

Lignin-Based Platform as a Potential Low-Cost Sorbent for the Direct Air Capture of CO₂

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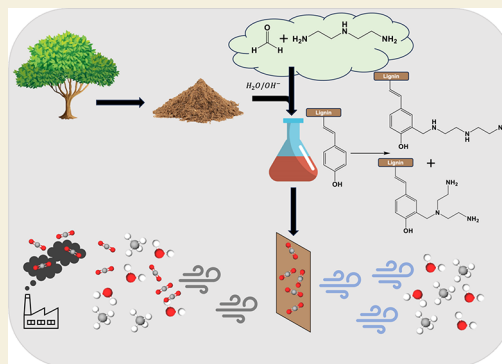
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ABSTRACT: The urgent need to address the current climate crisis has led to concerted efforts to develop low-cost and sustainable methods to remove carbon dioxide from the atmosphere. Carbon capture and storage (CCS) and negative emissions technologies (NET's) offer the most promising paths forward to offsetting global emissions. In this study, we explore the potential of kraft lignin, a readily available biomaterial, as a low-cost alternative for the development of a CO₂ sorbent. The approach leverages the known ability of amines to reacting with carbon dioxide and forming a stable compound. Commercially available kraft lignin was modified with diethylenetriamine (DETA), triethylenetetramine (TETA), and tetraethylenepentamine (TEPA) using a one-pot synthesis approach via the Mannich reaction. The sorbent was evaluated for porosity, accessible amine density, and nitrogen content. The CO₂ capture experiments revealed that the resulting sorbent can capture 0.80 (± 0.03) mmol of CO₂ per gram of sorbent.

KEYWORDS: lignin, carbon capture, amine, biomaterials, negative emissions technologies CO₂



1. INTRODUCTION

Since the onset of the industrial revolution, atmospheric concentrations of greenhouse gases (GHGs), predominantly carbon dioxide (CO₂), have risen at an unprecedented rate.¹ Their accumulation in the atmosphere have given rise to global warming, contributing to higher average surface temperatures, glacial mass loss, rising sea levels, and ocean acidification.² These rapid and unnatural changes have placed unprecedented strain on our environment. Delays in rollout of decarbonization technologies hampered the necessary mitigation efforts, deeming necessary not only the reduction of CO₂ emissions, but also proactively remove CO₂ already in the atmosphere.³ Two major directions are actively pursued: carbon capture and storage (CCS) and negative emissions technologies (NET's).

Carbon capture and storage (CCS) mitigate CO₂ emissions from heavy carbon producers through three major technologies: precombustion capture, postcombustion capture, and oxyfuel combustion.^{4–7} Precombustion capture focuses on the removal of CO₂ from fuels prior to their combustion by forming syngas, a mixture of carbon monoxide and hydrogen, which is separated and used as a benign fuel source. Postcombustion capture uses sorbents to remove CO₂ from flue gas streams immediately following combustion, while the CO₂ concentrations are still high. Oxyfuel combustion is a process that involves burning fuel in an oxygen-only environment, yielding high-purity CO₂ and water vapor that are easily separable and limits the production of toxic nitrous and sulfur oxide pollutants.

In contrast, negative emissions technologies (NETs) include direct air carbon capture and storage (DACCS), bioenergy with carbon capture and storage (BECCS), afforestation and reforestation, coastal blue carbon, and biochar among others.^{8–11} The natural NET approaches include afforestation and reforestation, BECCS and coastal blue carbon rely on photosynthesis to eliminate CO₂ from the atmosphere, while DACCS and other engineered approaches artificially speed up the carbon cycle by chemically or physically “stripping” CO₂ from the atmosphere. Natural approaches to decarbonization are more cost-effective and carry reduced environmental risks but require vast swaths of arable land be used for biomass and suffer from slow CO₂ removal. Engineered approaches offer more rapid CO₂ removal but suffer from high energy demands and higher costs.^{10,12} Recent efforts include engineered approaches that utilize renewable biomaterials like cellulose, vegetable starch, and chitosan to designing CO₂ sorbents.^{13–15} Among ubiquitous bio materials, lignin represents 25% of all nonfossil organic carbon on Earth and it is largely unutilized; its availability exceeds 300 billion tons,¹⁶ increasing annually by around 20 billion tons. Lignin is a three-dimensional

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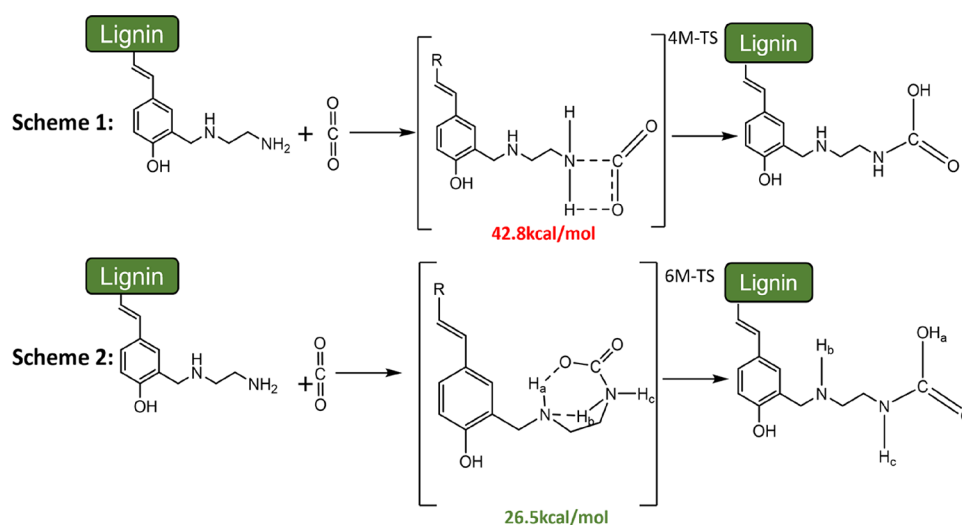


Figure 1. Formation of carbamic acid via commonly reported high energy (Scheme 1) and recently proposed lower energy (Scheme 2) transition states. Lignin modified with ethylene diamine on a coumaryl residue on lignin is shown in this model as an example. Adapted from ref 27, Copyright [2020] American Chemical Society.

biopolymer, which coexists in plants with hemicellulose and cellulose, filling the spaces between them and acting as an adhesive.^{17–21} Research efforts have focused on functionalization of lignin through amination, sulfonation, and phosphorylation to expand its potential applications.^{22–24} Significant advances have been reported on aminated lignin and its structural characteristics.^{25,26} This is significant as amines are commonly used as sorbents for carbon capture due to their ability to form strong and reversible bonds with CO₂.

There exists some uncertainty surrounding the mechanism by which amines interact with the compound CO₂. Until recently, the commonly accepted mechanism was believed to take place through a 1,3-zwitterionic transition state followed by the formation of either ammonium carbamate if undergoing proton transfer with a second amine, or carbamic acid if intramolecular proton transfer occurs (Figure 1, Scheme 1).²⁷ However, recent work has shown that this pathway is unlikely due to the high energy of the four-membered ring transition state (42.8 kcal/mol). Rather, a multistep mechanism through a 6-member ring transition state with a more energetically favorable pathway has been proposed (Figure 1, Scheme 2).²⁷

A previous work has shown that the modification of solid sorbents with amines via grafting or impregnation can improve sorbent capacity and selectivity for CO₂.^{8,28,29} Therefore, lignin modified with amine functional groups could be a promising source material for the design of a low-cost solid-state sorbent for carbon capture applications.

Herein, we report the modification of industrial softwood kraft lignin with diethylenetriamine (DETA), triethylenetetramine (TETA), and tetraethylenepentamine (TEPA) via the Mannich reaction in a facile one-pot synthesis. Lignin is a biopolymer composed of sinapyl alcohol, *p*-coumaryl alcohol, and coniferyl alcohol monomeric units (Figure 2) thus enabling amine addition via a Mannich-type condensation reaction on *p*-coumaryl and coniferyl alcohol units (Figure 3), as priory reported.^{30,31}

To the best of our knowledge, the covalent modification of lignin with various alkylamines for the investigation of their performance for the CO₂ capture has not been reported. The novel aminated lignin sorbents obtained herein were evaluated for determining the optimal alkylamine and amine density

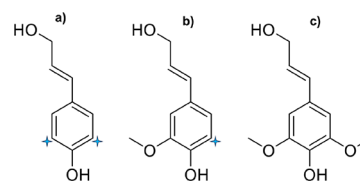


Figure 2. Monomeric units of (a) *p*-coumaryl, (b) coniferyl, and (c) sinapyl alcohol, components of the lignin polymer. Stars represent the reactive position on the phenolic –OH where amine addition may occur.

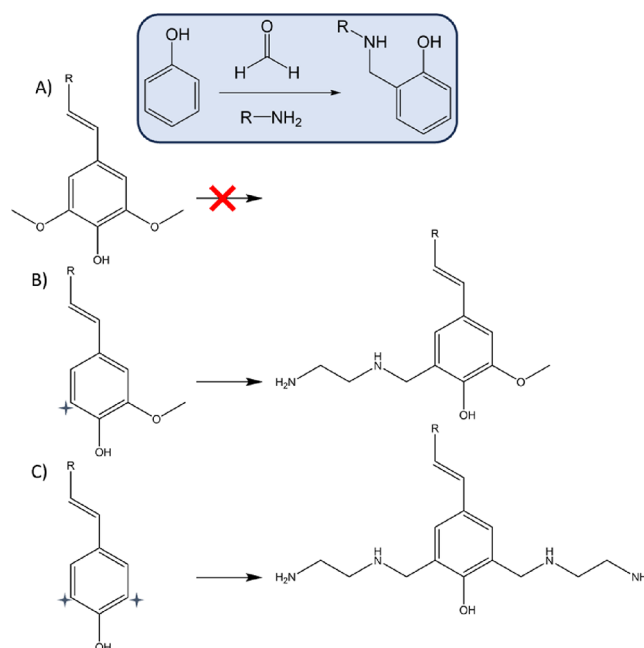


Figure 3. General scheme showing the addition of alkylamine to coniferyl (B) and *p*-coumaryl (C) using ethylenediamine as an example. Inset: Mannich reaction on the phenolic ring.

toward maximizing the CO₂ uptake based on the carbon dioxide adsorption–desorption isotherms.

2. MATERIALS AND METHODS

2.1. Materials

Triethylenetetramine (TETA, $C_6H_{18}N_4$) was purchased from TCI America. Tetraethylenepentamine (TEPA, $C_8H_{23}N_5$) was purchased from Acros Organics. Diethylenetriamine (DETA, $C_4H_{13}N_3$) and 2,2-dihydroxyindane-1,3-dione (ninhydrin) were supplied by Alpha Aesar. Dimethyl sulfoxide (DMSO), deuterated dimethyl sulfoxide (d_6 -DMSO), formaldehyde (H_2CO , 37% by weight), 99.5% 2-propanol (C_3H_8O), and sodium hydroxide pellets (NaOH) were purchased from Fisher Chemical. Type I deionized water was purchased from LabChem. Indulin AT kraft lignin was generously donated by Ingevity. All reagents were used without further purification unless otherwise stated.

2.2. Lignin Modification

In a typical experiment, Indulin AT kraft lignin (~ 2 g) was added to a 100 mL round-bottom flask containing 20 mL of 0.2 M aqueous NaOH solution and stirred for 30 min at 25 °C until fully dissolved. The temperature was increased to 65 °C, and an amount of 10.5 mmol of the selected amine, DETA (1.08 g), TETA (1.54 g), or TEPA (1.98 g), was added to the lignin solution. Formaldehyde (37% solution) in a 1:1 mol ratio with the specific amine was added dropwise under stirring. The flask was equipped with a reflux condenser to prevent the loss of volatiles and allowed to react for 4 h under stirring. The resulting product was dispersed via dropwise addition into 100 mL of 2-propanol, divided into 50 mL centrifuge tubes, and centrifuged at 8000 rpm for 10 min, yielding a compressed lignin pellet. The functionalized lignin was reconstituted via sonication and washed several times with 2-propanol to remove excess reagents and surface adsorbed amines. The final product was dried in a vacuum oven at 80 °C for 24 h, followed by 24 h of lyophilization. The dried lignin-amine was ground by hand to a fine powder and subjected to a qualitative visual ninhydrin test to confirm the presence of amine.

2.3. Amine Density Optimization

Previous studies on amine-functionalized sorbents have shown that high loading densities may reduce the performance of the sorbent due to steric effects, and in the case of porous materials, pore blockage or clogging leads to slow diffusion.^{32,33} Therefore, it was necessary to determine if the amount of amine used during the synthesis had any bearing on the capacity of the lignin sorbent. Sorbents were prepared in weight percent starting from 0 wt % (unmodified lignin) to 100 wt % (2 g of TEPA to 2 g of lignin) in 20% intervals. Synthesis was performed by dissolving ~ 2 g of lignin in 0.2 M aqueous NaOH via stirring at 25 °C for 30 min until fully dissolved. A predetermined amount of TEPA and 37% formaldehyde solution (Table 1) were

Table 1. Experimental Values Used for the Preparation of Density-Optimized Sorbents along with the Calculated Mass Percentage of Amine

sample name	lignin mass (g)	TEPA (mmol)	formaldehyde (mmol)	weight percent (wt %)
W00	2.00	0.00	0.00	0
W02	2.03	2.17	2.33	20.20
W04	2.12	4.38	4.32	39.15
W06	2.01	6.66	6.32	62.69
W08	2.10	8.45	8.66	76.19
W1	2.06	10.62	10.99	97.57

then added to the round-bottom flask and allowed to react at 65 °C for 4 h while stirring. The products were washed several times with 2-propanol and dried in a vacuum oven for 24 h, followed by lyophilization for an additional 24 h. The products were then hand-ground and subjected to a qualitative ninhydrin test to determine the presence of an amine. Samples were prepared in 0, 20, 40, 60, 80, and

100 wt % TEPA and were denoted as W00, W02, W04, W06, W08 and W1, respectively.

2.4. Characterization

Fourier Transform InfraRed Attenuated Total Reflectance spectroscopy (FTIR-ATR) was performed on a Shimadzu IRTracer-100 with QATR-10 module installed under nitrogen to interrogate functional groups before and after amine introduction. FTIR was collected over the course of 40 scans from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} . Nitrogen elemental analysis was performed by Atlantic Microlab (Norcross, GA) on a Carlo Erba 1108 Automatic Analyzer using a combustion tandem thermal conductivity detector. Ultra-violet–visible spectroscopy was performed using a Shimadzu 3600 Plus spectrophotometer with an integrating sphere installed in conjunction with a colorimetric ninhydrin assay to determine the concentration of amine present within lignin samples. Spectra were collected from 400 to 800 at 1.0 nm data intervals with medium scan speed and 5 nm slit width. FE-SEM imaging was taken with a JEOL/JSM-F100 Schottky field emission scanning electron microscope to determine changes in the particle size and surface morphology. Thermogravimetric analysis (TGA) measurements were performed under high-purity nitrogen gas on an SDT-Q600 AI from TA Instruments from room temperature to 700 °C with a 10°/min temperature ramp using an alumina crucible. The TGA was performed on unmodified and aminated lignin samples to compare the stability of the sorbent before and after modification. Carbon dioxide capture experiments were conducted for CO_2 uptake and measured using a Quantachrome Nova Touch LX2 gas adsorption analyzer using high-purity CO_2 as a sorbate gas. Isotherms were collected at 298.15K in partial pressures ranging from 0.005 to 0.995 P/P_0 and an equilibration time of 120 s. All samples were degassed for 16 h at 100 °C prior to measurements to remove surface adsorbed moisture. Carbon 13 nuclear magnetic resonance (^{13}C NMR) was performed by Pennsylvania State University on a Bruker NEO 600 MHz instrument. A zgpg30 pulse program was performed over 8192 scans with a spectral width of 236 ppm, and chemical shifts were referenced to the solvent peak DMSO (40 ppm).

3. RESULTS AND DISCUSSION

The modified lignin materials were analyzed for the successful amine addition and to interrogate the amine density, followed by carbon dioxide capture experiments.

3.1. FTIR-ATR

The FTIR spectra of lignin samples were collected before and after functionalization with the alkylamines to evaluate the changes in functional groups (Figure 4A). The broad peak ca. 3410 cm^{-1} is ascribed to alcohol and carboxylic acid O–H stretching and occupies the same region where N–H stretching from the introduced amines is expected, possibly masking the latter. Peaks at 2940 and 2850 cm^{-1} are ascribed to sp^2 and sp^3 C–H stretching from the lignin skeletal structure and ethylene linkers present within the alkylamine backbone. Peaks at 1710 and 1670 cm^{-1} are due to C=O stretching from ketones and carboxylic acids present throughout lignin. The peak at 1480 cm^{-1} corresponds to the C–H bending. Peaks in the region from 800 to 1200 cm^{-1} are characteristic of the lignin guaiacyl, syringyl, and *p*-hydroxy phenylpropane units.³⁴ Due to the rich variety of functional groups present in the lignin polymer, characteristic stretching and bending frequencies corresponding to N–H and C–N bonds were not apparent following functionalization.

3.2. Thermogravimetric Analysis

Unmodified and aminated lignin samples were heated under a nitrogen atmosphere with a flow rate of 100 mL/min from room temperature to 700 °C at a rate of 10 °C/min (Figure 4B). Inspection of the TGA curves shows an initial loss of mass

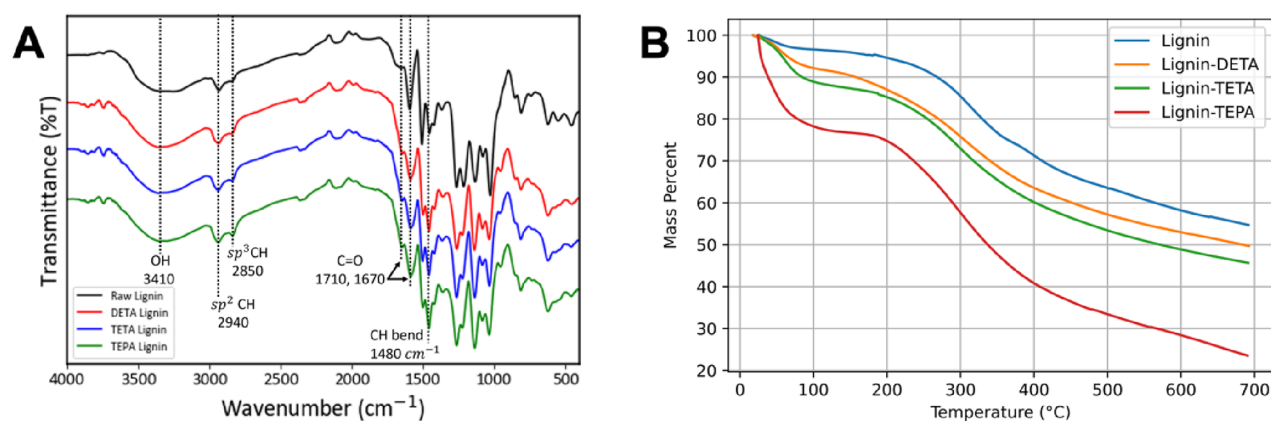


Figure 4. (A) FTIR-ATR spectra of unmodified lignin and lignin modified with the alkylamines DETA, TETA, and TEPA. (B.) TGA curves of unmodified lignin and lignin modified with alkylamines.

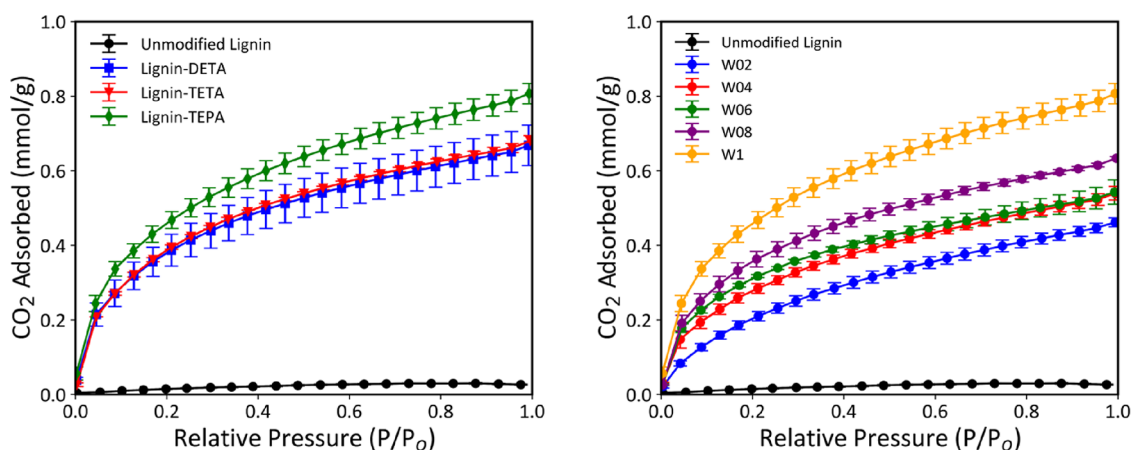


Figure 5. Carbon dioxide adsorption isotherms of: (A) unmodified lignin and aminated lignin sorbents; (B) carbon dioxide isotherms of lignin modified with different densities of TEPA.

between the starting temperature and 100 °C attributed to the evaporation of residual moisture. Mass loss due to water evaporation was greater for aminated lignin samples, in particular the TEPA-modified sample, suggesting a higher retained water content due to hydrogen bonding with the introduced amine side chains. A second mass loss beginning around 200 °C is attributed to the gradual decomposition of short lignin side chains releasing CO, CO₂, and CH₄ and loss of surface adsorbed amines.³⁵ The more rapid decomposition of aminated lignin is associated with breakdown of the amine side chains due to C–N bond cleavage, consistent with the results reported by Meng et al.³⁰

3.3. Carbon Dioxide Isotherms

3.3.1. Amine Selection. Carbon dioxide adsorption–desorption isotherms were collected using ultrahigh-purity carbon dioxide as a sorbate gas at 298.15 K. Sample temperatures were maintained constant using a recirculating Dewar of polyethylene glycol and water in a 1:1 ratio. Samples were prepared in triplicate and degassed under vacuum for 16 h at 100 °C prior to analysis to remove any surface adsorbed moisture. Analysis of the isotherms shows that aminated lignin samples adsorbed significantly more CO₂ than unmodified lignin, which shows marginal uptake (Figure 5A). Furthermore, the results suggest that the volume of the adsorbed CO₂ is proportional to the length of alkylamine used to modify the lignin. For example, lignin modified with 10.5 mmol of DETA

adsorbed less CO₂ than lignin modified with an equimolar amount of longer TEPA. This is attributed to the fact that the longer TEPA molecule has a greater number of secondary amine groups able to bind CO₂. The higher capacity of the TEPA-modified lignin may also be explained by the CO₂–amine binding mechanism proposed by Said et al. (2020).²⁷ The better performance of the TEPA-modified lignin may therefore be related to both the higher amine density and the increased flexibility of the TEPA molecule when compared with the shorter alkylamines. These two features increase the probability of proton transfer between adjacent amine groups in proximity, ultimately leading to improved uptake of CO₂. Lignin modified with 10.5 mM TEPA displayed optimal CO₂ uptake when compared to sorbents modified with the shorter DETA and TETA alkylamines. Based on these results, TEPA-modified lignin was selected for further studies.

3.3.2. Amine Density Optimization. Density optimization studies were conducted using TEPA as the target amine. Samples were prepared using procedures identical with those outlined in Section 3.3.1.

Analysis of the CO₂ isotherms shows that an increased volume of CO₂ uptake occurs as the amine density of the prepared sorbents increases, with seemingly no upper limit observed. This trend mirrors that shown by the UV–vis ninhydrin assay and the nitrogen content determined by elemental analysis. It should be noted that attempts were made to modify lignin with higher concentrations of amine (up to

200 wt %), but these resulted in heterogeneous products containing sticky, black agglomerates that could not be broken down. Adsorption of CO₂ reached a maximum for sorbent W1 (100 wt %), which adsorbed 0.80 (±0.03) mmol of CO₂/g of sorbent. These data suggest that there is no degradation in sorbent performance at high amine density, as is observed with some modified porous sorbents (Figure 5B).^{32,33}

3.4. Elemental Analysis

Nitrogen elemental analysis was performed by Atlantic Microlab (Norcross, GA) with a Carlo Erba 1108 automatic analyzer using a combustion tandem thermal conductivity detector. The innate nitrogen content of unmodified lignin was determined to be 0.36% and was subtracted from all other samples as background. The amount of TEPA corresponding to the mass of nitrogen was calculated and used to determine sorbent amine density (Table 2). As expected, the results

Table 2. Nitrogen Content Determined by Elemental Analysis and Corresponding Amine Density per Gram of Sorbent Using TEPA as an Example

sample	% nitrogen	mmol N	mmol TEPA/g
W00	0.36	25.70	0
W02	3.03	216.32	0.38
W04	3.86	275.58	0.50
W06	4.15	296.28	0.54
W08	4.54	324.12	0.60
W1	5.46	389.81	0.73

shown indicate that the nitrogen content increases as a function of amine concentration used during synthesis. Sample W1, prepared using 10.5 mmol of TEPA, contained the highest mass of nitrogen (5.46%), corresponding to 0.73 mmol of TEPA/g of lignin. These calculations suggest a low degree of amine incorporation, accounting for only 13.8% of the total amine used during the synthesis.

3.5. Scanning Electron Microscopy

Imaging was performed before and after modification of lignin with TEPA to probe any changes in particle morphology or surface features (Figure 6). As expected, pristine (unmodified) lignin particles showed heterogeneous particle size and a

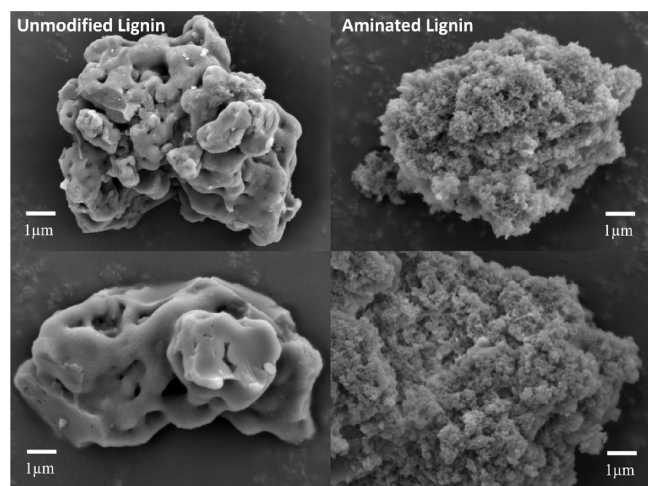


Figure 6. SEM images of lignin particles before (left) and after (right) modification with TEPA.

smooth surface with randomly distributed cratering. Following modification with amine, the surface features of the lignin present a rougher texture. Particle size and morphology remain heterogeneous and amorphous with no distinct features.

3.6. UV–Visible Spectroscopy

Elemental analysis alone is not an ideal technique to quantify the number of amine groups present within a sorbent and often leads to overestimates of nitrogen content.²⁶ This is due to the presence of ionically bound species and nonvolatile side products that remain after washing procedures. In addition, not every amine group present within the sorbent is accessible to chemically react with carbon dioxide, so a total nitrogen content is not an accurate reflection of predicting how much of the CO₂ may be adsorbed. Therefore, a more selective method to quantify only the amount of chemically accessible amine within each sorbent would be beneficial. In this work, attempts were made to use a colorimetric ninhydrin assay to quantify the amount of accessible amine within each sorbent. However, due to strong background absorbance of lignin and its many functional groups, the quantitative analysis, although correctly reflects the trend corresponding to the number of amine groups, it could overestimate the actual coverage (see the Supporting Information). Therefore, the UV–vis spectra of sorbent samples are discussed qualitatively. Unmodified lignin showed strong background signal in the same region as the absorbance maxima of Ruhemanns purple, which is formed upon dimerization of ninhydrin with primary and secondary amines. However, the absorbance trend shown by the ninhydrin assay is consistent with those seen in nitrogen elemental analysis, indicating a linear increase in sorbent amine density as a function of the TEPA used during the synthesis (Figure 7A,B).

3.7. Sorbent Regeneration

In efforts to lower the costs associated with manufacturing and minimize waste production, sorbents with long lifetimes that can be regenerated without significant degradation to sorbent performance are desirable. Therefore, the sorbent that showed optimal CO₂ uptake was selected to undergo adsorption/regeneration trials to investigate sorbent degradation (Figure 7C). Two samples comprising 100 mg of sorbent were degassed in accordance with the procedures in Section 3.2. Isotherms were collected from 0.005 to 0.995 *P/P*₀ at 298.15 K using high-purity CO₂ as the adsorbate gas. Regeneration was performed using thermal vacuum-swing desorption by placing the saturated sorbent under vacuum and heating to 100 °C for 60 min. Following regeneration, the isotherms were collected again. A total of 9 cycles were performed in duplicate on identically prepared samples. The volume of CO₂ adsorbed by each sample at maximum *P/P*₀ was recorded and plotted on a scatter plot. The sorbent shows an initial decrease in CO₂ uptake after 4 cycles of 15.68%, but remains stable after the fourth regeneration cycle, capturing an average of 0.56 mmol CO₂/g. Following the degradation from regeneration, this would translate to a calculated capacity of 1962 mol of CO₂/kg of lignin/year at 25 °C and 1 atm. However, high-purity CO₂ gas was used for analysis and is not reflective of how the sorbent would perform in a direct air capture or flue gas environment.

3.8. ¹³C NMR

Solutions of unmodified lignin and TEPA-aminated lignin (W1) were prepared in deuterated dimethyl sulfoxide (*d*₆-

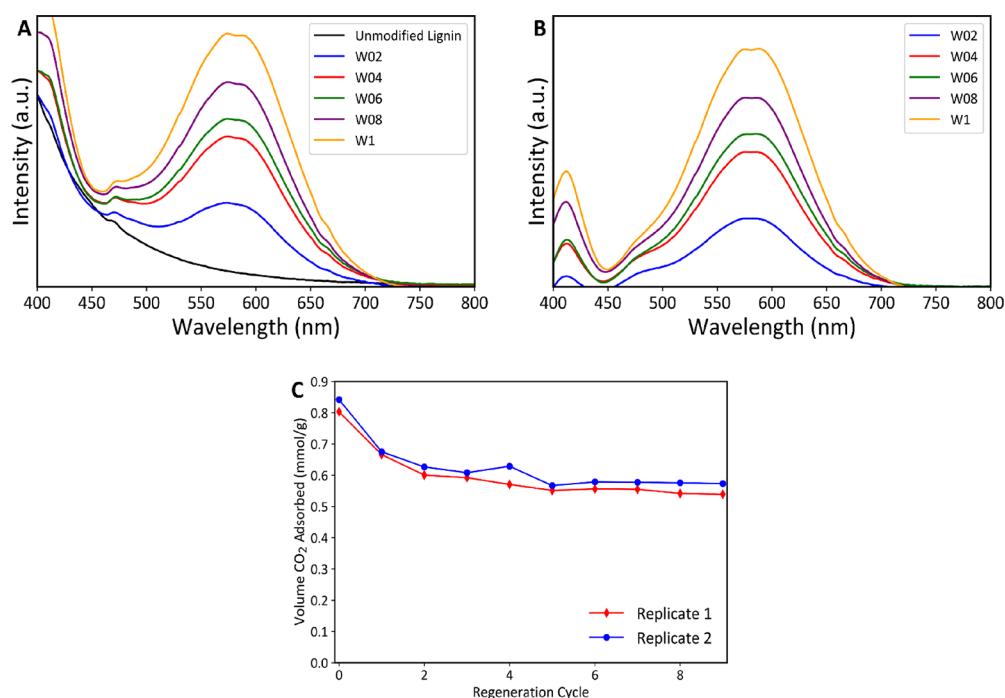


Figure 7. (A) UV–visible absorbance spectra of unmodified lignin and sorbents modified with different densities of TEPA following the colorimetric ninhydrin assay. (B) Corrected UV–visible absorbance spectrum of aminated lignin, subtracting the signal from unmodified lignin as a background. (C) Concentration of CO₂ adsorbed over several regeneration cycles of the best performing sorbent W1.

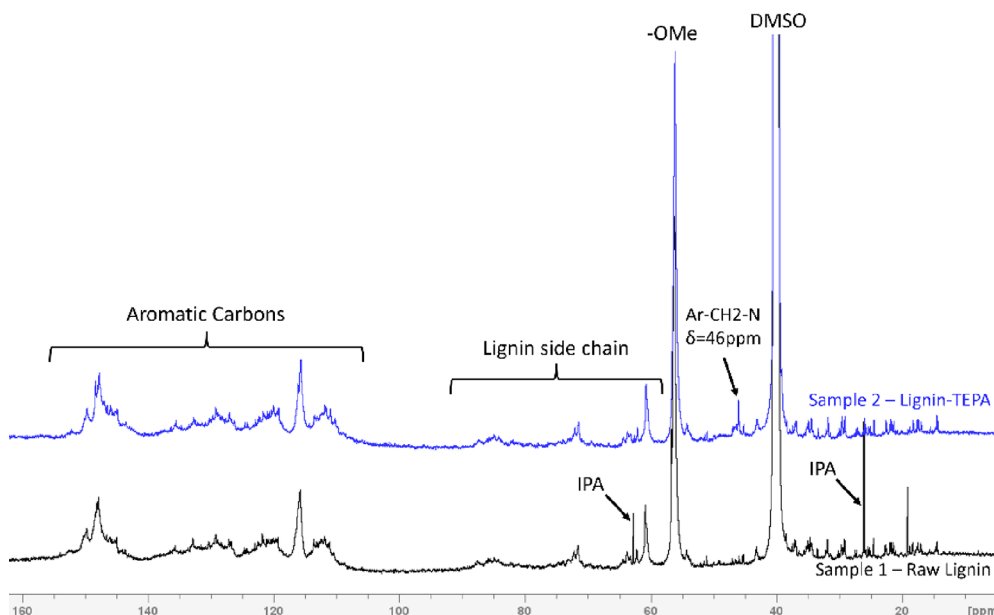


Figure 8. ¹³C NMR of lignin before and after functionalization with TEPA dissolved in *d*₆-DMSO.

DMSO) at a concentration of 200 mg/mL (Figure 8). Lignin modified with amine proved to be poorly soluble in DMSO and required several hours to dissolve. Due to the low concentration and poor signal-to-noise ratio, several hours were required before a usable signal could be obtained. The heterogeneous structure, high molecular weight, and poor solubility of lignin cause NMR peak assignment and quantitation to be quite challenging. Literature reports are referenced therefore for peak assignment.^{26,36,37} Chemical shift values are in reference to the solvent peak (DMSO) at 40 ppm. The broad signal at 56 ppm is assigned to the methoxy

(–OMe) substituent of the aromatic units from coniferyl and sinapyl alcohol monomer units. The unresolved peaks between 110 and 155 ppm are assigned to the aromatic carbons present throughout the lignin structure. Small resonances between 60 and 80 ppm are assigned to the carbons present throughout the lignin side chains and are barely distinguishable above the background. The peaks in the unmodified lignin structure at 27 and 63 ppm are attributed to residual 2-propanol (IPA). Following the modification of lignin with amine, a peak corresponding to the formaldehyde-derived Ar–CH₂–N

linking unit introduced to the *p*-coumaryl and coniferyl alcohol monomers emerges at 46 ppm (Figure 8).²⁶

4. CONCLUSIONS

In this work, we report the modification and characterization of IndulinAT kraft lignin with three different alkylamines possessing different numbers of amine groups and the ability to absorb carbon dioxide. The effect of the amine loading density on the performance of the sorbent is also investigated. Lignin was selected as a potential source material due to its low cost, sustainability, and wide availability, in strides to develop a low-cost and sustainable CO₂ sorbent for commercial-scale production. It was found that of the sorbents prepared, lignin modified with TEPA demonstrated the highest CO₂ uptake (0.80 mmol/g), more than 18% higher than lignin modified with DETA and TETA. This property is attributed to the greater number of amine groups present in the larger TEPA molecule, as well as the contribution of nearby secondary amines that may participate in proton transfer/exchange, lowering the activation energy required to absorb CO₂. This work shows that biomaterials such as lignin offer a promising avenue to low-cost and sustainable sorbents that could help reduce costs associated with large-scale sorbent production required to affect meaningful emissions mitigation. There remain promising research avenues to optimize reaction conditions, synthetic pathways, and characterization methods to improve our understanding of sorbent design and factors affecting sorbent performance.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenvironau.4c00008>.

Qualitative ninhydrin assay, UV–vis calibration curve, UV–vis calibration curve, and ¹³C NMR (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Jake Carrier** conceptualization, data curation, formal analysis, investigation, methodology, writing-original draft, writing-review & editing; **CHENG-YU LAI**

conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources, supervision, writing-review & editing; **Daniela R. Radu** conceptualization, formal analysis, funding acquisition, methodology, writing-original draft, writing-review & editing.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) EPA. *Inventory of U.S. Greenhouse Gas Emissions and Sinks 1990–2020*; U.S. Environmental Protection Agency, 2020.
- (2) *Climate Change: Evidence and Causes: Update 2020*; The National Academies Press, 2020. DOI: [DOI: 10.17226/25733](https://doi.org/10.17226/25733).
- (3) Core Writing Team; Lee, H.; Romero, J. IPCC, 2023: Climate Change 2023: Synthesis Report, Summary for Policymakers. *Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*; 2023, 1–34.
- (4) Pires, J. C. M.; Martins, F. G.; Alvim-Ferraz, M. C. M.; Simões, M. Recent developments on carbon capture and storage: An overview. *Chem. Eng. Res. Des.* **2011**, *89* (9), 1446–1460.
- (5) Chao, C.; Deng, Y.; Dewil, R.; Baeyens, J.; Fan, X. Post-combustion carbon capture. *Renewable Sustainable Energy Rev.* **2021**, *138*, No. 110490.
- (6) Gibbins, J.; Chalmers, H. Carbon capture and storage. *Energy Policy* **2008**, *36* (12), 4317–4322.
- (7) Leung, D. Y. C.; Caramanna, G.; Maroto-Valer, M. M. An overview of current status of carbon dioxide capture and storage technologies. *Renewable and Sustainable Energy Reviews* **2014**, *39*, 426–443.
- (8) Choi, S.; Drese, J. H.; Eisenberger, P. M.; Jones, C. W. Application of amine-tethered solid sorbents for direct CO₂ capture from the ambient air. *Environ. Sci. Technol.* **2011**, *45* (6), 2420–2427.
- (9) Fridahl, M.; Hansson, A.; Haikola, S. Towards Indicators for a Negative Emissions Climate Stabilisation Index: Problems and Prospects. *Climate* **2020**, *8* (6), 75.
- (10) McLaren, D. A comparative global assessment of potential negative emissions technologies. *Process Safety and Environmental Protection* **2012**, *90* (6), 489–500.
- (11) National Academies of Sciences, Engineering, and Medicine. *Negative Emissions Technologies and Reliable Sequestration: A Research Agenda*; The National Academies Press, 2019. doi: [DOI: 10.17226/25259](https://doi.org/10.17226/25259).
- (12) Ozkan, M.; Nayak, S. P.; Ruiz, A. D.; Jiang, W. Current status and pillars of direct air capture technologies. *iScience* **2022**, *25* (4), No. 103990.
- (13) Gebald, C.; Wurzbacher, J. A.; Tingaut, P.; Zimmermann, T.; Steinfeld, A. Amine-based nanofibrillated cellulose as adsorbent for CO(2) capture from air. *Environ. Sci. Technol.* **2011**, *45* (20), 9101–9108.
- (14) Aspromonte, S. G.; Tavella, M. A.; Albarracín, M.; Boix, A. V. Mesoporous bio-materials synthesized with corn and potato starches applied in CO₂ capture. *J. Environ. Chem. Eng.* **2023**, *11* (4), No. 109542.
- (15) Foong, S. Y.; Chan, Y. H.; Yiin, C. L.; Lock, S. S. M.; Loy, A. C. M.; Lim, J. Y.; Yek, P. N. Y.; Mahari, W. A. W.; Liew, R. K.; Peng, W.;

et al. Sustainable CO₂ capture via adsorption by chitosan-based functional biomaterial: A review on recent advances, challenges, and future directions. *Renewable Sustainable Energy Rev.* **2023**, *181*, No. 113342.

(16) Delmas, M. Vegetal Refining and Agrochemistry. *Chem. Eng. Technol.* **2008**, *31* (5), 792–797.

(17) Patil, P. T.; Armbruster, U.; Richter, M.; Martin, A. Heterogeneously Catalyzed Hydroprocessing of Organosolv Lignin in Sub- and Supercritical Solvents. *Energy Fuels* **2011**, *25* (10), 4713–4722.

(18) Gosselink, R. J.; Teunissen, W.; van Dam, J. E.; de Jong, E.; Gellerstedt, G.; Scott, E. L.; Sanders, J. P. Lignin depolymerisation in supercritical carbon dioxide/acetone/water fluid for the production of aromatic chemicals. *Bioresour. Technol.* **2012**, *106*, 173–177.

(19) Zakzeski, J.; Bruijninx, P. C. A.; Jongerius, A. L.; Weckhuysen, B. M. The Catalytic Valorization of Lignin for the Production of Renewable Chemicals. *Chem. Rev.* **2010**, *110* (6), 3552–3599.

(20) Haveren, J. v.; Scott, E. L.; Sanders, J. Bulk chemicals from biomass. *Biofuels, Bioproducts and Biorefining* **2008**, *2* (1), 41–57.

(21) Sjöström, E. Chapter 4 - LIGNIN. In *Wood Chemistry*; 2nd ed.; Academic Press, 1993; pp 71–89.

(22) Gao, C.; Zhou, L.; Yao, S.; Qin, C.; Fatehi, P. Phosphorylated kraft lignin with improved thermal stability. *Int. J. Biol. Macromol.* **2020**, *162*, 1642–1652.

(23) Pan, H.; Sun, G.; Zhao, T. Synthesis and characterization of aminated lignin. *Int. J. Biol. Macromol.* **2013**, *59*, 221–226.

(24) Xiao, X.; Jiang, J.; Wang, Y.; Wang, B.; Yuan, T.-Q.; Shi, Q.; Liao, X.; Shi, B.; Sun, R.-C. Microwave-Assisted Sulfonation of Lignin for the Fabrication of a High-Performance Dye Dispersant. *ACS Sustainable Chem. Eng.* **2021**, *9* (27), 9053–9061.

(25) Du, X.; Li, J.; Lindström, M. E. Modification of industrial softwood kraft lignin using Mannich reaction with and without phenolation pretreatment. *Industrial Crops and Products* **2014**, *52*, 729–735.

(26) Kollman, M.; Jiang, X.; Thompson, S. J.; Mante, O.; Dayton, D. C.; Chang, H. -m.; Jameel, H. Improved understanding of technical lignin functionalization through comprehensive structural characterization of fractionated pine kraft lignins modified by the Mannich reaction. *Green Chem.* **2021**, *23* (18), 7122–7136.

(27) Said, R. B.; Kolle, J. M.; Essalah, K.; Tangour, B.; Sayari, A. A Unified Approach to CO₂-Amine Reaction Mechanisms. *ACS Omega* **2020**, *5* (40), 26125–26133.

(28) Chen, C.; Xu, H.; Jiang, Q.; Lin, Z. Rational design of silicas with meso-macroporosity as supports for high-performance solid amine CO₂ adsorbents. *Energy* **2021**, *214*, No. 119093.

(29) Darunte, L. A.; Walton, K. S.; Sholl, D. S.; Jones, C. W. CO₂ capture via adsorption in amine-functionalized sorbents. *Current Opinion in Chemical Engineering* **2016**, *12*, 82–90.

(30) Meng, X.; Scheidemantle, B.; Li, M.; Wang, Y. Y.; Zhao, X.; Toro-Gonzalez, M.; Singh, P.; Pu, Y.; Wyman, C. E.; Ozcan, S.; et al. Synthesis, Characterization, and Utilization of a Lignin-Based Adsorbent for Effective Removal of Azo Dye from Aqueous Solution. *ACS Omega* **2020**, *5* (6), 2865–2877.

(31) Dai, K.; Zhang, J.; Kou, J.; Yang, P.; Li, M.; Tang, C.; Zhuang, W.; Ying, H.; Wu, J. Tunable synthesis of polyethylene polyamine modified lignin and application for efficient adsorption of Fe²⁺ in super acid system. *Sep. Purif. Technol.* **2021**, *272*, No. 118950.

(32) Song, T.; Zhao, H.; Hu, Y.; Sun, N.; Zhang, H. Facile assembly of mesoporous silica nanoparticles with hierarchical pore structure for CO₂ capture. *Chin. Chem. Lett.* **2019**, *30* (12), 2347–2350.

(33) Guo, Y.; Luo, L.; Zheng, Y.; Zhu, T. Optimization of CO₂ Adsorption on Solid-Supported Amines and Thermal Regeneration Mode Comparison. *ACS Omega* **2020**, *5* (17), 9641–9648.

(34) Shi, Z.; Xu, G.; Deng, J.; Dong, M.; Murugadoss, V.; Liu, C.; Shao, Q.; Wu, S.; Guo, Z. Structural characterization of lignin from *D. sinicus* by FTIR and NMR techniques. *Green Chemistry Letters and Reviews* **2019**, *12* (3), 235–243.

(35) Amit, T. A.; Roy, R.; Raynie, D. E. Thermal and structural characterization of two commercially available technical lignins for

potential depolymerization via hydrothermal liquefaction. *Curr. Res. Green Sustainable Chem.* **2021**, *4*, No. 100106.

(36) Hu, Z.; Du, X.; Liu, J.; Chang, H. -m.; Jameel, H. Structural Characterization of Pine Kraft Lignin: BioChoice Lignin vs Indulin AT. *Journal of Wood Chemistry and Technology* **2016**, *36* (6), 432–446.

(37) Lancefield, C. S.; Wienk, H. L. J.; Boelens, R.; Weckhuysen, B. M.; Bruijninx, P. C. A. Identification of a diagnostic structural motif reveals a new reaction intermediate and condensation pathway in kraft lignin formation. *Chem. Sci.* **2018**, *9* (30), 6348–6360.