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High Purity Lignin Extraction Approach via Heat-Treated Black Liquor


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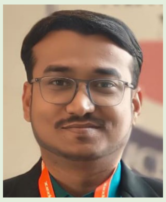
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Abstract: *Lignin is considered a potential precursor for the biorefinery industry. The black liquor produced from the pulp and paper industry is a major feedstock for lignin extraction. However, its strong association with carbohydrates and inorganic impurities in black liquor limit its extraction into a highly pure form. The present study investigates lignin extraction from sugarcane bagasse-derived agro-based black liquor (ABBL) via heat treatment followed by acid precipitation. Heat treatment of ABBL caused the breakage of bonds between lignin and carbohydrates in Lignin Carbohydrate Complexes (LCCs), thereby improving purity ~ 57.6% and yield ~ 17%. The sophisticated instrumental analyses performed in this study provided strong support for the favourable effect of heat treatment on the structural, thermal, and morphological characteristics of lignin. This study provides an industry-oriented, scalable approach for extracting more pure lignin from black liquor for high-end applications.*

Keywords: *Pulp and Paper, Black Liquor, Heat-treatment, Lignin, Biorefinery, Sustainable Development Goal*

Introduction

Lignin, as a natural biopolymer, is surpassed only by cellulose in terms of biospheric abundance [1, 2]. It accounts for 10-35% of the lignocellulosic biomass and is a vital structural constituent of plant cell walls, offering rigidity, helping the transport of minerals, and providing protection against microbial attack [3-6]. It is a renewable feedstock for biofuels, biogas, and advanced energy storage materials such as supercapacitor electrodes and organic flow batteries [7-12]. The unique three-dimensional structure of lignin has increased its importance as soil conditioners, biopesticides, food packaging material, adhesives, and as a precursor for fine chemicals and carbon fibres [8-10, 13]. It is estimated that lignin production may reach 225 million tons worldwide by 2030, which supports its growing significance as a renewable resource [14].

Currently, the primary source of lignin is pulp and paper mill black liquor. Almost 1.3 billion tons of black liquor are produced annually [15]. However, only a small fraction, just 0.075 million tons, is extracted annually through biorefineries and soda processes [16]. Various processes such as enzyme purification, membrane filtration/ultrafiltration, solvent fractionalisation, and organic and inorganic acid precipitation [17-21] are available for lignin extraction from black liquor. Among these, acid precipitation is used worldwide. However, the greatest challenge in acid precipitation is balancing yield with purity. Inorganic salts such as thiosulfates, sulfides, carbohydrates, metals, organosulfur moieties, silica, and resins present in black liquor might precipitate with lignin, hindering its applicability. Among these, carbohydrates are not easily separated from lignin due to the formation of Lignin Carbohydrate Complexes (LCCs). LCCs contain strong covalent and non-covalent bonds between lignin and hemicelluloses, which prevent the effective separation of lignin into an independent phase [22-25]. Heat treatment can result in highly pure lignin up to 96–98%, according to studies, by disrupting robust linkages in LCCs [26, 27]. Various studies reported a significant reduction in the viscosity of black liquor following heat-treatment, which also supports breakdown of LCCs [23, 24, 28].

Heat treatment promotes demethylation and demethoxylation of polymeric phenols, converting them to catechols and methoxy catechols [26, 27]. 94% demethylation of black liquor can be achieved by thermal treatment [29]. During demethylation, methoxy groups react with sulfur species present in Kraft black liquor to form dimethyl sulfide and increase the number of free phenolics –OH groups. These free phenols increased the reactivity of lignin towards oxygen and formaldehyde, and also increased its solubility in organic solvents [29]. Studies reported that thermally treating black liquor increases phenolic OH contents by 31% [28, 30, 31]. Heat treatment improves the filtration properties of black liquor before carbonation, thereby reducing the investment costs of a lignin separation plant [32]. Heat treatment of agro-residue-based black liquor as a purification strategy for lignin extraction has not been adequately studied. This study introduces a unique strategy for isolating high-purity lignin, a value-added biopolymer, from renewable

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sugarcane bagasse derived black liquor bioresource by targeted heat treatment of ABBL for advanced applications.

2. Materials and Methods

2.1. Heat-treatment of black liquor:

Sugarcane-based, Weak Agro-Based Black Liquor (W-ABBL) and Semi-Concentrated Agro-Based Black Liquor (SC-ABBL) samples were collected from a North-Indian pulp and paper mill. The heat treatment of SC-ABBL was performed at 180˚C for 20 minutes, as described in our previous work [23, 24]. The heat-treated SC-ABBL was further used for lignin extraction.

2.2. Procedure for lignin extraction:

A known amount of W-ABBL and heat-treated SC-ABBL were separately taken for acid precipitation. Liquors were initially placed in the hot-water bath at 70-80 °C, and 98% pure H_2SO_4 was gradually added drop-by-drop to the black liquor with stirring to reach the targeted pH of 2-3. The acidified black liquor was then centrifuged at 2500 rpm for 50 minutes. The settled lignin was collected in petri dishes for drying in the sun, and the filtrate was collected separately. Once dried, the lignin granules were ground and then sieved using a 52-mesh sieve, as shown in Figure 1. The mass balance of the lignin extraction process from the black liquor was also performed.

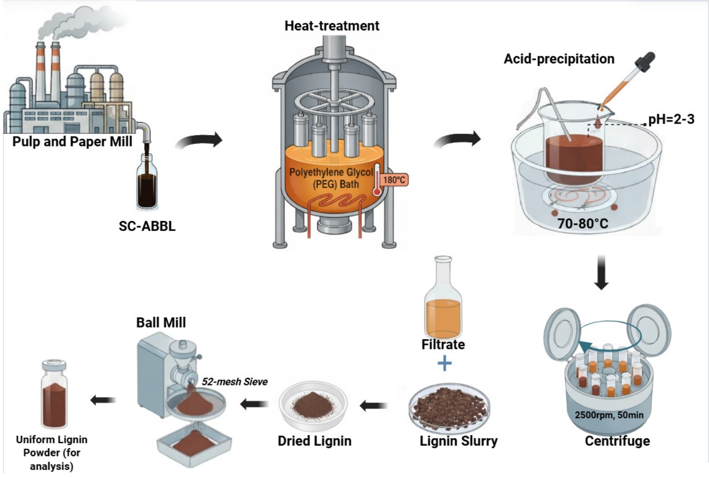

Figure 1. Schematic representation of lignin extraction from heat-treated black liquor

2.3. Physicochemical and instrumental analysis of lignin:

The isolated lignin samples were analysed for moisture (TAPPI T 264), ash (TAPPI T 211), silica (TAPPI T 245 cm-07), Gross Calorific Value (Bomb calorimeter, Parr Instrument, USA), CHNS (Elemental analyser, Vario EL cube, Elementar, Germany), sodium and potassium (flame photometer, FF-200, Cole-Parmer, USA), calcium and magnesium (TAPPI T 625 cm-14), acid-insoluble lignin (TAPPI T 222 om-06), acid-soluble lignin (UV-Vis spectroscopy, TAPPI UM 250), chloride (Mohr's argentometric titration) and bulk density (graduated-cylinder tapping method). The extracted lignin samples were also analysed for morphology using SEM (MIRA 3 LMH, TESCAN, USA), functional groups using FTIR (Spectrum Two, Perkin Elmer, USA), crystallinity using XRD (Ultima IV, Rigaku, Japan) and thermal stability using TGA/DSC (Model 55/25, TA Instruments, USA).

3. Results and Discussion

3.1. Physicochemical properties of W-ABBL and heat-treated SC-ABBL Lignins

The mass balance of the lignin extraction process is shown in Figure 2, and the physicochemical properties of the extracted lignin specimens are reported in Table 1. The lignin yield enhanced significantly ~ 17% after heat-treatment. This is consistent with reports that elevated temperature and acidic/auto-hydrolytic conditions cleave β-O-4 and other LCC linkages [33, 34]. The 12.65% and 15% declines in carbon content and GCV post heat-treatment, respectively, indicate that the carbohydrate and hemicellulose fractions present in lignin dissolve in the filtrate during acid precipitation, without co-precipitating with lignin. The C/H ratio increased from 7.55 to 9.56 after heat treatment, which is indicative of aromatic condensation or an increased degree of unsaturation. Conversely, the decrease of H/C ratio from 0.133 to 0.105, suggests increased aromaticity in the extracted lignin. The highly aromatic nature of black liquor-extracted lignin makes it feasible for the synthesis of biochemicals, biofuels, and bioelectricity [35]. A similar trend is also observed for lignin under hydrothermal carbonisation or thermal modification, where higher temperatures increase aromaticity and the formation of char-like structures [36, 37]. Additionally, slightly reduced O/C ratios in heat-treated lignin improve suitability for thermochemical conversion.

A technical Kraft lignin contains 2–3% total sulphur primarily due to the cooking process [38]. The increase in sulphur content of lignin from 5.31 to 5.88 after heat- treatment is due to the increased consumption of sulphuric acid. Lignin having sulphur >5 % (w/w) finds application as a bio-filler/reinforcement in polymer composites and as an excellent dispersion and antioxidant protection in pesticide compositions [36, 39-42]. The heat-treated SC-ABBL lignin showed a noticeable increase in ash content with respect to the W-ABBL lignin. This may be due to co-precipitation of inorganic salts during acidification even after heat treatment. The slight variations in the concentrations of sodium, potassium, calcium, magnesium, and chlorides are possibly due to subsequent dissolution of entrapped inorganic species within lignin and hemicelluloses. The silica remained almost constant in both lignins. Lower moisture content in heat-treated SC-ABBL lignin is advantageous for downstream handling, storage, and thermochemical conversion. Heat-treated SC-ABBL lignin showed higher bulk density than W-ABBL lignin as a result of an increase in surface area with degradation of the LCC bond. Reduction in volatile matter in heat-treated SC-ABBL lignin as compared to W-ABBL lignin is an outcome of the escape of volatiles during thermal treatment, thereby increasing fixed carbon content in heat-treated SC-ABBL by 24.88%. The filtrate obtained after lignin separation can be used to produce chemicals, such as lactic acid, glycolic acid, and carboxylic acids, via chromatographic separation, hemicellulose recovery, and NaOH recovery [43, 44].

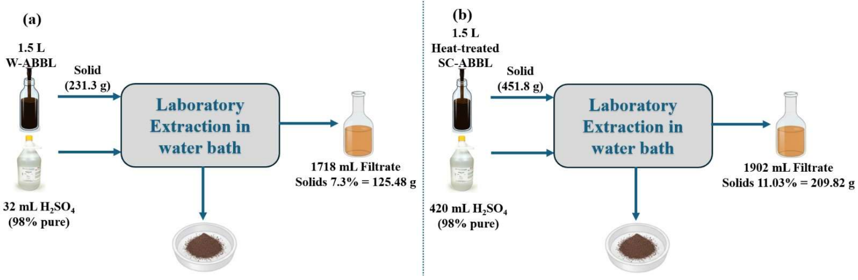

Figure 2. Mass Balance of Lignin Extraction Process from (a) W-ABBL (b) Heat-treated SC-ABBL

Table 1. Physicochemical properties of W-ABBL and Heat-treated SC-ABBL Lignin.

Parameter	W-ABBL lignin	Heat-treated SC-ABBL lignin
Moisture, %w/w	17.34	7.77
Silica as SiO_2, %w/w	2.78	2.77
Acid Insoluble Lignin, %w/w	39.67	42.09
Acid Soluble Lignin, %w/w	6.08	1.47
Lignin yield, %w/w	45.75	53.56
GCV, cal/gm	3538.86	3010.29
Lignin Purity, %w/w	55.5	87.5
Calcium as Ca, %w/w	0.07	0.14
Magnesium as Mg, %w/w	0.04	0.09
Potassium as K, %w/w	10.18	9.91
Sodium as Na, %w/w	11.86	10.39
Chloride as Cl-, %w/w	1.23	1.89
Carbon as C, %w/w	36.39	31.79
Hydrogen as H, %w/w	4.81	3.33
Nitrogen as N, %w/w	0.14	0.23
Sulphur as S, %w/w	5.31	5.88
Ash, %w/w	12.30	15.74
Oxygen as O, %w/w	14.05	12.04
C/H	7.54	9.56
H/C	0.13	0.11
C/N	276.47	142.67
O/C	0.39	0.38
Bulk density (g/mL)	0.75	0.83
Volatile matter (%)	40.18	38.80
Fixed Carbon (%)	30.18	37.69

3.2. Instrumental Analysis

3.2.1. Functional Group Analysis:

The FTIR spectra for the isolated lignin specimens are shown in Figure 3. The aliphatic and aromatic OH stretching bands are observed in the broad absorption band at 3600-3000 cm^{-1}; however, a less intense O–H band (nearly 3400 cm^{-1}) was observed after heat treatment. This may be due to dehydration/condensation reactions. The phenolic fraction also increased as β–O–4 and methoxyl groups cleave, generating free phenolic OH, which is evident in the broadening of the band. A hypsochromic blue shift in the peak from 2921 cm^{-1} to 2978 cm^{-1} after heat treatment is likely due to demethylation and demethoxylation reactions, which alter the environments of $CH_3/CH_2/OCH_3$ groups[27]. Additionally, the peaks originating from aromatic ring vibrations as mentioned in Table 2 decreased in intensity after the heat treatment due to the partial degradation of aromatic units and structural rearrangements. A relative change at 1600 / 1510 cm^{-1} for lignin samples after heat treatment indicates condensation/cross-linking of aromatic units in black liquor, also observed in some heat-treated wood/lignin systems [45-47]. The most notable feature is the emergence of a characteristic peak at 1718 cm^{-1}, which confirms the presence of C=O stretching in esters/carboxylic acids (oxidised side chains or residual hemicellulose/fats). The thermal processing of black liquor leads to an increase in carbonyl signals due to the formation of carboxylic acid and ester groups [27, 48, 49]. Hence, heat treatment results in the formation of non-conjugated carbonyls (ketones/aldehydes/esters) via oxidation and side chain reactions. This can also be due to the transformation of LCCs to low-molecular-weight organic acids (acetic, lactic, glycolic, and oxalic acids). The reduction in intensity and relative migration of the peak from 1108 to 1120 cm^{-1} are consistent with degradation of S/G units and enrichment in H- and catechol-type lignin in heat-treated SC-ABBL lignin [26, 27, 50].

Table 2. FTIR characteristics of W-ABBL and Heat-treated SC-ABBL Lignin

Absorption Band / Peak Centre	Assignment of Bands	Mode of vibration	References
3390 / 3409 cm^{-1}	phenolic and aliphatic/aromatic OH	Stretching	[51, 52]
2978 / 2921 cm^{-1}	C–H bond in CH_3/CH_2 of side chains and methoxy groups	Stretching	[52, 53]
1718 cm^{-1}	C=O in esters/carboxylic acids (oxidised side chains or residual hemicellulose/fats)	Stretching	[53, 54]
1606 / 1603 and 1517 /1509 cm^{-1}	aromatic ring skeletal vibration; conjugated C=O / lignin aromatics; G ring (etherified guaiacyl)	Stretching	[52-55]
1120 / 1108 cm^{-1}	syringyl ring / aromatic C-H	In-plane Deformations	[56, 57]
804 cm^{-1}	aromatic C–H	Out-of-Plane Deformations	[53]

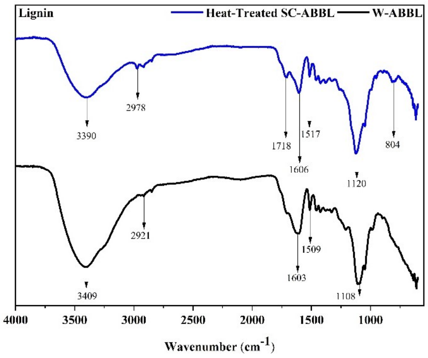

Figure 3. FTIR characteristics of Lignins

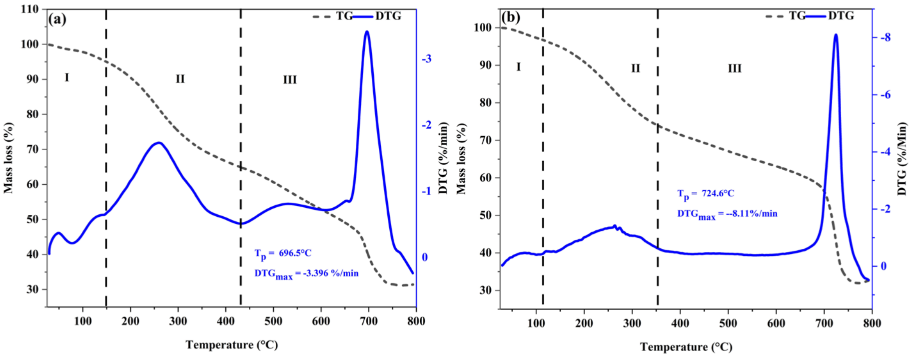

Figure 5. TGA/DTG characteristics of
(a) W-ABBL and (b) Heat-treated SC-ABBL Lignin

3.2.2. Surface Morphology

Morphology of lignin extracted from the W-ABBL and heat-treated SC-ABBL is provided in Figure 4. The W-ABBL lignin shows a dense, layered structure with log- and wide-bar-shaped formations. Such findings are consistent with bimodal particle distributions and intricate pore networks common in acid-extracted Kraft lignin [58, 59]. In contrast, heat-treated SC-ABBL lignin forms a highly porous network resembling a "beehive cluster" of distorted polygonal and spherical shapes. This blistering of structures, here, is primarily attributed to the thermal degradation of LCC bonds and subsequent release of volatile components, thereby transforming the morphology from a dense structural matrix into a more porous network [24].

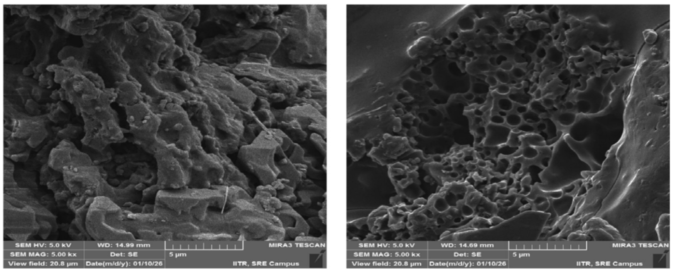

Figure 4. SEM characteristics of W-ABBL lignin (left),
and Heat-treated SC-ABBL lignin (right).

3.2.3. TG/DTG analysis:

Figure 5 shows that the thermal degradation profiles of lignin samples occur in three stages: moisture removal (Stage I), carbohydrate degradation (Stage II), and lignin decomposition (Stage III). In Stage I (25–200°C), mass loss is due to the evaporation of surface-bound moisture and volatiles, with heat-treated SC-ABBL lignin showing a lower moisture content (3.25%) than W-ABBL lignin (4.91%) [60]. In Stage II (150–450°C), W-ABBL lignin shows greater mass loss in comparison to heat-treated SC-ABBL lignin, indicating a higher presence of residual hemicellulose and cellulose in W-ABBL lignin and the heat-treated SC-ABBL lignin being the purer one [61]. Stage III (345°C to completion) refers to the strong pyrolytic zone where lignin degradation dominates [62]. The peak decomposition temperature (T_p) for heat-treated SC-ABBL lignin (724.25°C) is notably higher than that of W-ABBL lignin (695.81°C), signalling a more condensed aromatic structure and superior thermal stability [63]. Heat-treated SC-ABBL lignin has a higher maximum mass-loss rate (DTG_{max}) of -8.11 %/min compared to -3.34 %/min for W-ABBL, confirming a more uniform and stable molecular framework resulting from heat treatment [64].

3.2.4. DSC analysis:

Figure 6 shows DSC thermograms of W-ABBL and Heat-treated SC-ABBL lignin. Temperature-dependent heat capacity (C_p), glass transition (T_g), crystallinity, and melting zones were estimated from these thermograms to identify key thermal transitions in lignin [65]. The T_g for W-ABBL lignin (76.92°C) was higher than that of heat-treated SC-ABBL lignin (62.70°C), showing that likely a more intact aromatic network, higher molecular weight, and stronger inter-chain interactions like π–π stacking and hydrogen bonding are present in W-ABBL lignin. Instead, the lower T_g in SC-ABBL lignin suggests that heat treatment resulted in partial depolymerisation, thereby increasing phenolic hydroxyl groups and chain mobility. In the crystallinity zone, both samples exhibited endothermic peaks related to structural reorganisation. W-ABBL showed a peak at 208.43°C, while SC-ABBL peaked at 206.81°C. This reduction in SC-ABBL is attributed to cleavage of ether linkages and decreased molecular ordering, which requires less thermal energy for the transition. The melting temperatures (T_m) of 248.02°C for W-ABBL and 249.79°C for SC-ABBL, with a smaller difference, indicate that while heat treatment modifies side chains and mobility, the stable aromatic backbone of the lignin remains largely intact [66].

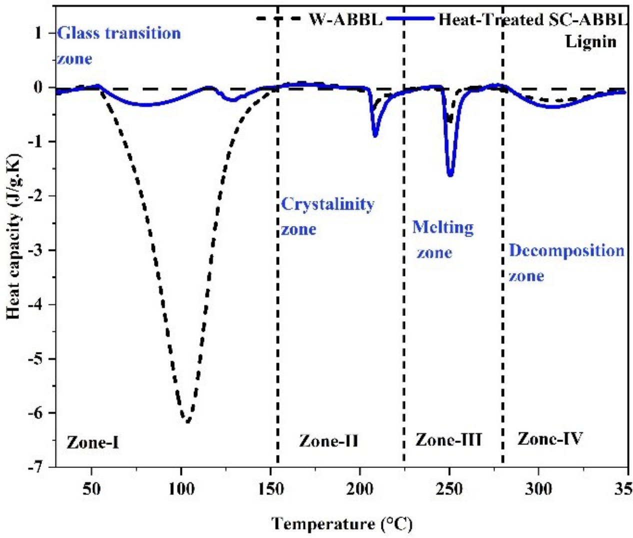

Figure 6. DSC characteristics of W-ABBL and Heat-treated SC-ABBL Lignin.

3.2.5. XRD analysis

Figure 7 shows that both W-ABBL and heat-treated SC-ABBL lignin show the diffraction peaks in the 2θ range around 30°. These peaks are relatively broad and more intense than those observed in black liquor by Anupam et al. [24]. This is because black liquor contains inorganic salts, sodium-based compounds, and other organics, in addition to lignin. Lignin extracted from heat-treated SC-ABBL exhibited a sharper and more distinct peak near 30°, reflecting reduced inorganic content, higher purity, and improved structural ordering [67]. Although lignin remains predominantly amorphous, the more explicit peak definition highlights the effectiveness of heat treatment in separating and refining lignin compared to black liquor.

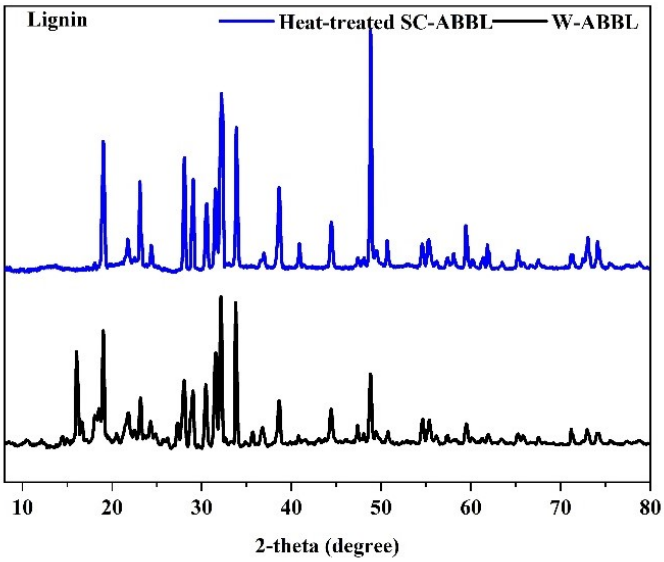

Figure 7. XRD graph of Lignins

4. Conclusion

Though black liquor is generally used for lignin extraction, the LCCs present in it increases its impurity. Hence, this paper examined the potential to increase lignin purity via heat treatment of black liquor, which efficiently breaks the LCC bond. Heating the black liquor at 180°C for 20 minutes before lignin extraction makes lignin precipitate easier, lowers the pH, increases the phenolic groups, promotes demethylation/ demethoxylation reactions, and, more significantly, results in a 58% surge in its purity along with a 17% rise in yield. The FTIR analysis confirmed that thermal treatment modifies lignin structures by partially degrading the aromatic units. SEM analysis revealed a dense structural matrix transforming into a porous network-like structure upon thermal degradation of LCCs during heat treatment. The higher maximum mass-loss rate (DTG_{max}) of -8.11 %/min compared to -3.34%/min untreated black liquor lignin supports the uniform and stable molecular framework resulting from heat treatment.

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