several monosaccharide units. XAD-16N macroporous resin has been shown to selectively adsorb lignin and LCC structures (Persson *et al.* 2010), but it exhibits no adsorption of hemicellulose (Zhang *et al.* 2018); therefore, the adsorbed hemicellulose in the present study likely originates from LCC structures. Furthermore, the glucose content was greater

than the xylose content, which contrasts with reports claiming bagasse hemicellulose primarily comprises xylose (Yao *et al.* 2015). The increased glucose content in the mild alkaline extracts of the present work was likely a result of cellulose dissolution (Farhat *et al.* 2017).

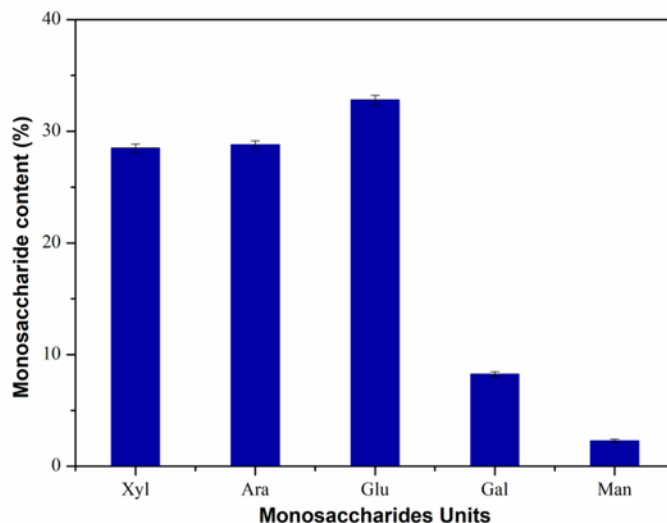


Fig. 2. The amount of sugar from adsorbate

Analysis of the Lignin Structure

The adsorbates were detected by ^1H NMR spectroscopy, as shown in Fig. 3 (Perez *et al.* 1998; Sun *et al.* 2003; Strahan *et al.* 2022; Krivdin 2025), where the clear signals from δ 7.4 to 7.8 ppm were attributed to the aromatic and olefinic protons in ferulic acids (FAs) and *p*-coumaric acids (PCAs), respectively. Signals of this type are generally observed in grass lignin. The peak at δ 4.7 to 4.8 ppm indicates that the compound was mainly connected to a β -O-4' structure. A strong signal at δ 3.7 ppm represented the methoxy protons, and the sharp septet at δ 2.5 ppm was from the DMSO- d_6 solvent. The aliphatic protons afforded signals from δ 0.8 to 2.1 ppm, and a peak at δ 9.7 ppm was possibly due to the formyl protons of cinnamaldehyde and aromatic formate groups. These signals indicate that the adsorbates are primarily those of lignin found in grass material.

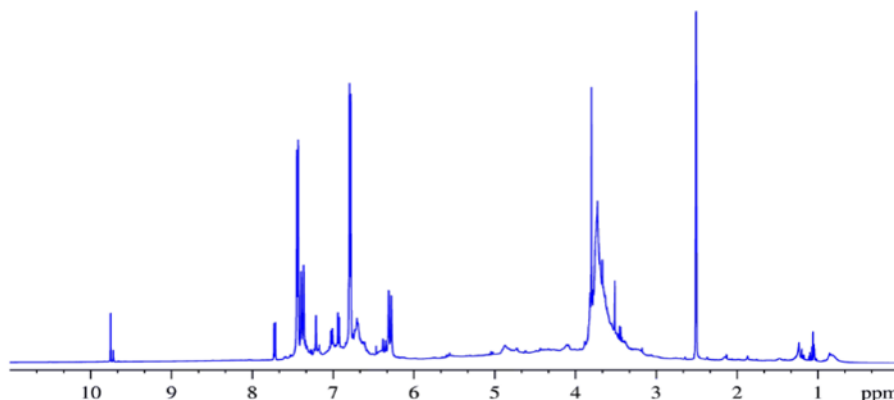


Fig. 3. ^1H NMR spectrum from adsorbate

The ^{13}C NMR signals were interpreted (Chen 1998; Sun *et al.* 2003; Cipriano *et al.* 2020; Krivdin 2025) to further elucidate the adsorbate structure (Fig. 4). The region

between δ 104.2 and 169.1 ppm was indicative of the bagasse lignin aromatic carbons, including syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) units. These signals showed that the bagasse lignin was an SGH grass-type lignin, which agrees with lignin characteristics that were observed from the ^1H NMR spectroscopic analysis. The signal at δ 122.2 ppm corresponded to etherified FAs, while esterified PCAs afforded a signal at δ 129.6 ppm. These results indicated that FAs were connected to lignin by both ether and ester bonds and PCAs were connected to lignin *via* ester bonds only. The ^{13}C NMR spectrum confirmed that β -O-4' linkages were the main bonds within lignin structure units, but signals indicative of 5-5' and β - β' structures were also found. Therefore, bagasse lignin predominantly comprised β -O-4' ether bonds, as well as 5-5' and β - β' linkages (Sun *et al.* 2003; Narron *et al.* 2017). Furthermore, the ^{13}C signal at δ 18.5 ppm was attributed to the CH_3 group of acetyl lignin, the peak at δ 190.8 ppm corresponded to aldehydes, and the signals at δ 164.8 ppm and 159.4 ppm arose from aromatic groups. The methoxy carbon of the syringyl and guaiacyl units was observed at δ 55.6 ppm. There was also a lack of signals near δ 175.0 ppm. In addition, the signals at δ 69.8 ppm is attributed to 4-O-Me- β -D-GlcpA (Chaikumpollert *et al.* 2004; Sun *et al.* 2003). The ^{13}C NMR results demonstrated that the lignin separated by the XAD resin contained trace amounts of hemicellulose that originated from LCCs (Persson *et al.* 2010), and the adsorption content is consistent with lignin found by IC.

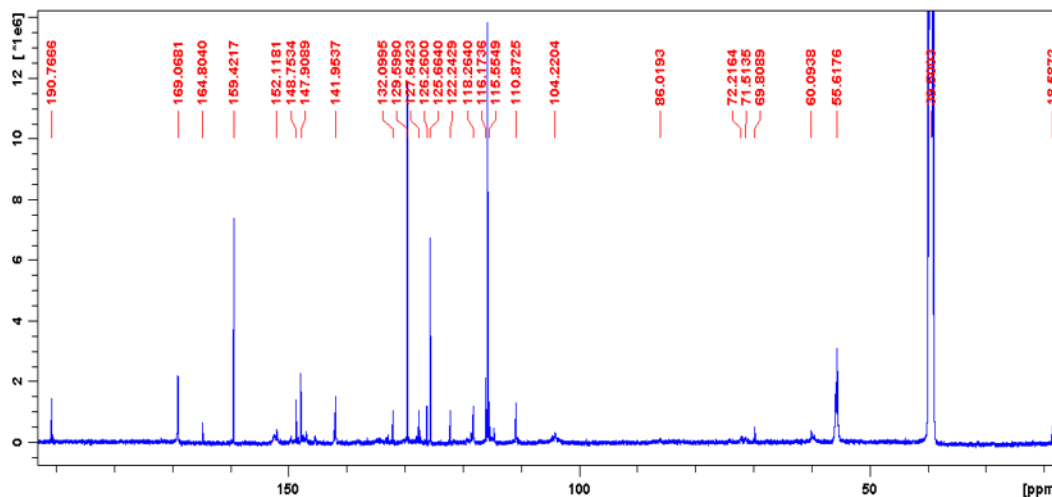


Fig. 4. ^{13}C NMR spectrum from adsorbate

The bagasse lignin structures were also determined by 2D-NMR experiments, spectra from which can be found in Fig. 5 (Yuan *et al.* 2011; Sun *et al.* 2015; Chen *et al.* 2019; Xiao *et al.* 2025). Signals from the methoxy groups and β -O-4' substructures (A) were prominently observed in the adsorbed lignin, and those of the phenylcoumaran substructure (B) were also observed. Other substructures, including resinol (C), were found at ($\delta\text{C}/\delta\text{H}$ 53.5/3.06, 71.0/3.82, 71.0/4.18, and 84.8/4.65). Furthermore, relatively low amounts of a *p*-hydroxycinnamyl alcohol end group (I) were represented by the signal at $\delta\text{C}/\delta\text{H}$ 61.3/4.09 ($\text{C}_\gamma\text{-H}_\gamma$) and spirodienone substructures (D) were identified by a signal at $\delta\text{C}/\delta\text{H}$ 81.2/5.07 ($\text{C}_\alpha\text{-H}_\alpha$). Moreover, several signals of carbohydrates from adsorbate were detected, including X_2 , X_3 , X_4 , and X_5 of the β -D-xylopyranoside unit. The adsorbate content was mainly lignin and trace amounts of carbohydrates, including glucan and xylan. The results also showed that lignin and hemicellulose from the LCC structure, which were abundant in the bagasse, were selectively absorbed by the XAD resin (Narron *et al.* 2017;

Zhang *et al.* 2018). The signals from the 2D-NMR spectra agreed with the lignin features observed *via* IC and the ^{13}C analyses.

The linkages between lignin and carbohydrate are primarily phenyl glycoside (PhGlc), benzyl ether (BE), and benzyl ester (Est) bonds (Zhang *et al.* 2010). The ester bond was not stable under alkaline conditions, so it was not maintained in the adsorbate. PhGlc signals were also not observed in the adsorbate of mild alkaline extracts of bagasse, but they were observed in sugarcane bagasse treated with hot-water extraction (Narron *et al.* 2017; Miyamoto *et al.* 2018). Therefore, the presence of the PhGlc bonds may be dictated by the treatment method. The γ -ester linkages were easily broken during the weak alkaline extraction of sugarcane bagasse, so they were not observed in the 2D-NMR spectra (Balakshin *et al.* 2011; Kumar *et al.* 2023). The BE LCC linkages were divided into two types: BE₁ linkage and BE₂ linkage, which connect primary and secondary hydroxyl groups of carbohydrates, respectively (Balakshin *et al.* 2011; Yuan *et al.* 2011; Narron *et al.* 2017). The benzyl ether (BE) linkages were stable under alkaline conditions.

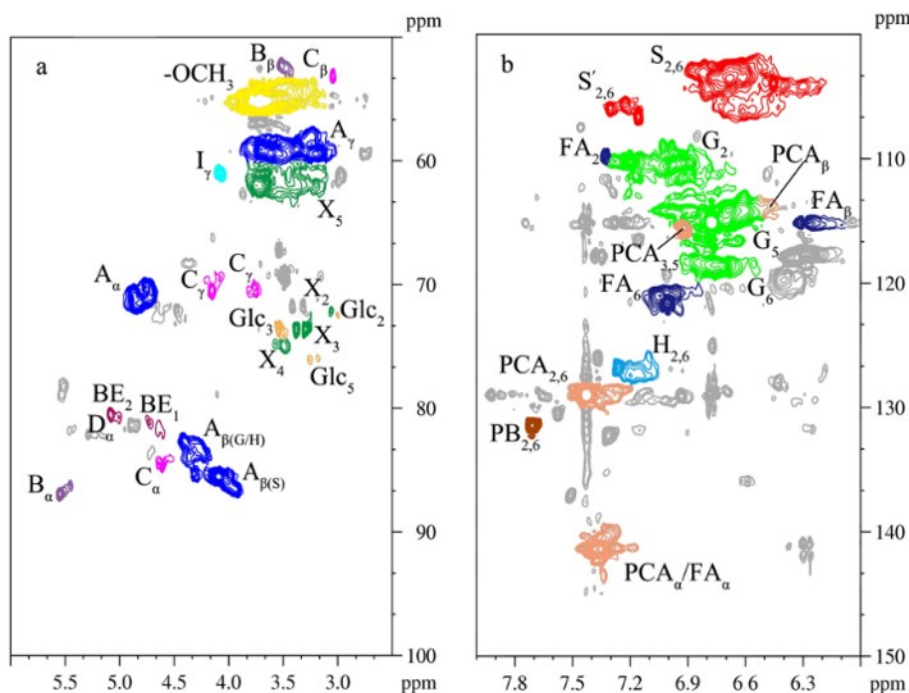


Fig. 5. a: Side-chain ($\delta\text{C}/\delta\text{H}$ 45-100/2.5-6.0; and b: aromatic region ($\delta\text{C}/\delta\text{H}$ 100-150/6.0-8.0 in the 2D HSQC NMR spectra from adsorbate

The S, G, and H units of lignin from different signals were observed in 2D-NMR spectra. Meanwhile, significant *p*-coumarate and ferulate signals were detected in the NMR spectra of grasses (Yuan *et al.* 2011; Río *et al.* 2012), which further confirmed that the adsorbate was lignin found in the grass. The strong FA signal in the lignin may have been due to lignin degradation during the mild alkaline extraction of bagasse, as FA acts as a cross-linker between lignin and arabinoxylan polymers (Ralph 2009; Wang *et al.* 2019). This also implies that lignin and LCC structures were selectively adsorbed by the resin. Additionally, the weak signal of *p*-hydroxybenzoate (PB) indicated that it partially acylated the bagasse. In combination with ^{13}C NMR signals, prominent 2D-NMR signals corresponding to β -O-4', β -5', β - β' , and β -1' structures in the side chain region, those of

major lignin units (S, G, and H), as well as those of FA and PCA residues were clearly observed. However, the β -1' structure was not found in bagasse subjected to hot-water extraction (Narron *et al.* 2017), the pretreatment method likely being the cause of this. These observations showed that adsorbate of bagasse extracts mainly consists of S, G, and H structures, which confirms the resin exhibited a strong lignin adsorption capacity.

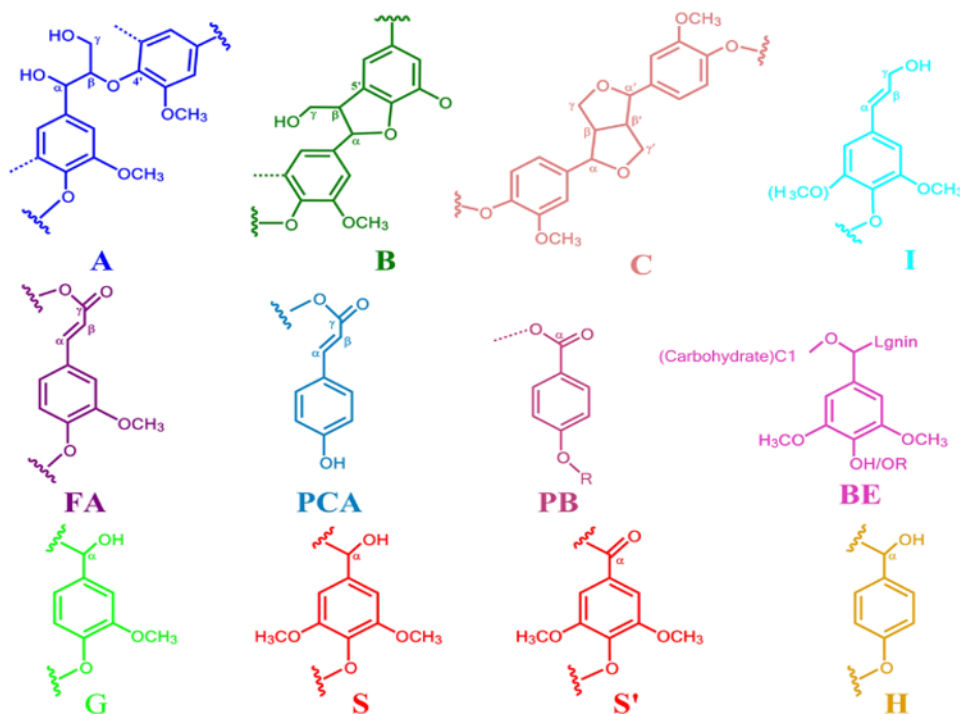


Fig. 6. Lignin and LCC substructure units: (A) β -O-4' substructures; (B) phenylcoumarane substructures; (C) resinol substructures; (I) *p*-hydroxycinnamyl alcohol end groups; (FA) ferulate residues; (PCA) *p*-coumarate residues; (PB) *p*-hydroxybenzoate substructures; (BE) benzyl ether; (G) guaiacyl units; (S) syringyl units; and (S') oxidized syringyl units; (H) *p*-hydroxyphenyl units

The relative, quantitative analysis of main lignin substructures and LCC linkages in sugarcane bagasse obtained in this work is summarized in Table 1. The sugarcane bagasse is characterized by high amounts of the β -O-4' substructure (41.4%). The other substructures present are those of phenylcoumaran (5.4%) and spirondienones (2.30%). Resinol (5.18%) and β -O-4' structures were also observed, probably because β - β' linkages were preferentially solubilized during the alkaline pretreatment (Yuan *et al.* 2011; Miyamoto *et al.* 2018). The *p*-hydroxycinnamyl alcohol end groups had a concentration of 4.90 per 100 Ar-units. The BE concentration was 3.33 per 100 Ar, which was higher than that of the groups obtained *via* hot-water pretreatments and likely due to this choice of pretreatment method (Narron *et al.* 2017). The S/G ratio was estimated to be 0.94, showing a strong predominance of G units that indicated lignin groups rich in S units were preferentially solubilized in the alkaline pretreatment. This may be related to the structure and molecular mass of the S and G units in sugarcane bagasse and agreed with the ratios reported by previous studies (Río *et al.* 2012; Miyamoto *et al.* 2018).

Table 1 Quantification of Lignin and LCC Substructures from Adsorbate by 2D-NMR (% , based on 100 Ar)

Characteristic	Sugarcane Bagasse
β -O-4' Aryl Ether (A)	41.39
Phenylcoumaran (B)	5.40
Resinol (C)	5.18
Spirodienones (D)	2.30
<i>p</i> -Hydroxycinnamyl Alcohol End Groups (I)	4.90
S/G Ratio	0.94
Benzyl Ether (BE)	3.33

Analysis of Functional Groups of Lignin

The signals of the different hydroxyl groups of lignin were efficiently separated by ^{31}P NMR, displaying the chemical shifts in distinct regions (Araneda *et al.* 2022; Pajer *et al.* 2025). The aliphatic hydroxyl group, phenolic hydroxyl group, and carboxyl group in bagasse lignin could clearly be distinguished (Zhang *et al.* 2010). The unstable H-atoms in lignin (-OH and -COOH hydrogens) were replaced by P-atoms to form a phosphorus-containing lignin-MDP derivative. The derivative P-atoms are surrounded by oxygen atoms during ^{31}P NMR spectroscopy, and the ^{31}P NMR signals were uncoupled single peaks that could be used to quantify the functional group content (Argyropoulos 1994; Wang *et al.* 2019). The formula for calculating the hydroxyl content is as follows (Araneda *et al.* 2022):

$$A = \frac{\frac{\rho \times 150 \times 10^{-6}}{100.16} \times \frac{A_2}{A_1}}{m} \times 100\% \quad (1)$$

Here, A is the hydroxy group content (unit), ρ represents cyclohexanol concentration (unit), A_1 is the integral area of the hydroxyl group (unit) in cyclohexanol, A_2 is the integral area of the hydroxyl group (unit) in the lignin structure, m is the quantity of the lignin sample (unit), 150 is the volume of cyclohexanol added to lignin, and 100.16 is the cyclohexanol molar mass.

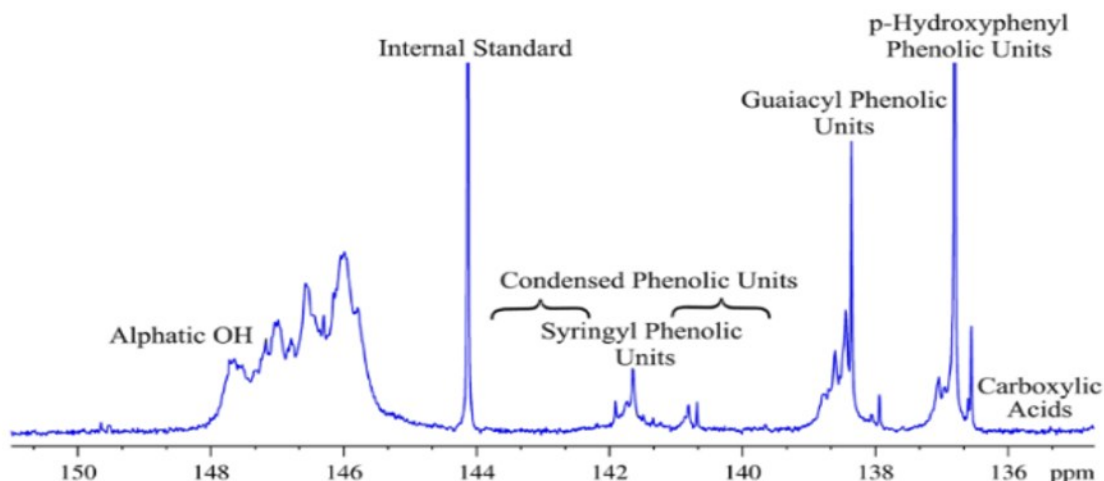
**Fig. 7.** ^{31}P NMR spectrum of lignin from adsorbate

Table 2 ^{31}P NMR Analysis of Lignin from Adsorbate

Chemical Shift, δ (ppm)	Functional Group	Functional Group Content (mmol/g)
148.22-144.51	Aliphatic hydroxyl group	10.28
143.71-142.26 141.09-140.04	Condensed phenolic hydroxyl group	0.16
142.16-141.31	Syringyl (S) phenolic hydroxyl group	0.48
139.51-137.68	Guaiacyl (G) phenolic hydroxyl group	1.53
137.54-136.32	<i>p</i> -Hydroxyphenyl (H) phenolic hydroxyl group	1.81
-	Total phenolic hydroxyl	3.98
136.47-135.03	Carboxyl group	0.10

The different functional groups of lignin were analyzed (Fig. 7 and Table 2), and the aliphatic hydroxyl content of bagasse lignin desorption was found to be the highest, up to 10.3 mmol/g. The signals of the primary and secondary hydroxyl groups were contained in the aliphatic region of the ^{31}P NMR spectrum, but their signals overlapped; therefore, their individual content could not be determined. However, the overall aliphatic hydroxyl content was determined by adding the primary and secondary hydroxyl group contents. The S, G, and H groups accounted for most of the total phenolic hydroxyl content, which was low and agreed with that of lignin (Moghaddam *et al.* 2017; Wang *et al.* 2019). This indicated that bagasse lignin did not possess a strong, condensed structure. The results also showed that bagasse lignin was the same as SGH grass lignin, which was consistent with the findings of the appeal study on the ^1H NMR spectroscopic and ^{13}C NMR spectroscopic. Moreover, the hydroxyl content of lignin obtained from the mild alkaline extracts of bagasse by XAD resin was almost higher than that of lignin extracted from triploid of *Populus tomentosa* Carr., as determined by ^{31}P NMR, especially that of aliphatic and phenolic hydroxyl contents (Zhang *et al.* 2010). The G and H phenolic hydroxyl groups were more abundant in bagasse than in wheat straw soda lignin (Ahvazi *et al.* 2011). The wheat straw soda lignin was chemically modified, and the results indicated that lignopolyol with higher aliphatic hydroxyl content was prepared more efficiently. This implies that the diverse and abundant hydroxyl lignin of bagasse that was extracted by resin under mild alkaline conditions can be used to manufacture value-added products by hydroxyl-modified lignin (Argyropoulos 1994; Shi *et al.* 2019). Methylation, phenylation, etherification, and esterification are common chemical methods used to modify the hydroxyl groups of lignin. For example, Lin *et al.* (2018) studied hydroxyl and carbonyl groups of lignin, which provide cross-linking sites for formaldehyde by electrophilic addition and aldol condensation reactions, produces lignin-formaldehyde cryogel.

Thermal Analysis of Lignin

The TGA-DTG curves of centrifuged lignin and lignin adsorbed from bagasse are shown in Fig. 8. In the first phase, the thermal decomposition occurred between 120 and 200 °C. The comparison between resin adsorption and the direct centrifugation of lignin showed that the adsorbed lignin appeared in a gentle phase and the weight loss obtained by direct centrifugation was continuous. Possibly, the directly-centrifuged lignin had small molecules, such as monosaccharides (xylose, glucose, *etc.*), in the biomass. It has been reported that xylose undergoes thermal decomposition at 167 to 180 °C (Geng *et al.* 2003), and the thermal decomposition temperature of glucose is below 200 °C (Sun *et al.* 2013). This was consistent with the sugar content that was determined after XAD-resin adsorption.

In the second phase, decomposition occurred over the range of 200 to 800 °C. The weight loss at this stage was due to the combined decomposition of lignin and hemicellulose.

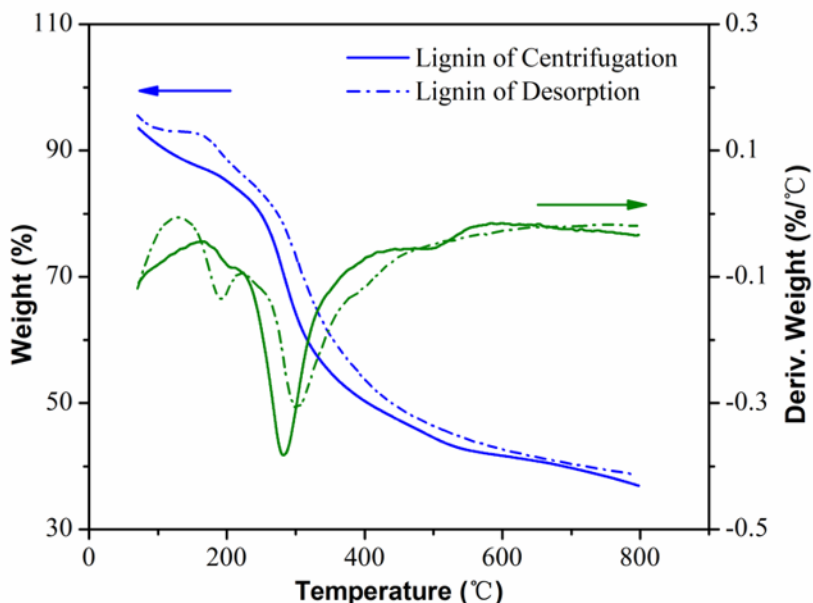


Fig. 8. Thermogravimetric curves of centrifuged and resin-adsorbed lignins

The maximum mass loss rates of the centrifuged lignin and adsorbed lignin were detected at 282.8 and 300.7 °C, respectively, which demonstrated the superior thermal stability of the adsorbed lignin to that of the centrifuged lignin. This likely indicates that the adsorbates contained less hemicellulose and the lignin was highly pure. In the second phase, the thermal decomposition of hemicellulose was observed from 200 to 400 °C. The weight loss of lignin was obvious and was mainly due to the disruption of unstable β -O-4' lignin linkages (Wang *et al.* 2019). This thermal decomposition process could be due to the fracture and detachment of C–C bonds and C–O bonds attached to the main hemicellulose backbone. Moreover, decarbonylation and decarboxylation might have occurred (Sun *et al.* 2013), as hemicellulose was broken down into CO₂, CO, and light hydrocarbons (Yang, *et al.* 2007).

The various functional groups with different thermal stabilities were contained by the lignin structure, which accounts for the wide range of thermal decomposition temperatures associated with lignin. The decomposition of the polymer structure in the lignin began at 200 to 275 °C, and it has been reported that the propane side chain of lignin begins to degrade at 230 to 260 °C (Fiddler *et al.* 1967). Additionally, the β - β and C-C linkages of bagasse lignin were cracked at 273 to 350 °C (Sarkanen and Ludwig 1971). The main process of thermal decomposition of lignin occurred at around 400 °C. The aromatic hydrocarbons, hydroxyphenols, phenols, and G/S compounds were formed, and phenolic hydroxyl groups were present in most compounds. The lignin substituents and aliphatic structures were decomposed, where H₂O was released from lignin hydroxyl groups and CO₂ was derived from the lignin carboxyl group (Brebu *et al.* 2010).

CONCLUSIONS

The separation of lignin from mild alkaline extracts of sugarcane bagasse was achieved using an aromatic-selective resin. The adsorbate was analyzed by various techniques.

1. In the adsorbates, trace amounts of hemicellulose originating from lignin-carbohydrate complex (LCC) structures were identified.
2. Various linkage distributions of lignin polymers were studied. In the adsorbates there were major S, G, and H lignin units; PCA and FA structures in the aromatic region; and β -O-4', β -5', β - β ', and β -1' structures in the side chain. The BE content observed was mainly from linkages in the LCC structure. However, the β -1' structure was not detected when a hot-water extraction was used on the sugarcane bagasse, and the BE content was considerably lower than that from the alkaline extraction.
3. The hydroxyl group content of mild alkaline lignin obtained from the bagasse was generally higher than that of lignin obtained *via* other pretreatment methods.
4. The thermal stability of the adsorbed lignin was superior to that of the centrifuged lignin.
5. New, structural characteristics of lignin and LCC structures subjected to different pretreatment and purification conditions were elucidated in this study. This lignin, which mainly comprises hydroxyl groups, can expand the line of value-added lignin products, reduce the effects of bagasse waste on the environment, and provide economic benefits.

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