

Article

Sustainable Upscaling of High-Purity Lignin Production from Kraft Black Liquor Waste via a Green Chemical Process

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Abstract

Lignin present in black liquor represents a major renewable resource that can be valorized into high-value bio-based materials; however, its recovery typically relies on strong mineral acids that pose environmental and corrosion concerns. In this study, citric acid was employed as a greener and less corrosive alternative for lignin precipitation from black liquor. Laboratory-scale experiments were conducted to optimize recovery conditions, identifying a precipitation pH of 2.0 and a lignin-to-deionized water washing ratio of 1:100 as the optimal parameters. Under these conditions, the recovered lignin exhibited high purity ($91.69 \pm 0.23\%$), with very low ash ($0.11 \pm 0.02\%$) and volatile content ($5.01 \pm 0.51\%$). Bench-scale validation confirmed the reproducibility of the optimized process, yielding lignin with comparable purity ($91.30 \pm 1.28\%$) and recovery yield ($14.05 \pm 0.21\%$). Gel permeation chromatography revealed that the isolated lignin possessed a relatively high molecular weight ($M_w \approx 45,000\text{--}47,000 \text{ g mol}^{-1}$) with a narrow molecular weight distribution ($PDI = 1.09$), which remained consistent during scale-up. Structural characterization by elemental analysis, FTIR, and ^1H NMR further confirmed that the chemical composition and functional groups of lignin were preserved across both processing scales. These findings demonstrate that citric-acid-based precipitation is a promising approach for recovering structurally consistent lignin from kraft black liquor and provide valuable insights into the bench-scale implementation of green lignin recovery processes.

Keywords: bench-scale validation; black liquor; citric acid precipitation; green chemical; high-purity lignin; scalable green process



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1. Introduction

Black liquor, a major byproduct of the pulp and paper industry, is one of the largest underutilized biomass streams worldwide [1–3]. An estimated 1.2–1.3 billion tons of black liquor are generated each year, of which approximately 98% is still burned as low-grade fuel, while only a small fraction is valorized into commercial products [4–6]. Notably, black liquor contains up to 45% lignin, a carbon-rich aromatic biopolymer with high thermal stability and abundant functional groups, making it a promising renewable feedstock [7–9]. However, efficient and scalable methods for lignin recovery and purification remain limited [10–12]. Recovering lignin from black liquor offers significant environmental and

economic benefits, including reduced carbon emissions and the production of high-value materials such as activated carbon, carbon fibers, biofuels, and phenolic resins [13–15]. In addition, lignin shows strong potential for advanced applications such as energy storage materials and separation technologies [16,17].

Among the methods for lignin recovery, acid precipitation is the most widely used due to its simplicity and cost-effectiveness [9,18,19]. This method involves lowering the pH of black liquor by adding acid, which causes lignin to coagulate and precipitate [20,21]. Despite its effectiveness, this approach often results in low-purity lignin unless it undergoes additional purification procedures [22–24]. Nevertheless, acid precipitation remains the preferred method due to its scalability, adaptability to various black liquor types, and compatibility with industrial processes [25,26].

The growing interest in lignin valorization from black liquor highlights the importance of examining recovery processes that have already been implemented on an industrial scale. Currently, five major industrial-scale processes are employed to recover lignin from kraft black liquor: the WestVaco process, the LignoBoost process, the LignoForce System™, the Soda (Protobind 2400), and the Sequential Liquid–Lignin Recovery and Purification (SLRP) process [27–29]. All these technologies utilize strong acids, most commonly sulfuric acid, as the acidifying agent during precipitation to get high lignin yields. These methods, however, pose several drawbacks, including low durability of equipment, potential health hazards for operators, and the generation of waste streams that are more difficult to handle and neutralize [30,31].

In response to these drawbacks, research efforts have shifted toward identifying greener and less corrosive chemicals. Among the most promising options, weak organic acids are considered greener alternatives for lignin precipitation [32–34]. At the laboratory scale, weak acids, particularly citric acid, have demonstrated the ability to reduce corrosion risks and minimize environmental impact while still enabling efficient lignin precipitation from both hardwood and softwood black liquors. The obtained lignin typically contains lower sulfur content and reduced inorganic ash compared to precipitation using strong acids [32,34,35]. However, this promising method has not yet been widely implemented on an industrial scale. This underscores the need for further research into process optimization, scalability, and integration with existing recovery systems.

Although research on lignin recovery using weak organic acids has increased considerably, most studies remain limited to laboratory-scale investigations conducted under controlled conditions. In contrast, pilot- and industrial-scale lignin recovery has predominantly relied on strong-acid precipitation processes, such as those implemented in the LignoBoost and LignoForce technologies, owing to their proven process robustness and industrial feasibility. Several pilot-scale studies have demonstrated the technical feasibility of lignin recovery from kraft black liquor; however, these investigations have primarily focused on conventional acid precipitation systems using mineral acids and product characterization, whereas scale-up studies employing weak organic acids remain scarce. Consequently, the scalability of environmentally friendly precipitation systems has not yet been adequately validated.

Furthermore, systematic comparisons between laboratory- and bench-scale lignin recovery using weak organic acids are still lacking. In particular, there is limited information regarding whether the lignin yield, purity, ash content, volatile matter, molecular characteristics, and overall process performance achieved under laboratory conditions can be consistently maintained during process scale-up. In addition, although water washing has frequently been employed as a purification step, comprehensive optimization of hot deionized water purification to produce high-purity lignin has received relatively little attention.

To address these knowledge gaps, the present study systematically investigates lignin recovery from kraft black liquor using citric acid as a green precipitating agent at both laboratory and bench scales. In addition, the purification process was optimized through hot deionized water treatment to maximize lignin purity while minimizing inorganic impurities. By integrating laboratory-scale optimization, bench-scale validation, and comprehensive physicochemical characterization, this work provides practical insights into the scalability of green lignin recovery and demonstrates the feasibility of replacing conventional strong-acid precipitation with a more environmentally benign alternative.

2. Materials and Methods

2.1. Materials

The kraft black liquor used in this study was obtained from the hardwood kraft pulping process. Technical-grade citric acid supplied by Brataco Chemical Inc. (Bandung, Indonesia) was used for acid precipitation. Analytical-grade sulfuric acid (95–97%) was purchased from Smart Lab, Inc. (Banten, Indonesia). In addition, demineralized water (DM water) was used to dilute the black liquor, whereas deionized water (DI water) was utilized for lignin purification.

2.2. Black Liquor Characterization

The physicochemical properties of black liquor were analyzed to optimize lignin recovery. The moisture content of black liquor was determined by oven-drying the sample at 105 °C for 5 h. Lignin concentration was quantified according to TAPPI T-222, while pH was measured using a calibrated pH meter.

2.2.1. Lignin Content Measurement

Lignin content was determined according to TAPPI T-222. The testing procedure was as follows: 1 g of dry sample (**a**) was dissolved in 15 mL of 72% (*w/w*) sulfuric acid and stirred at 250 rpm using a magnetic stirrer for 2 h. After dissolution, the sample was diluted until the acid concentration reached 3% (*w/w*) and then boiled for 4 h. The resulting precipitate was then separated using Whatman No. 42 filter paper (Cytiva, Marlborough, MA, USA). The residue was washed with deionized water until a neutral pH of 7 was achieved. It was then dried and weighed periodically until a constant mass was obtained (**b**). This process was repeated three times for each variation, and the lignin percentage was calculated using Equation (1).

$$\text{Lignin content} = \frac{b}{a} \times 100\% \quad (1)$$

2.2.2. Fourier Transform Infrared (FTIR) Spectroscopy of Black Liquor

FTIR analysis was conducted to identify and compare the functional groups present in the black liquor samples using Bruker Alpha II (Bruker Optics GmbH & Co. KG, Ettlingen, Germany). The samples were prepared using the KBr pellet method, and the spectra were recorded between 4000 and 400 cm^{−1} with a resolution of 4 cm^{−1} in absorbance mode.

2.3. Laboratory-Scale Lignin Recovery

Lignin recovery from black liquor at the laboratory scale was conducted in two main stages: acid precipitation and purification. In the first stage, lignin was precipitated from the black liquor by adjusting the pH with citric acid, while in the second stage, the precipitated lignin was purified using deionized water to remove soluble impurities. These sequential steps were designed to establish optimal operating parameters that could later be validated in the bench-scale system.

2.3.1. Acid Precipitation

Kraft black liquor (15 g) was diluted with 187.5 mL of demineralized (DM) water, corresponding to a solid-to-liquid ratio of 1:12.5, to facilitate precipitation. Lignin was then precipitated by gradually adding a 50% (*w/w*) citric acid solution until target pH values of 2, 3, and 4 were achieved. The precipitate was separated using Whatman No. 41 filter paper and washed with DI water until a neutral pH of 7.0 was achieved. The recovered solids were air-dried under a fan for 24 h, followed by drying in a food dryer at 80 °C for 12 h to obtain a constant weight.

2.3.2. Lignin Purification

The dried lignin obtained from the precipitation process was purified by refluxing in DI water at various lignin-to-DI water weight ratios (1:50, 1:100, 1:150, 1:200, 1:250, and 1:300) at 100 °C for 2 h to remove soluble impurities and enhance lignin purity. The purified lignin was subsequently filtered using Whatman No. 41 filter paper and dried in a food dryer at 80 °C for 12 h to obtain a constant weight. The sample codes used for lignin purification are listed in Table 1.

Table 1. Sample code of lignin purification.

Sample Code	Lignin and DI Water Weight Ratio	
	Lignin	DI Water
LW0	1	0
LW50	1	50
LW100	1	100
LW150	1	150
LW200	1	200
LW250	1	250
LW300	1	300

2.4. Bench-Scale Process Validation

The optimized laboratory-scale parameters were validated using a bench-scale reactor system. The reactor consisted of a 34 L SS-316 tank equipped with a mechanical stirrer and a temperature controller and was operated at a working volume of 25 L, as illustrated in Figure 1a. For each batch, 1 kg of kraft black liquor was diluted with 12.5 L of demineralized (DM) water, maintaining the optimized solid-to-liquid ratio of 1:12.5 established during the laboratory-scale study. The suspension was continuously stirred at 300 rpm throughout the precipitation process. Subsequently, a total of 7.425 L of 50 wt% citric acid solution was manually added at an estimated rate of approximately 100 mL s^{−1} (within the approximate range of 50–150 mL s^{−1}) until the optimized precipitation pH of 2.0 was achieved. After reaching the pH target, the suspension was maintained under continuous stirring for an additional 30 min to ensure complete lignin precipitation.

Following acid precipitation, the recovered lignin slurry (approximately 20.9 L) was separated using a gravity-filtration system equipped with Whatman No. 41 filter paper (50 cm diameter). The initial filtration step required approximately 10 h. The recovered lignin filter cake was subsequently transferred to a washing vessel and washed with deionized (DI) water in five consecutive washing cycles, using 5 L of DI water per cycle (25 L in total). Each washing cycle was allowed to drain completely before the subsequent washing step was initiated. The washing process required approximately an additional 10 h and was continued until the filtrate reached neutral pH (≈7), ensuring the removal of residual citric acid and other soluble impurities. The neutralized lignin was then dried in a food dryer at 80 °C for 12 h to obtain a constant weight.

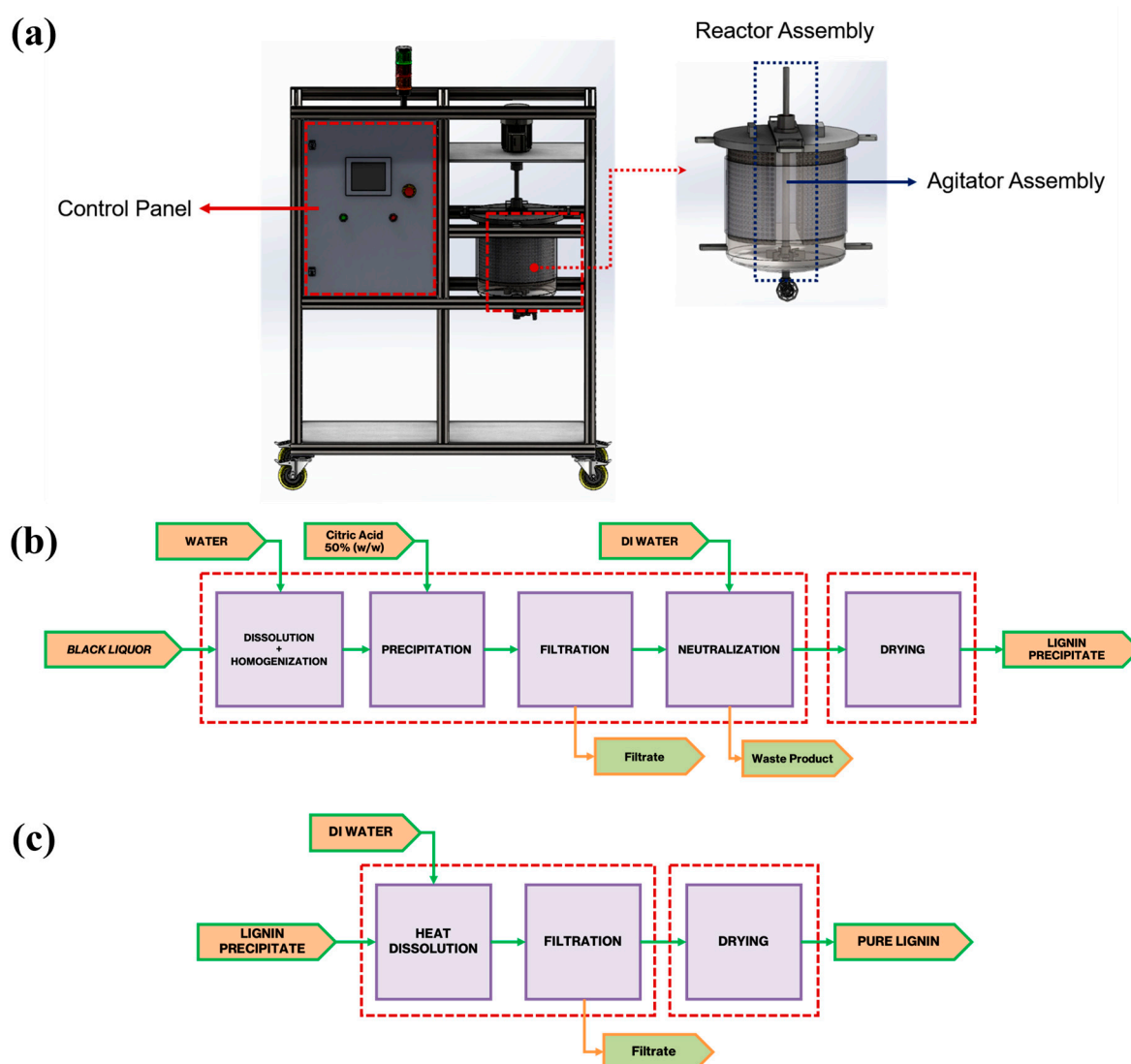


Figure 1. (a) 3D design of the bench-scale reactor and simplified schematic of the bench-scale process for lignin recovery: (b) precipitation of lignin and (c) purification of the recovered lignin. The orange boxes indicate the process inputs, the purple boxes represent the processing units or equipment, the green arrows indicate the direction of material flow through each processing unit, and the orange arrows indicate the by-products or waste streams generated during the process. The red dashed boxes indicate integrated process stages that should be considered as inseparable units. In panel (a), the red and blue arrows identify the control panel and reactor assembly components, respectively.

For the purification stage, the dried lignin was reintroduced into the same bench-scale reactor and mixed with DI water using the optimized lignin-to-DI water ratio of 1:100. The suspension was heated at 100 °C for 2 h to remove residual soluble impurities. After purification, the lignin was again separated using the same gravity filtration system, washed with DI water as required, and dried in a food dryer at 80 °C for 12 h until a constant weight was obtained. A simplified process flow diagram (PFD) of the complete bench-scale recovery process is presented in Figure S1, while simplified schematics of the precipitation and purification stages are shown in Figure 1b and Figure 1c, respectively.

2.5. Assessment of Recovery Efficiency and Lignin Characterization

The lignin samples obtained from both scales were characterized to assess the reproducibility and scalability of the recovery and purification methods. Identical analytical techniques were applied to maintain consistency and comparability across scales. Further-

more, a comparative assessment was carried out to verify that the lignin characteristics from the bench-scale process retained the quality and properties observed at the laboratory scale. The evaluation encompassed yield percentage, purity, ash content, and volatile content, detailed in the following sections.

2.5.1. Yield Percentage

The lignin yield was evaluated based on the recovery efficiency after the precipitation and purification processes. The initial lignin content in the black liquor was determined prior to recovery. The mass of recovered lignin after drying to constant weight was recorded as **(b)**, while the initial lignin content was taken as **(a)**. The measurement was repeated three times for each variation, and Equation (2) was used to determine the lignin yield.

$$\text{Lignin yield} = \frac{b}{a} \times 100\% \quad (2)$$

2.5.2. Purity of Lignin Measurement

The purity of lignin was determined using the Klason lignin method, according to TAPPI T-222. This method provides a reliable measure of lignin content and highlights potential impacts of scaling on the recovery process. The details of the testing procedure are provided in Section 2.2.1.

2.5.3. Evaluation of Ash Content

Ash content was evaluated according to TAPPI T-211. A 1 g dry lignin sample **(a)** was weighed and placed in a crucible. The sample was heated in a furnace at 700 °C for 6 h. After heating, the remaining residue was weighed **(b)**. The measurement was repeated three times for each variation, and Equation (3) was used to determine the ash content.

$$\text{Ash content} = \frac{b}{a} \times 100\% \quad (3)$$

2.5.4. Evaluation of Volatile Content

A 1 g lignin sample **(a)** was placed in a crucible and then heated at 220 °C for 6 h. Afterward, the final mass **(b)** was recorded, and the weight loss percentage was calculated using Equation (4). Each variation in the sample was tested three times.

$$\text{Volatile content} = \frac{(a - b)}{a} \quad (4)$$

2.5.5. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed using a Hitachi STA7300 TG/DTA analyzer (Hitachi High-Tech Corporation, Tokyo, Japan) to evaluate the thermal behavior of the recovered lignins. Approximately 10–15 mg of dried lignin was placed in an alumina crucible for each measurement. Two independent TGA measurements were conducted under different atmospheric conditions. For moisture and volatile matter determination, the sample was heated from room temperature to 300 °C under a nitrogen atmosphere at a heating rate of 10 °C min^{−1} to prevent oxidative degradation during thermal decomposition. In a separate experiment, another aliquot of the sample was heated from room temperature to 700 °C under an oxygen atmosphere at the same heating rate to completely oxidize the organic constituents and determine the residual ash content. The oxidation residue at 700 °C was recorded and compared with the ash content obtained using the TAPPI standard method. The sample mass was continuously monitored throughout each heating

program to obtain the corresponding thermal degradation profiles under nitrogen and oxygen atmospheres.

2.5.6. Fourier Transform Infrared (FTIR) Analysis for Comparison of Laboratory- and Bench Scale Lignin

FTIR analysis was conducted to identify and compare the functional groups present in the recovered lignin samples using Bruker Alpha II (Bruker Optics GmbH & Co. KG, Ettlingen, Germany). The spectra, recorded between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1} in absorbance mode, were prepared using the KBr pellet method.

2.5.7. Nuclear Magnetic Resonance (NMR)

The structural features and proton environments of the isolated lignin samples were analyzed by ^1H NMR spectroscopy. Approximately 20 mg of dried lignin from both laboratory- and bench-scale preparations was dissolved in 0.5 mL of deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$). The spectra were recorded on an Agilent 500 MHz NMR spectrometer (Agilent Technologies, Inc., Santa Clara, CA, USA) at 298 K.

2.5.8. Elemental Analyzer (CHNS/O)

The elemental composition of the isolated lignin samples was determined using a Thermo Scientific FlashSmartTM Elemental Analyzer (Thermo Fisher Scientific, Bremen, Germany). Carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) contents were quantified via combustion analysis, while oxygen (O) content was calculated by difference. Prior to analysis, the samples were dried at 80 °C to remove residual moisture. All measurements were performed in triplicate to ensure reproducibility, and the results are reported as weight percentages.

2.5.9. Gel Permeation Chromatography (GPC)

The molecular weight distribution of the lignin samples was determined by Gel Permeation Chromatography (GPC). Prior to analysis, the samples were dissolved in tetrahydrofuran (THF) to ensure complete solubilization. Measurements were carried out using a TSKgel SuperAW5000 (Tosoh Corporation, Tokyo, Japan) column with THF as the mobile phase at a flow rate of 0.3 mL min^{-1} . The column and pump temperatures were maintained at 40 °C. An injection volume of 20 μL was used, and detection was performed using a refractive index (RI) detector. Calibration was conducted using polystyrene standards, and the reported number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) are expressed as polystyrene-equivalent values.

3. Results and Discussion

3.1. Feedstock Characterization: Kraft Black Liquor for Lignin Recovery

The black liquor obtained from the kraft pulping process exhibited a pH of 14, confirming its highly alkaline nature. This strong alkalinity is primarily attributed to residual sodium hydroxide (NaOH) and sodium sulphide (Na_2S), which play a critical role in the degradation of lignocellulosic biomass and the solubilization of lignin during pulping. The lignin content, determined according to TAPPI T-222, was $32.20 \pm 1.39\%$, which falls within the typical range of 25–35% reported for kraft black liquor [36]. This relatively high lignin fraction highlights the strong potential of black liquor as a feedstock for lignin recovery and valorization.

The chemical structure of lignin present in the black liquor was further analyzed using Fourier-transform infrared (FTIR) spectroscopy, as shown in Figure 2. The spectra display characteristic absorption bands that confirm the presence of lignin and the preservation of its key structural features. A broad absorption band centered around 3439 cm^{-1} is

observed, corresponding to O–H stretching vibrations from phenolic and aliphatic hydroxyl groups. The aromatic backbone of lignin is clearly indicated by a prominent peak at 1595 cm^{-1} , which is attributed to aromatic skeletal (C=C) vibrations. In the fingerprint region ($1800\text{--}1000\text{ cm}^{-1}$), several lignin-specific bands are clearly identified. The peak around 1229 cm^{-1} is associated with guaiacyl (G) ring breathing combined with C–O stretching, while the band near 1115 cm^{-1} corresponds to syringyl (S) units, related to aromatic C–H in-plane deformation and C–O stretching. Additionally, bands in the range of $1030\text{--}1120\text{ cm}^{-1}$ indicate the presence of C–O–C ether linkages, which are characteristic of aryl ether bonds in lignin. The simultaneous presence of guaiacyl (G) and syringyl (S) units suggests that the lignin can be classified as syringyl–guaiacyl (S–G) type, which is commonly associated with hardwood-derived lignin. These structural features are consistent with previously reported spectra of technical lignins [37,38].

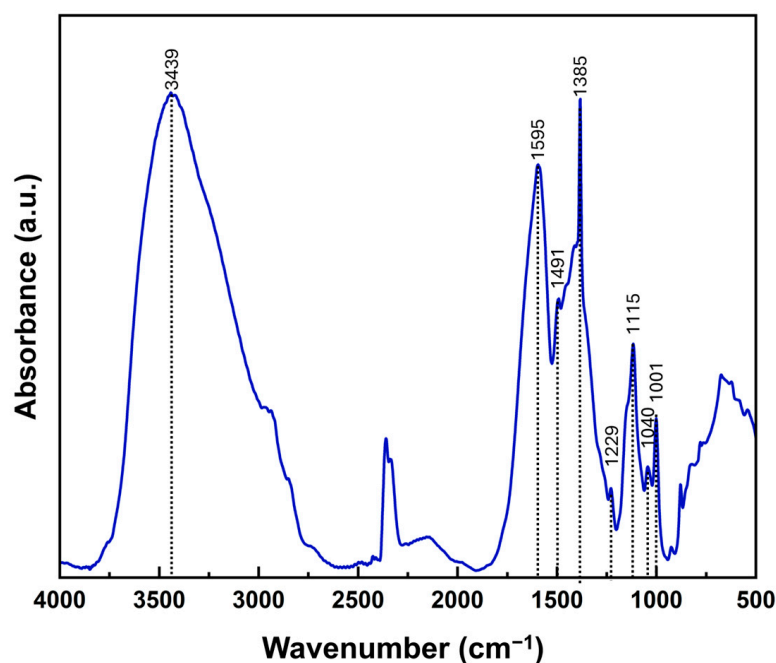


Figure 2. Fourier-transform infrared (FTIR) spectroscopy analysis of lignin in kraft black liquor.

Overall, the FTIR analysis confirms that the fundamental aromatic framework and functional groups of lignin remain intact despite the harsh alkaline conditions of the kraft process. This structural preservation is beneficial for subsequent recovery and purification, as it maintains chemical functionality and reactivity of lignin for downstream applications.

Subsequently, lignin recovery was first optimized at the laboratory scale to identify the optimum operating conditions. The following section first discusses the optimization of lignin recovery at the laboratory scale, including the influence of operating parameters on lignin yield and properties. Thereafter, the optimized conditions were applied at the bench scale to evaluate the scalability of the proposed process, followed by comparative characterization of lignin recovered from both laboratory- and bench-scale systems to validate process consistency. Finally, the properties of the recovered lignin were benchmarked against reported commercial and industrial lignin specifications to evaluate its suitability as a precursor for high-value bio-based materials.

3.2. Optimizing Lignin Recovery: Laboratory-Scale Investigations

Laboratory-scale investigations were conducted to systematically evaluate the influence of key process parameters on lignin recovery performance. Particular attention was given to lignin recovery yield and purity, as these parameters are essential for assessing the

effectiveness of the precipitation process and the quality of the recovered lignin. The effects of precipitation conditions were therefore analyzed to identify the most favorable recovery environment prior to scale-up and process validation.

The effect of precipitation pH on lignin recovery performance is presented in Figure 3a,b. Lowering the precipitation pH from 4.0 to 2.0 resulted in a significant improvement in both lignin recovery yield and purity. At pH 4.0, the recovery remained relatively low due to incomplete protonation of ionizable functional groups in lignin. As the pH decreased, the protonation of phenolic and carboxyl groups increased, reducing electrostatic repulsion and promoting the aggregation of lignin macromolecules. This enhanced aggregation led to improved coagulation and separation efficiency, resulting in the highest recovery yield of 18.85% at pH 2.0, accompanied by a maximum lignin purity of 87.67%. The underlying mechanism of this pH-dependent behavior is illustrated in Figure 4, where acid-induced protonation facilitates the transition from dispersed lignin molecules to aggregated clusters, ultimately leading to precipitation. These observations are consistent with previous studies reporting that lignin precipitation becomes more effective under strongly acidic conditions because protonation reduces electrostatic stabilization of dissolved lignin molecules, thereby promoting particle aggregation and coagulation [27–29]. Similar precipitation behavior has been reported for both mineral acids and weak organic acids, although the recovery efficiency depends on the composition of the kraft black liquor and the operating conditions employed [32–34].

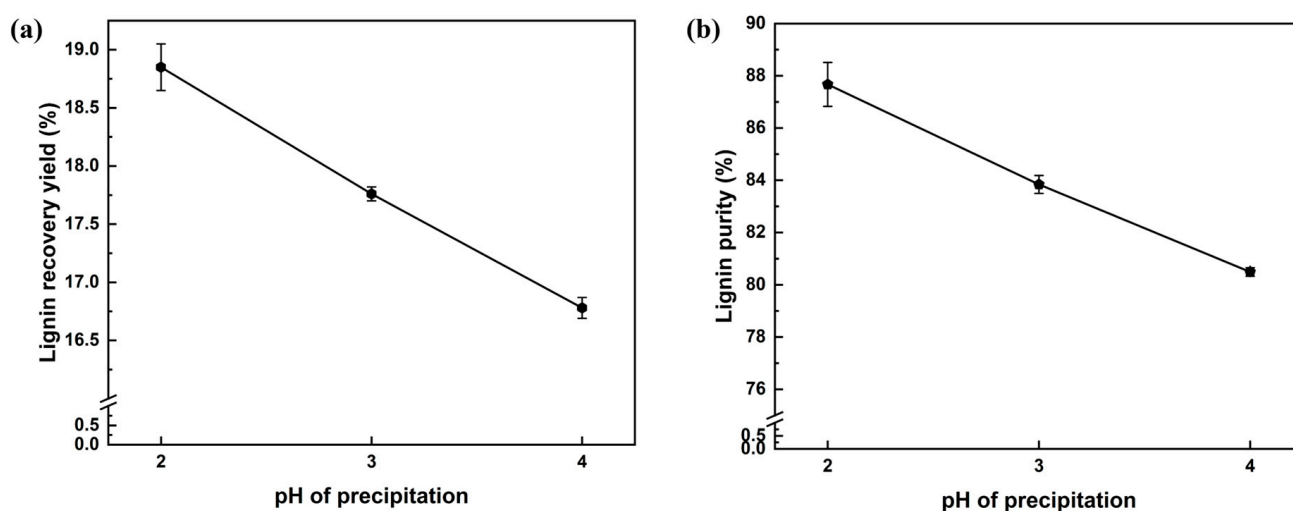


Figure 3. Effect of precipitation pH on lignin recovery performance, showing (a) lignin recovery yield and (b) lignin purity.

Based on these findings, pH 2.0 was selected as the most favorable precipitation condition within the investigated pH range and was therefore used for the subsequent purification and bench-scale validation. Although lower pH values were considered, further reduction below pH 2.0 could not be achieved with reproducibility despite continued addition of 50 wt% citric acid solution. This limitation is attributed to the high buffering capacity of kraft black liquor, which resists further decreases in pH due to the presence of alkaline inorganic species and ionizable organic compounds. Consequently, additional citric acid consumption did not produce any measurable reduction in pH but instead increased the process liquid volume, residual citrate content, filtration load, and washing-water requirement. Therefore, pH 2.0 is regarded as the lowest practically achieved pH under the investigated operating conditions rather than a universally optimum precipitation pH.

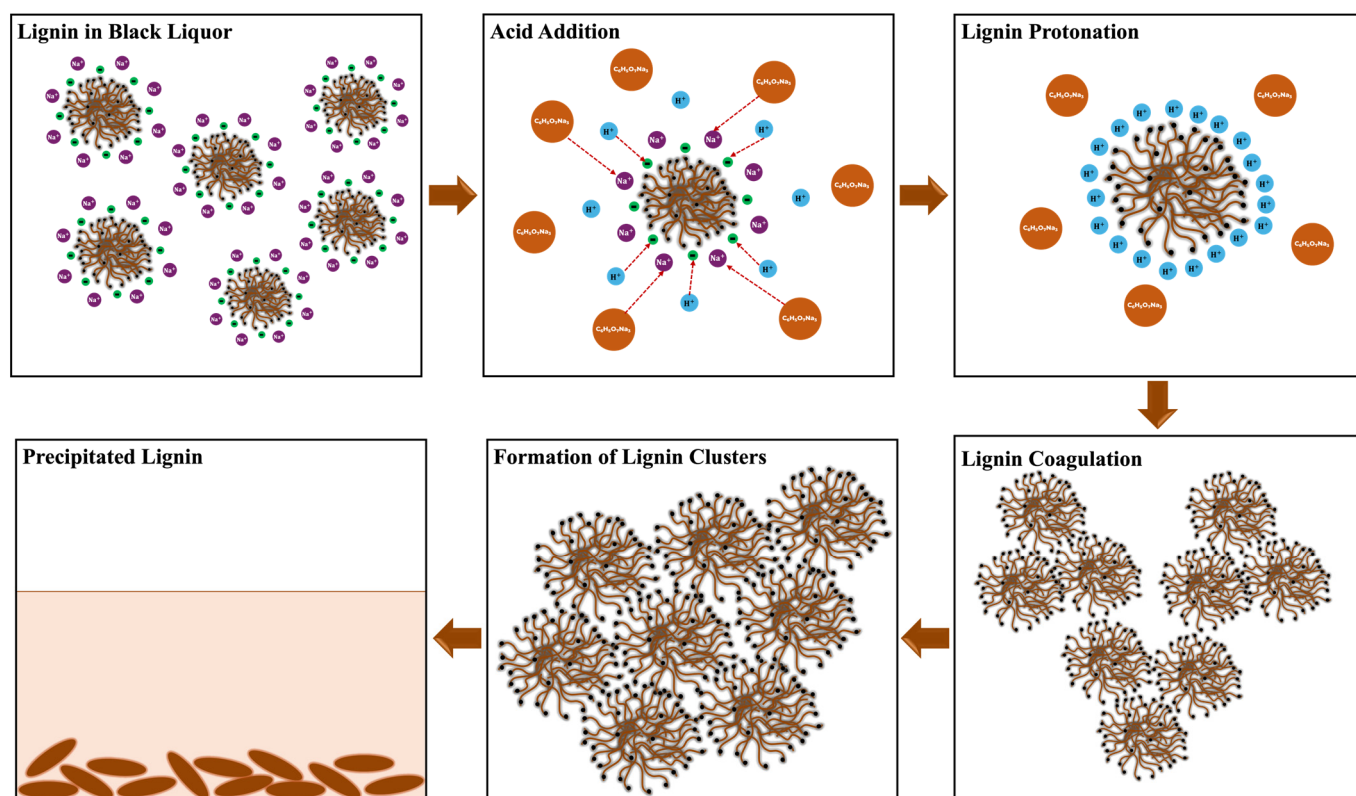


Figure 4. Schematic illustration of the lignin precipitation mechanism at low pH, including lignin dispersion in black liquor, acid-induced protonation, cluster formation, coagulation, and final precipitation.

Following precipitation, purification using deionized (DI) water was performed to improve lignin quality by removing residual inorganic and volatile impurities. As shown in Figure 5a, the lignin yield decreased from 18.85% at LW0 (before purification) to 15.67% at LW100 (lignin-to-water ratio of 1:100), indicating the removal of soluble non-lignin components. Although this reduction reflects a trade-off in yield, it is accompanied by significant improvements in lignin quality.

At LW100, the lignin purity increased to 91.69% (Figure 5b), while the volatile content decreased from 14.41% to 5.01% (Figure 5c), and the ash content was reduced from 1.10% to 0.11% (Figure 5d). These changes confirm the effective removal of hemicellulosic residues, dissolved salts, and volatile compounds during purification. Increasing the washing ratio beyond LW100 resulted in only marginal improvements, indicating that most soluble impurities had already been removed during the initial purification stage. Therefore, further increases in the lignin-to-DI water ratio provided only limited additional purification while substantially increasing water consumption, indicating that LW100 represents a practical optimum for balancing purification efficiency and process sustainability.

Although the use of a lignin-to-DI water ratio of 1:100 increases water consumption during the purification process, this condition was selected to establish the optimum purification performance prior to bench-scale validation. From a practical perspective, minimizing freshwater consumption through water recycling and appropriate wastewater treatment will be essential for future industrial implementation. These aspects are currently being investigated as part of our ongoing research and will be reported in future studies once comprehensive technical and environmental evaluations have been completed.

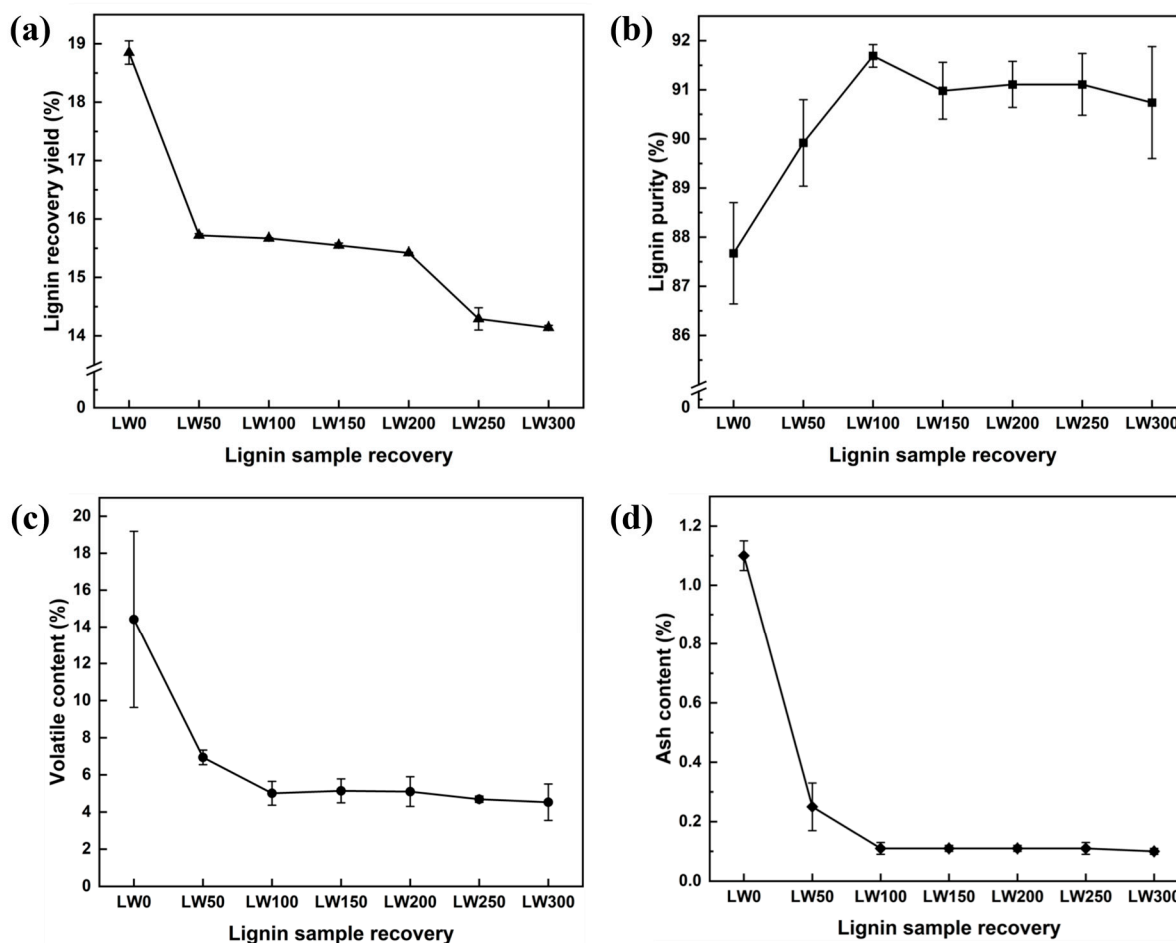


Figure 5. Variation of (a) lignin recovery yield, (b) lignin purity, (c) volatile content, and (d) ash content as a function of lignin purification at different lignin-to-DI water ratios.

3.3. Results of Bench-Scale Process Validation

The bench-scale validation was carried out to evaluate the scalability of the optimized laboratory process under larger-scale processing conditions. The optimized operating parameters established from the laboratory-scale study, including a precipitation pH of 2.0 and a lignin-to-DI water ratio of 1:100 during the purification stage, were directly applied to the bench-scale process. The laboratory-scale experiment was conducted using 15 g of kraft black liquor, whereas the bench-scale validation processed 1 kg of kraft black liquor, corresponding to a scale-up factor of approximately 67. A comparison of the overall recovery performance between the laboratory- and bench-scale processes is summarized in Table 2.

Table 2. Comparison of lignin recovery parameters between the laboratory-scale and bench-scale processes.

Parameter	Laboratory Scale	Bench Scale
Yield (%)	15.67 ± 0.32	14.05 ± 0.21
Purity of lignin (%)	91.69 ± 0.23	91.30 ± 1.28
Volatile content (%)	5.01 ± 0.51	5.77 ± 0.65
Ash content (%)	0.11 ± 0.02	0.13 ± 0.02

As summarized in Table 2, the lignin recovery yield at the bench scale reached 14.05 ± 0.21%, which is slightly lower than the yield obtained at the laboratory scale (15.67 ± 0.32%). This minor reduction (approximately 1.62 percentage points) can be at-

tributed to operational challenges associated with larger processing volumes, such as filter clogging and marginal particle losses during solid–liquid separation. Despite these challenges, the relatively small decrease in recovery yield demonstrates that the precipitation kinetics and separation efficiency were largely maintained during scale-up. This finding indicates that the optimized laboratory conditions can be successfully translated to larger processing volumes without substantial deterioration in process performance, highlighting the robustness and scalability of the proposed lignin recovery process.

In terms of quality, the lignin purity obtained at the bench scale was $91.30 \pm 1.28\%$, which is almost identical to the purity recorded at the laboratory scale ($91.69 \pm 0.23\%$). This strong consistency demonstrates that both precipitation and purification steps maintained their effectiveness during scale-up, resulting in lignin of comparable and stable purity. The volatile content showed a slight increase from $5.01 \pm 0.51\%$ to $5.77 \pm 0.65\%$ upon scaling up, likely due to particle aggregation at larger processing volumes, which may reduce the efficiency of volatile removal. However, this value remains well within the acceptable range. Similarly, the ash content increased only marginally from $0.11 \pm 0.02\%$ to $0.13 \pm 0.02\%$, confirming that inorganic contaminants were effectively removed during the recovery process. Overall, these results indicate that the scale-up process successfully preserved the compositional quality of the recovered lignin. To further verify whether the compositional similarity was accompanied by comparable thermal behavior, thermogravimetric analysis (TGA) was performed under both nitrogen and oxygen atmospheres to evaluate the thermal behavior of the recovered lignins while determining their proximate characteristics. The nitrogen atmosphere was employed to quantify the moisture and volatile contents without oxidative degradation, whereas the oxygen atmosphere was used to completely oxidize the remaining carbonaceous material, leaving only the oxidation residue. The resulting TGA curves are presented in Figure 6.

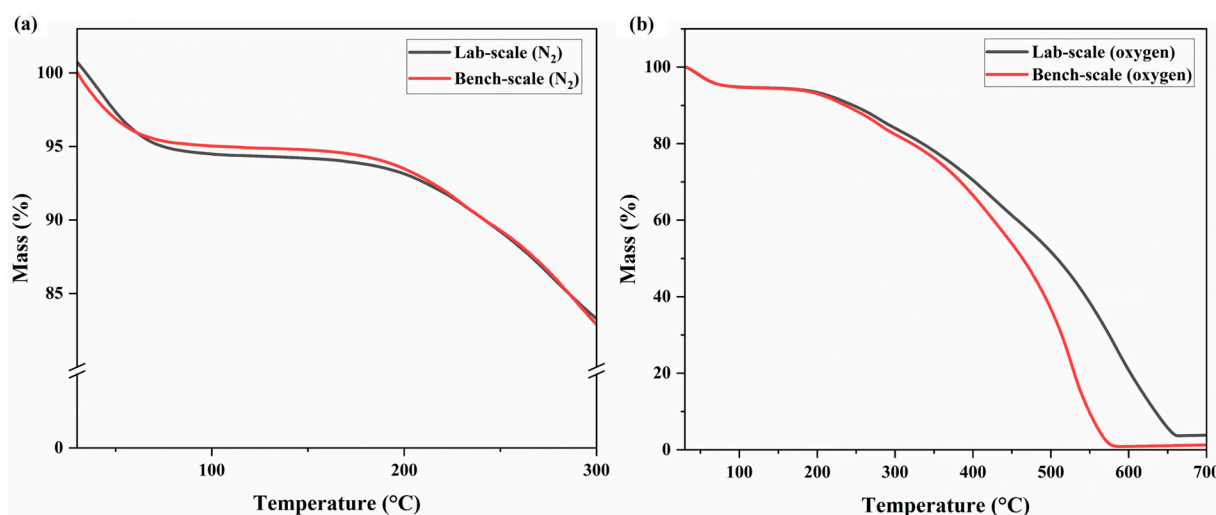


Figure 6. Comparison of the thermogravimetric analysis (TGA) curves of lignin recovered at laboratory and bench scales under (a) nitrogen (N_2) and (b) oxygen atmospheres. The nitrogen atmosphere was used to evaluate moisture evaporation, volatile matter evolution, and thermal decomposition behavior, whereas the oxygen atmosphere was employed to assess oxidative degradation and the residual mass after complete oxidation.

Under a nitrogen atmosphere (Figure 6a), both laboratory- and bench-scale lignins exhibited nearly identical thermal degradation profiles, indicating that the thermal behavior of the recovered lignin was largely preserved after scale-up. The first mass-loss stage, occurring below approximately $100\text{ }^{\circ}\text{C}$, corresponds to the evaporation of physically adsorbed moisture. The laboratory-scale lignin exhibited a moisture loss of 5.09% , while

the bench-scale sample showed a comparable value of 4.89%, indicating that the drying and purification procedures produced lignins with similar moisture contents.

The second degradation stage, extending from approximately 100 to 300 °C, is attributed to the release of volatile matter, including low-molecular-weight lignin fragments and oxygen-containing functional groups. The bench-scale lignin exhibited a slightly higher volatile content (8.44%) than the laboratory-scale sample (7.73%), consistent with the proximate analysis results. In addition, the bench-scale lignin showed a slightly earlier onset of thermal degradation, as evidenced by the subtle leftward shift in the TGA curve. This behavior suggests the presence of a slightly greater proportion of thermally labile structures that require lower activation energy for decomposition. Nevertheless, the difference was minor, and both samples followed nearly identical degradation pathways throughout the heating process, demonstrating that the overall thermal stability of the recovered lignin was successfully maintained during scale-up.

Under an oxygen atmosphere (Figure 6b), the remaining carbonaceous material was progressively oxidized until only the oxidation residue remained at 700 °C. The laboratory-scale lignin exhibited a residual mass of 3.75%, whereas the bench-scale lignin retained only 1.31%. The lower oxidation residue observed for the bench-scale sample suggests that fewer oxidation-resistant constituents remained after combustion, reflecting the effectiveness of the recovery and purification processes at the larger processing scale. Despite this slight difference, both samples displayed comparable oxidation profiles over the entire temperature range, indicating that their combustion behavior remained largely unchanged following scale-up. The subtle variations observed in both nitrogen and oxygen atmospheres, however, imply that minor differences in the molecular architecture may still exist between the recovered lignins.

Overall, the TGA results demonstrate that scaling up the lignin recovery process did not significantly alter the thermal behavior of the recovered lignins. Both laboratory- and bench-scale lignins exhibited comparable moisture loss, volatile evolution, and oxidation characteristics, confirming that the optimized recovery process successfully preserved the thermal stability of the recovered lignin. Although the trends observed from the TGA are consistent with those obtained from the compositional characterization, the absolute values of moisture, volatile matter, and oxidation residue differ from those presented in Table 2 because the two methods are based on fundamentally different measurement principles.

It should be noted that the moisture, volatile matter, and ash values obtained from TGA are not directly comparable to those reported in Table 2. The values in Table 2 were determined using standardized TAPPI methods, in which moisture, volatile matter, and ash are measured independently under specific temperatures, atmospheres, and holding times to provide quantitative compositional data. In contrast, TGA continuously records the mass change in a sample during programmed heating under controlled atmospheres, allowing the thermal degradation behavior of lignin to be monitored as a function of temperature. Consequently, the values obtained from TGA represent mass-loss events and oxidation residue under dynamic heating conditions rather than standardized compositional parameters. Therefore, the TAPPI methods provide the reference values for determining the moisture, volatile matter, and ash contents of the recovered lignins, whereas TGA serves as a complementary technique for evaluating their thermal stability and decomposition behavior.

Beyond demonstrating consistent recovery performance during scale-up, it is equally important to evaluate whether the recovered lignin meets the quality requirements of commercially available technical lignins. Therefore, the physicochemical quality of the bench-scale lignin was benchmarked against representative industrial lignin products reported in the literature, as summarized in Table 3. The purity of the bench-scale lignin

reached $91.30 \pm 1.28\%$, which is comparable to Indulin AT ($92 \pm 2\%$) and LignoBoost lignin ($91 \pm 1\%$), while being considerably higher than Protobind 2400 soda lignin ($79 \pm 1\%$) [38]. More importantly, the ash content of the recovered lignin ($0.13 \pm 0.02\%$) was substantially lower than that reported for all commercial lignins considered in this comparison. Although commercial lignins are generally produced through highly optimized industrial processes, the proposed citric-acid-based recovery process achieved comparable purity while producing lignin with exceptionally low ash content. This demonstrates the effectiveness of the purification strategy in removing inorganic impurities and highlights the potential of the proposed process for producing high-quality lignin suitable for downstream chemical conversion, carbon materials, and polymer-based applications.

Table 3. Comparison of lignin recovery parameters between this study and commercial lignin recovery processes in the literature.

Lignin Recovery Process	Scale	Purity of Lignin (%)	Ash (%)
This study	Bench scale	91.30 ± 1.28	0.13 ± 0.02
Indulin AT from Ingevity Corporation [38]	Industrial	92 ± 2	3.59 ± 0.70
Soda (Protobind 2400) from GreenValue SA [38]	Industrial	79 ± 1	1.61 ± 0.06
LignoBoost from Valmet Corporation [38]	Industrial	91 ± 1	0.73 ± 0.08

The benchmark comparison presented above evaluates the quality of the recovered lignin product obtained from the bench-scale process. Likewise, the subsequent comparison between the laboratory- and bench-scale lignin samples is intended to assess the consistency and reproducibility of the recovered lignin products obtained using the same recovery and purification procedure. Since both samples had already undergone acid precipitation and purification prior to characterization, the following analyses evaluate the consistency of the recovered products between processing scales rather than the preservation of the complete structure or composition of the lignin species originally dissolved in the kraft black liquor.

3.3.1. Chemical Structure and Functional Group Consistency

The FTIR spectra of lignin recovered from black liquor at both laboratory and bench scales are shown in Figure 7. Overall, the spectra obtained from the two processing scales showed very similar absorption patterns, indicating highly comparable structural characteristics after scale-up. A broad absorption band centered at approximately 3415 cm^{-1} is observed in both samples, corresponding to O–H stretching vibrations associated with phenolic and aliphatic hydroxyl groups in the lignin structure [39,40]. The presence of aliphatic C–H stretching bands at 2917 and 2847 cm^{-1} further reflects the contribution of methoxylated side chains commonly present in lignin macromolecules [33,41].

The aromatic nature of the polymer backbone is confirmed by characteristic absorption peaks at 1605 and 1515 cm^{-1} , which are attributed to aromatic skeletal (C=C) vibrations [33,41]. In addition, the band at 1458 cm^{-1} is assigned to C–H deformation of methyl and methylene groups [39,40]. Within the carbonyl region, the band at 1707 cm^{-1} appears with comparable intensity in both samples, suggesting that the scale-up procedure did not induce significant additional oxidation or condensation reactions [33,39,40].

In the fingerprint region (1800 – 1000 cm^{-1}), several characteristic lignin bands are clearly observed. The peaks at 1215 cm^{-1} and 1112 cm^{-1} correspond to ring vibrations associated with guaiacyl (G) and syringyl (S) units, respectively, while the band at 1032 cm^{-1} is attributed to C–O stretching in ether and alcohol groups [9,33,42]. The similar positions and relative intensities of these peaks for both samples indicate that the relative distribution of lignin structural units was highly comparable between the laboratory- and bench-scale recovered lignin samples.

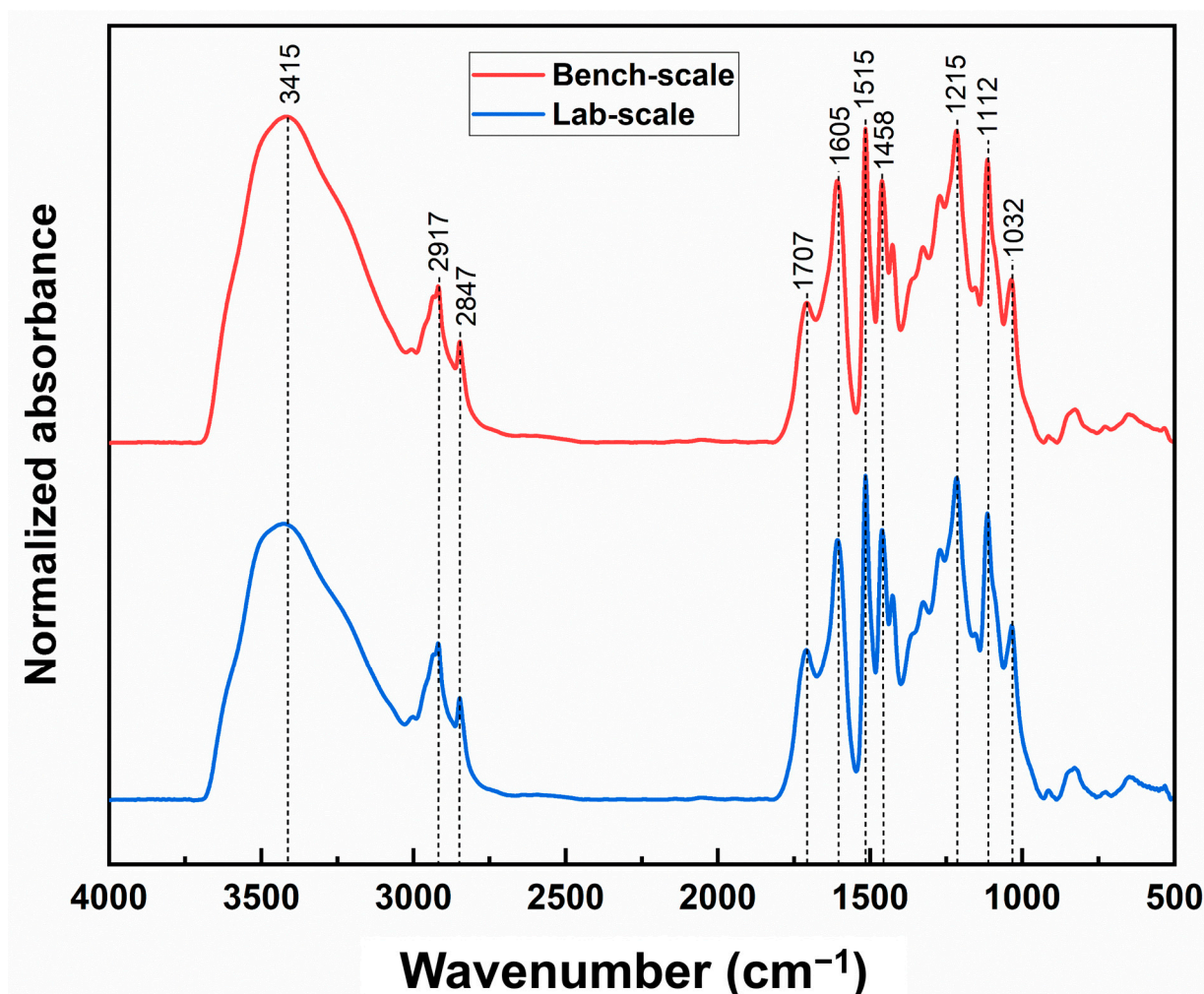


Figure 7. Comparative FTIR spectra of lignin recovered from black liquor at laboratory and bench scales.

The simultaneous presence of S- and G-associated absorption features suggests that the recovered lignin can be classified as syringyl–guaiacyl (S–G) type lignin, which is typical for lignin derived from hardwood sources [9,42]. The absence of additional absorption bands or noticeable shifts in the characteristic lignin peaks after scale-up further indicates that citric acid precipitation did not introduce detectable chemical modification of the lignin backbone. The presence of these functional groups is particularly advantageous for downstream applications requiring reactive phenolic and ether functionalities, such as polymer synthesis, carbon-material production, and other lignin valorization processes. Overall, the close similarity between the spectra obtained at laboratory and bench scales demonstrates that the developed isolation protocol produced recovered lignin products with highly consistent structural characteristics across processing scales. This observation also indicates that the slight shift in the TGA degradation profile of the bench-scale lignin is unlikely to arise from changes in the major functional groups of lignin, but rather from more subtle variations in its molecular structure that cannot be fully resolved by FTIR analysis.

Since FTIR confirmed that the principal functional groups of lignin remained unchanged after scale-up, ^1H NMR spectroscopy was subsequently employed to investigate whether more subtle differences in the molecular structure could account for the slight variation in thermal degradation behavior observed by TGA and to examine the structural characteristics of lignin obtained from black liquor at both laboratory and bench scales using DMSO-d_6 as the solvent, as shown in Figure 8. The spectra of the two samples exhibit

highly comparable resonance patterns, indicating similar proton environments within the macromolecular frameworks of the laboratory- and bench-scale recovered lignin products.

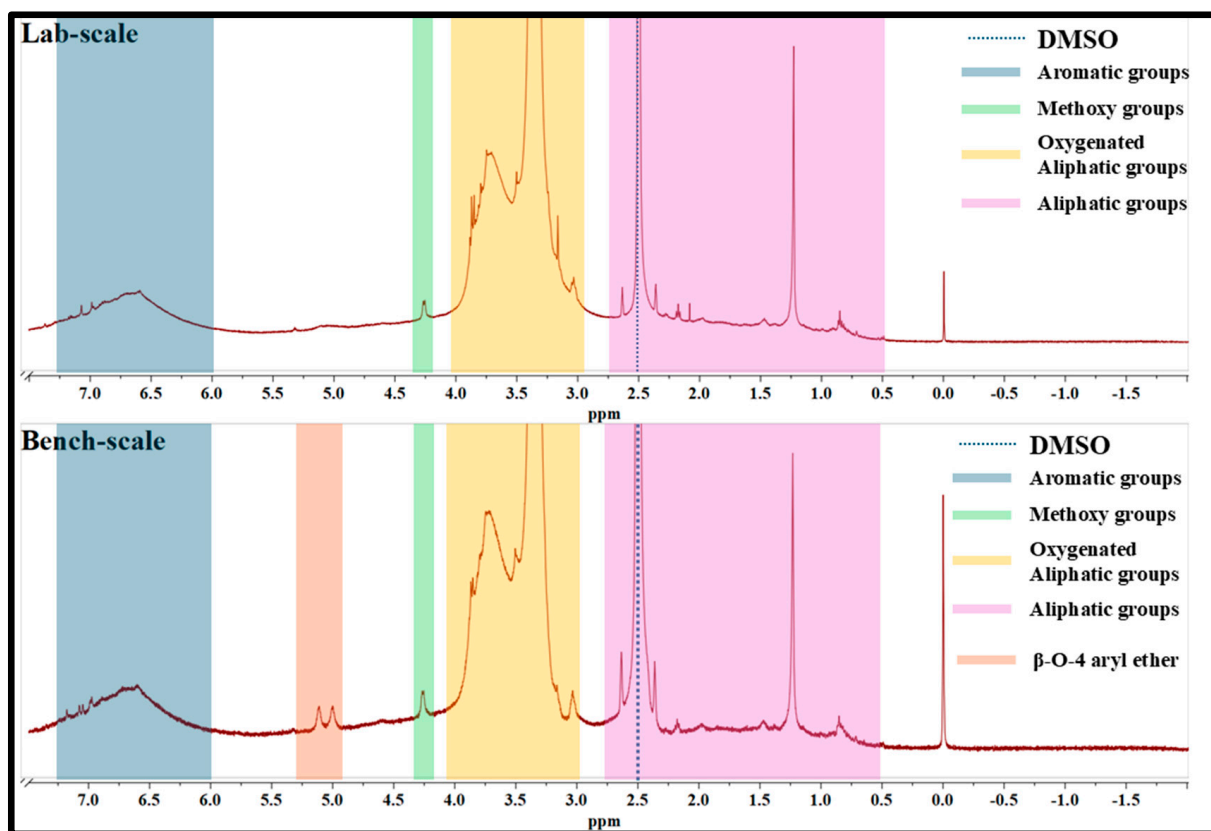


Figure 8. Comparison of ^1H NMR spectra of lab-scale and bench-scale lignin recorded in DMSO-d_6 (500 MHz).

The most prominent resonance in both spectra appears at 4.0–4.5 ppm, which corresponds to methoxyl protons ($-\text{OCH}_3$), a characteristic structural feature of lignin [39,43]. In the aromatic region (6.0–7.5 ppm) [44], signals attributed to syringyl (S) units around 6.59 ppm and guaiacyl (G) units within 6.97–7.37 ppm are observed, indicating that the isolated lignin belongs to the typical syringyl–guaiacyl (S–G) type commonly associated with hardwood lignin [43,45,46]. Signals within the range of 3.0–4.0 ppm are associated with oxygenated aliphatic protons originating from lignin side chains linked through ether functionalities [39,43,44,46].

A notable difference is observed in the bench-scale lignin spectrum, where additional signals appear at approximately 5.006 and 5.111 ppm. These resonances are attributed to protons associated with $\beta\text{-O-4}$ aryl ether linkages, which represent the most abundant interunit bonds in lignin [43,45,46]. The presence of these ether linkages in the bench-scale recovered lignin suggests that the scale-up process retained a slightly different distribution of interunit bonding without altering the overall lignin framework. Such subtle structural variations may explain the slightly earlier onset of thermal degradation observed in the TGA, as differences in the abundance and accessibility of ether-containing structural motifs can influence the activation energy required to initiate thermal decomposition. Moreover, the preservation of $\beta\text{-O-4}$ linkages is particularly advantageous because these interunit bonds serve as important reactive sites for catalytic depolymerization and the production of value-added aromatic chemicals. Their presence may also contribute to the slightly higher molecular weight observed for the bench-scale lignin by limiting excessive bond cleavage during the isolation process [46].

Overall, the strong similarity between the spectra obtained at both processing scales confirms that the principal structural characteristics of lignin were highly comparable during scale-up. The additional β -O-4 aryl ether signals detected in the bench-scale lignin indicate that the scale-up process produced recovered lignin with comparable subtle structural features without altering the overall chemical framework. Together with the FTIR and TGA results, these findings demonstrate that the optimized recovery process successfully maintained consistent chemical characteristics in the recovered lignin products while introducing only minor variations in molecular architecture that had a limited influence on its purity and thermal degradation behavior.

3.3.2. Elemental Composition

Elemental (CHNS/O) analysis was performed to evaluate whether the scale-up process altered the elemental composition of the recovered lignin. In addition to determining the carbon, hydrogen, oxygen, nitrogen, and sulfur contents, the elemental data were used to calculate the H/C and O/C atomic ratios, which provide useful indicators of the aromaticity and degree of oxygenation of lignin. Comparable elemental characteristics after scale-up are essential because these characteristics strongly influence the physicochemical properties, thermal behavior, and potential applications of the recovered lignin. The elemental composition and calculated atomic ratios of the recovered lignins are summarized in Table 4.

Table 4. Comparison of elemental compositions and atomic ratios of lignin recovered between laboratory and bench scales.

Parameter	C (%)	H (%)	N (%)	S (%)	O (%)	H/C	O/C
Lab-scale	64.60 $\pm$ 3.10	5.76 $\pm$ 0.02	-	0.39 $\pm$ 0.21	20.68 $\pm$ 0.93	1.06 $\pm$ 0.05	0.24 $\pm$ 0.01
Bench-scale	66.05 $\pm$ 0.11	5.84 $\pm$ 0.07	-	0.66 $\pm$ 0.13	20.91 $\pm$ 0.08	1.05 $\pm$ 0.01	0.24 $\pm$ 0.00

The carbon content increased slightly from 64.60 $\pm$ 3.10% for the laboratory-scale lignin to 66.05 $\pm$ 0.11% for the bench-scale sample, while the hydrogen content remained nearly unchanged at approximately 5.8% for both samples. Likewise, the oxygen content showed only a marginal variation, ranging from 20.68 $\pm$ 0.93% to 20.91 $\pm$ 0.08%. A slight increase in sulfur content was also observed, from 0.39 $\pm$ 0.21% to 0.66 $\pm$ 0.13%, which is likely associated with minor variations in residual sulfur-containing species originating from the kraft black liquor. Overall, the relatively small differences in elemental composition indicate that the recovery process resulted in highly comparable elemental compositions of lignin during scale-up.

The calculated H/C atomic ratio decreased only slightly from 1.06 $\pm$ 0.05 for the laboratory-scale lignin to 1.05 $\pm$ 0.01 for the bench-scale sample, while the O/C atomic ratio remained unchanged at 0.24. These highly comparable atomic ratios indicate that the relative elemental composition of the recovered lignins was maintained despite the increased processing scale. This observation is further supported by the FTIR and ^1H NMR analyses, which revealed comparable structural characteristics for the recovered lignins obtained at laboratory and bench scales. Collectively, these results demonstrate that the optimized recovery process produced recovered lignin products with consistent elemental composition and physicochemical characteristics during the transition from laboratory to bench scale.

3.3.3. Scalability Performance: Consistency of Molecular-Weight Distribution Uniformity

Following the structural confirmation obtained from FTIR, ^1H NMR, and elemental analyses (CHNS/O), the macromolecular characteristics of the isolated lignin were further evaluated using Gel Permeation Chromatography (GPC). The laboratory-scale recovered lignin was used as the baseline reference, while the bench-scale recovered lignin was analyzed to evaluate whether the scale-up process affected the molecular-weight distribution and polymer architecture. Since the objective of this study was to assess the scalability of the lignin recovery process, comparison between the laboratory- and bench-scale recovered lignin provides a direct evaluation of the consistency of the molecular-weight distribution during process scale-up.

The molecular weight distribution of the isolated lignin is summarized in Table 5. The laboratory-scale lignin exhibited a weight-average molecular weight (M_w) of $45,581\text{ g mol}^{-1}$, a number-average molecular weight (M_n) of $41,829\text{ g mol}^{-1}$, and a PDI of 1.090. Following the scale-up, only a slight increase was observed, with M_w and M_n reaching $46,762\text{ g mol}^{-1}$ and $42,713\text{ g mol}^{-1}$, respectively, while the PDI increased marginally to 1.095. The corresponding GPC chromatograms for both samples are presented in Figure S2, showing comparable elution profiles and molecular-weight distributions.

Table 5. Comparative molecular weight parameters and PDI of the isolated lignin across different processing scales.

Parameter	$M_w\text{ (g mol}^{-1}\text{)}$	$M_n\text{ (g mol}^{-1}\text{)}$	$M_z\text{ (g mol}^{-1}\text{)}$	$M_p\text{ (g mol}^{-1}\text{)}$	PDI
Lab scale	45,581	41,829	49,946	39,294	1.090
Bench scale	46,762	42,713	51,492	41,685	1.095

From a macromolecular standpoint, the low PDI values obtained for both samples (1.090 for the laboratory-scale lignin and 1.095 for the bench-scale lignin) indicate a relatively narrow molecular-weight distribution with only a marginal increase after scale-up. This observation suggests that the optimized recovery and purification process maintained a high degree of molecular uniformity while minimizing excessive depolymerization and condensation reactions, which are commonly associated with broader molecular-weight distributions during lignin isolation. The close agreement between the laboratory- and bench-scale PDI values further demonstrates that the scale-up process did not introduce significant changes in the molecular architecture of the recovered lignin. Such molecular uniformity is advantageous because it contributes to more consistent processing behavior and predictable performance in subsequent lignin valorization, including polymeric materials, carbon fibers, and other high-value lignin-derived products.

It should be noted that the GPC measurements were performed under controlled dissolution conditions using appropriate calibration standards, thereby minimizing potential artifacts associated with lignin aggregation or incomplete solubilization. The M_w values obtained in this study fall within the upper range of those commonly reported for lignin derived from black liquor. The observation of both high molecular weight and narrow distribution after scale-up suggests that the isolation protocol effectively limits excessive depolymerization while avoiding significant condensation reactions. This structural consistency is advantageous for applications requiring controlled macromolecular architecture, including the development of carbonaceous precursors and high-performance polymer composites.

Overall, these findings highlight that the optimized process can be reliably scaled up, as bench-scale validation provided results consistent with those observed at the laboratory scale. Moreover, these results also emphasize the strong potential for industrial-scale implementation of lignin recovery and purification using weak organic acids. By transforming

black liquor, a major byproduct of the pulp and paper industry, into a high-value, low-ash, and high-purity material, this approach advances waste valorization, supports sustainable process development, and reduces dependence on fossil-based resources.

From an industrial perspective, the economic feasibility of the proposed process should also be considered alongside its technical performance. Although citric acid is generally more environmentally benign and less corrosive than the strong mineral acids commonly employed in conventional lignin recovery processes, the purification step requires a relatively high volume of deionized water, which may increase water consumption and wastewater generation. Likewise, filtration of larger slurry volumes may become a significant operational consideration during further scale-up. Therefore, future process development should focus on optimizing citric acid utilization, reducing water demand through water recycling, improving solid–liquid separation efficiency, and implementing appropriate wastewater treatment strategies. A comprehensive techno-economic assessment, together with life-cycle and environmental evaluations, will be essential in future studies to determine the overall industrial feasibility and sustainability of the proposed green lignin recovery process.

4. Conclusions

This study successfully established and validated a green lignin recovery process from kraft black liquor through citric acid precipitation followed by deionized water purification. Laboratory-scale optimization identified a precipitation pH of 2.0 and a lignin-to-DI water ratio of 1:100 as the optimum operating conditions, yielding lignin with high purity ($91.69 \pm 0.23\%$) and low ash content ($0.11 \pm 0.02\%$). Application of these optimized conditions at the bench scale produced lignin with comparable recovery yield, purity, moisture, volatile matter, and ash contents, demonstrating that the compositional quality of the recovered lignin was successfully maintained during scale-up. Thermogravimetric analysis further confirmed that both laboratory- and bench-scale lignins exhibited similar thermal degradation and oxidation behaviors, indicating that the thermal stability of the recovered lignin was largely preserved.

Structural characterization by FTIR and NMR revealed that the fundamental chemical structure of lignin remained intact following the scale-up, while CHNS/O elemental analysis showed only minor variations in elemental composition and maintained H/C and O/C atomic ratios. Furthermore, GPC analysis demonstrated that the molecular-weight characteristics of the recovered lignin were retained after scale-up, confirming that the optimized recovery process preserved both the structural integrity and molecular properties of lignin despite the increased processing scale.

Overall, these findings demonstrate the technical feasibility of scaling up citric acid-based lignin recovery from kraft black liquor while maintaining the compositional, thermal, structural, elemental, and molecular characteristics of the recovered lignin. The proposed process therefore represents a promising and environmentally friendly alternative to conventional mineral-acid precipitation for sustainable lignin valorization. Future work should focus on water recycling, wastewater management, and techno-economic assessment to further evaluate the industrial applicability and long-term sustainability of the proposed process.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/macromol6030052/s1>, Figure S1: The PFD of lignin precipitation and purification from black liquor; Figure S2: GPC chromatogram of the recovered lignin obtained from the laboratory-scale process; Figure S3: GPC chromatogram of the recovered lignin obtained from the bench-scale; Table S1: Detailed GPC molecular-weight distribution.

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