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Extraction and Depolymerization of Lignin from Pine Sawdust and Pistachio Shells

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Abstract: Lignocellulosic biomass is a renewable resource that contains three major constituents: cellulose, hemicellulose, and lignin. Lignin is a potential source of aromatic phenols. The extraction and subsequent depolymerization of lignin was studied using pine sawdust and pistachio shells. Lignin extraction used 70:30 methyl isobutyl ketone:ethanol followed by 0.1M H_2SO_4. The extraction yield of lignin was 15.78 ± 3.38% from pistachio shells and 18.86 ± 1.52% from pine sawdust. The extracted lignin was characterized using Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and ^{1}H-NMR spectroscopy. The extracted lignin was depolymerized using subcritical water and a Ni-Graphene catalyst at 240 °C for 10 min. The depolymerization products were identified as phenolic monomers, such as phenol, guaiacol, vanillin, syringol, guaiacylpropane, syringaldehyde, coniferaldehyde, synapyl alcohol, and synapyl aldehyde, using GC-MS.

Keywords: depolymerization; subcritical water; lignocellulosic biomass; pistachio shells; pine sawdust; extraction; characterization; phenolic monomers; GC-MS; lignin

Citation: Jadhav, B.; Roy, R.; Rahman, M.S.; Raynie, D.E. Extraction and Depolymerization of Lignin from Pine Sawdust and Pistachio Shells. *Biomass* **2022**, *2*, 348–357. https://doi.org/10.3390/biomass2040023

Academic Editor: Lasse Rosendahl

Received: 4 September 2022
Accepted: 23 November 2022
Published: 28 November 2022

1. Introduction

Biomass is the most abundant renewable biological material, grows everywhere, and provides clean resources, including fuel, power, and chemicals. The utilization of biomass for the production of chemicals and fuels is a major part of the U.S. bioeconomy. Concerns arising from fossil fuel consumption, e.g., climate change, global warming, and negative impacts on human health, are driving modern biomass utilization [1]. Lignocellulosic biomass is a most abundant and low-cost renewable source to produce the value-added chemicals [2]. The main components of biomass are cellulose, hemicellulose, and lignin [3]. This is an alternative source to replace fossil fuels and reduce the global warming [4]. Biomass includes food crops, grassy and woody plants, residues from agriculture or forestry, oil-rich algae, and the organic components of municipal and industrial wastes [5].

Lignin is a complex amorphous aromatic polymer with a three-dimensional structure composed of polypropane units, including guaiacylpropane (G), syringylpropane (S), and p-hydroxyphenypropane (H), bonded with C-C, β-β, β-1, β-5, and β-O-4 linkages [6,7]. Lignin is a source of aromatic phenolic monomers, which are widely used in the preparation of resins and polymers. Lignin is used in binders and additives in cement and applicable in many areas, such as emulsifiers, dyes, synthetic flooring, dispersal agents, and paints [8]. The lignin content varies depending on the plant species and contains up to 25–30%. The pulp and paper industries produce approximately 50 million tons of lignin annually, and only one million tons of lignin is used for the production of value-added chemicals [1]. Lignin is crosslinked with strong inter- and intramolecular hydrogen bonds because of prevalent polar and hydroxyl groups. The conversion of lignin into small aromatic phenols occurs by breaking the β-O-4 bond under specific reaction conditions and solvents (temperature, pressure, time, and solvents).

There are several methods reported for the depolymerization of lignin, including pyrolysis [9], acid-catalyzed depolymerization [10], base-catalyzed [11], enzymatic depoly-

merization [12], depolymerization with ionic liquids [13], supercritical CO_2 depolymerization [14], and metal-catalyzed depolymerization [15]. Acid-catalyzed depolymerization requires extreme reaction conditions and toxic chemicals and produces corrosive waste, which significantly increases the cost of the process and pollution prevention concerns. Other methods also use hazardous reaction conditions and organic solvents for the depolymerization of lignin.

In this study, subcritical water and a Ni-Graphene catalyst are used for the depolymerization of lignin from our previous studies [16]. The depolymerization of lignin was performed at 240 °C for 10 min. The products were identified using gas chromatography–mass spectrometry (GC-MS). The utilization of a green solvent (subcritical water) and minimal reaction conditions for lignin depolymerization is considered a greener approach.

In this study, pistachio shells and pine sawdust are used as feedstocks for the extraction of lignin.

Pine sawdust is a common waste material from the forestry and industrial sector [17]. Pine sawdust is an excellent raw material for biorefinery [18]. It contains 22.65% lignin [19]. Pistachio shells (PS) are a potential alternative lignocellulosic biomass and are generated in considerable amounts, as the annual production of pistachios in the last 10 years is between 800 and 900 ktonnes [20]. Pistachios are cultivated in Iran, the Middle East, the United States, and Mediterranean countries [21]. Iran is the largest pistachio producer in the word, yielding about 40% of the global production in the year 2009 [22]. The U.S. is the second largest producer, with 27% of the total global marketplace [22]. Pistachio shells are agricultural wastes mostly used for animal feed or fuel [21]. Pistachio shells contain 16.33% lignin [23]. Pistachio shells are used for the production of activated carbon by pyrolysis and gasification [21].

The isolation of lignin from biomass can be performed in two ways. One method is to extract cellulose and hemicellulose, leaving most of the lignin as solid residue. The second method is to extract lignin using solvent fractionation, leaving the other components. There are several techniques reported for the extraction of lignin from biomass, such as using ionic liquids [24], acid [19], alkali [25], organic solvents [26], deep eutectic solvents (DESs) [27], and hydrogen peroxide [28].

In this study, methyl isobutyl ketone and ethanol (7:3 v/v) followed by 0.1M H_2SO_4 are used for the extraction of lignin from pine sawdust and pistachio shell biomass using accelerated solvent extraction (ASE). The structural characterization of the extracted lignin was performed with Fourier-transform infrared spectroscopy (FTIR), ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectroscopy, and thermogravimetric analysis (TGA), and the depolymerization products were characterized using GC-MS. The main objective of this work is to extract lignin from biowaste materials and perform depolymerization using subcritical water and a catalyst to convert lignin into aromatic phenols.

2. Materials

Pine sawdust and pistachio shells were obtained from the Department of Agricultural and Biosystems Engineering at South Dakota State University. These samples were homogenized and the particle size was reduced to 850 µm. The extraction solvents methyl isobutyl ketone, ethanol, H_2SO_4, and DMSO-d_6 were purchased from the Fisher Scientific Store (Fair Lawn, New Jersey, USA). The catalyst (Ni-Graphene) was obtained from the Department of Agricultural and Biosystems Engineering [16].

3. Experimental procedure:

3.1. Extraction of Lignin from Pine Sawdust and Pistachio Shells

Accelerated solvent extraction (Dionex ASE model 350, Thermo-Fisher, Sunnyvale, CA, USA) was used for the extraction of lignin from the biomass. Stainless steel cells (34 mL) were used for loading 0.5–1.0 g of the biomass, and the balance of the vessel was packed with diatomaceous earth. The samples were extracted with methyl isobutyl ketone and ethanol (7:3 (v/v %)) followed by a second extraction with 0.1 M H_2SO_4. The

extraction temperature was 200 °C at a pressure of 1500 psi with nine minutes of heating, sixty minutes of static time, five minutes of purge time, and the rinse volume was 100%.

Water was added to the extract, allowed to separate, and the organic phase was collected. The organic phase concentrated overnight in a fume hood, was oven dried at 50 °C for 30 min, and was weighed. The extracted lignin was characterized with ^{1}H NMR spectroscopy, FTIR, and TGA. Figure 1 shows the stepwise process for the extraction of lignin from the biomass.

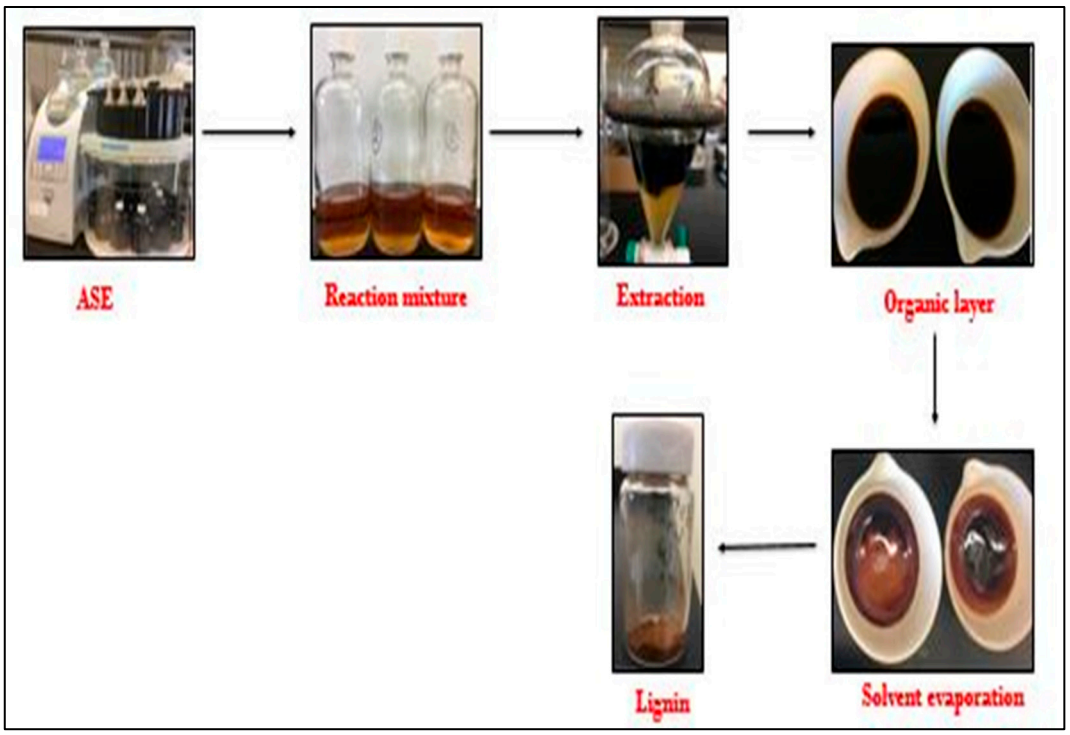

Figure 1. Extraction of lignin from the biomass using accelerated solvent extraction (ASE).

3.2. Depolymerization of Extracted Lignin from Pistachio Shells and Pine Sawdust

Depolymerization of the extracted lignin was performed with a Helix Subcritical H_2O instrument (Applied Separations, Allentown, PA, USA) using subcritical water and a catalyst. The optimized conditions from previous studies were applied [16]. The Ni-Graphene catalyst (0.025 g) was used for the depolymerization of 0.2500 g of lignin in a 24-mL stainless steel vessel. Distilled water passed into the stainless-steel vessel at 21 mL/min. Depolymerization was performed at 240 °C for 10 min with constant stirring. The pressure was 22.5 MPa. The reaction mixture was collected after the reaction and filtered under vacuum. Acetic acid was added to the filtrate to protonate the extract. The phenolic monomers were isolated from the extract using ethyl acetate. The samples were concentrated under N_2 gas. The concentrated samples were analyzed using GC-MS.

4. Results and Discussion

4.1. Extraction of Lignin from the Pine Sawdust and Pistachio Shell Biomass

The extraction of lignin from the pine sawdust and pistachio shells was performed at 140 °C, 170 °C, and 200 °C using accelerated solvent extraction (ASE). The extraction yield from the pistachio shells was found to be 6.63% at 140 °C, 13.3% at 170 °C, and 15.78% at 200 °C. The extraction yield from the pine sawdust was found to be 6.52% at 140 °C, 14.4% at 170 °C, and 18.86% at 200 °C. The highest yield was achieved at 200 °C for 60 min for both the pine sawdust and pistachio shell biomass. Figure 2 shows the extraction of lignin from the pine sawdust biomass at different temperatures. The yield of the extracted lignin was calculated by using Equation (1). The extraction yield increases

with the increasing temperature. Because organic solvents and sulfuric acid are used for the breakage of covalent bonds in lignocellulosic biomass at higher temperatures, the yield of lignin increases with temperature [29].

$$\% \text{ Yield} = \frac{Weight\ of\ Extracted\ Lignin}{Weight\ of\ Biomass} \times 100 \quad (1)$$

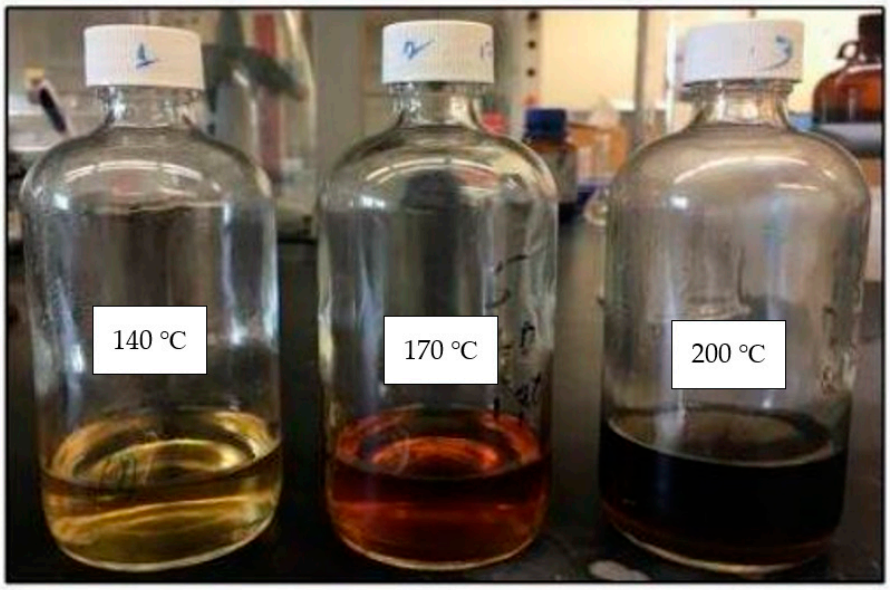

Figure 2. Extraction of lignin from the pine sawdust biomass at different temperatures.

4.2. Characterization of Extracted Lignin

The extracted organosolv lignin structure was confirmed with Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and ^{1}H NMR spectroscopy. These techniques provide detailed qualitative information on structural features, including functional groups and types of chemical bonds.

4.2.1. FTIR Spectroscopy

The extracted samples were dissolved in DMSO for FTIR analysis. FTIR measurements of the extracted lignin were taken using a Nicolet iS5 Thermo Scientific instrument. The typical functional groups present in lignin were identified in the FTIR spectrum. Figure 3 shows the FTIR spectrum of commercial lignin and the extracted lignin from the pine sawdust and pistachio shell samples. Table 1 shows the identified functional groups and their frequency ranges. The absorption bands at 3450–3210 cm^{-1} appeared for the strong O-H bond stretching and are attributed to the presence of -OH groups in the aromatic and aliphatic structures. The absorption bands at 2358–2997 cm^{-1} indicate the C-H stretching vibrations of methyl and methylene groups. Peaks at 1660 cm^{-1} are attributed to C=O for unconjugated ketones. Peaks at 1437 cm^{-1} are attributed to aliphatic -CH_2 vibrations, and peaks at 1056.16 cm^{-1} indicate aliphatic ether C-O and alcohol C-O stretching. The peaks at 954.53 cm^{-1} correspond to aromatic C-H out-of-plane deformations of asymmetric methyl and methylene groups [30].

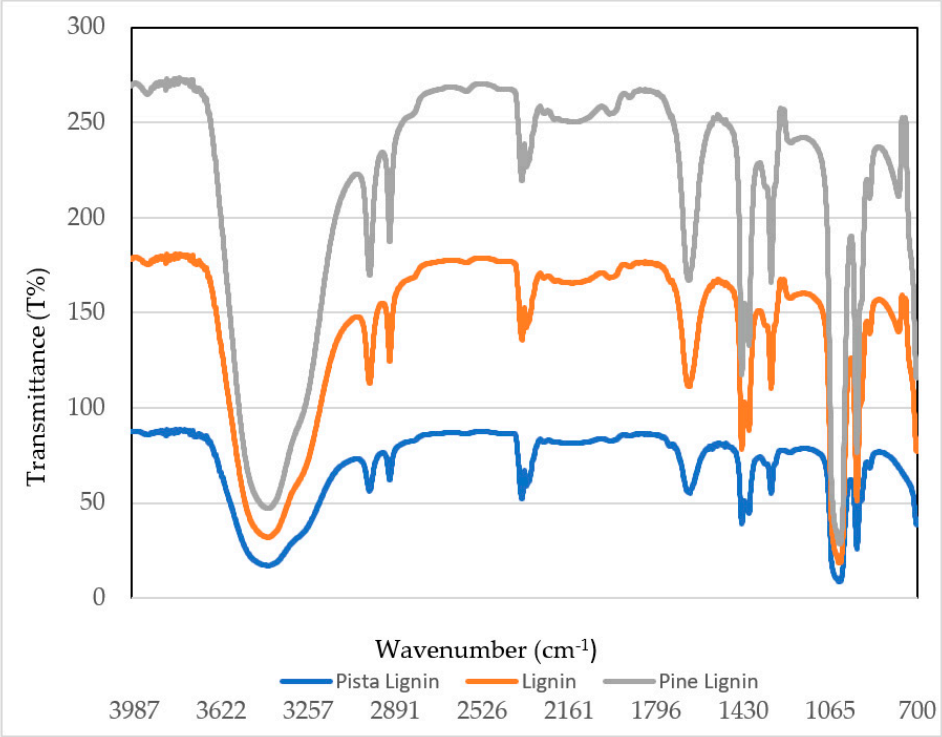

Figure 3. FTIR spectrum of extracted lignin from the pistachio shell and pine sawdust biomass and compared with commercial lignin.

Table 1. Functional group assignment of FTIR analysis of extracted lignin from pine sawdust and pistachio shells.

Absorption Bands (cm^{-1})	Functional Groups
3445	O-H stretching vibration due to alcohols
2358–2997	C-H stretching in methyl and methylene groups
1660.76	C=O stretching in aromatic carbonyl
1437.15	Aliphatic CH_2 vibrations
1407.46	Aromatic skeletal vibrations and C-H in-plane deformation
1311.38	Aliphatic C-H stretch in CH_3
1056.16	Aliphatic ether C-O and alcohol C-O stretching
954.53	Aromatic C-H out-of-plane deformation

4.2.2. NMR Spectroscopy

^{1}H-NMR spectroscopic methods possess much higher resolution and provide larger amounts of information from lignin compared with the other techniques. The extracted lignin samples were dissolved in DMSO-d_6 for analysis. A 600 MHz Bruker Spectrospin NMR spectrometer was used for the characterization of lignin. ^{1}H NMR spectroscopy provides the qualitative assay for the frequencies of linkages and the composition of H/G/S units in the lignin analysis. In the spectrum, the signal observed around 7.5 ppm can be assigned to the aromatic protons in H units, the other two chemical shifts at 7.0 ppm and 6.5 ppm are attributed to the aromatic protons in G and S units, respectively, and the signals at 5.75–6.25 ppm are from the H-α with α-O-Ac in β-O-4. The signals in the range of 3.95–4.50 ppm emanate from the H-γ in β-O-4, β-5, β-1, and β-β. The signals in the range of 4.0–3.0 ppm are attributed to methoxy protons. The signals in the range of 2.50–3.55 ppm are from the H-β in β-1 and β-β protons, and chemical shifts in the range of 2.20–2.50 ppm are from the H in Ar-OAc. The chemical shifts in the range of 1.50–2.20 ppm are from

the H-in aliphatic-OAc and Ar-OAc in 5-5 units in lignin. Figure 4 shows the ^{1}H NMR spectrum of the lignin extracted from the pistachio shells, pine sawdust, and commercial lignin. Table 2 shows the assigned functional groups and their chemical shifts for the extracted lignin from the pine sawdust and pistachio shells compared with commercial lignin chemical shifts.

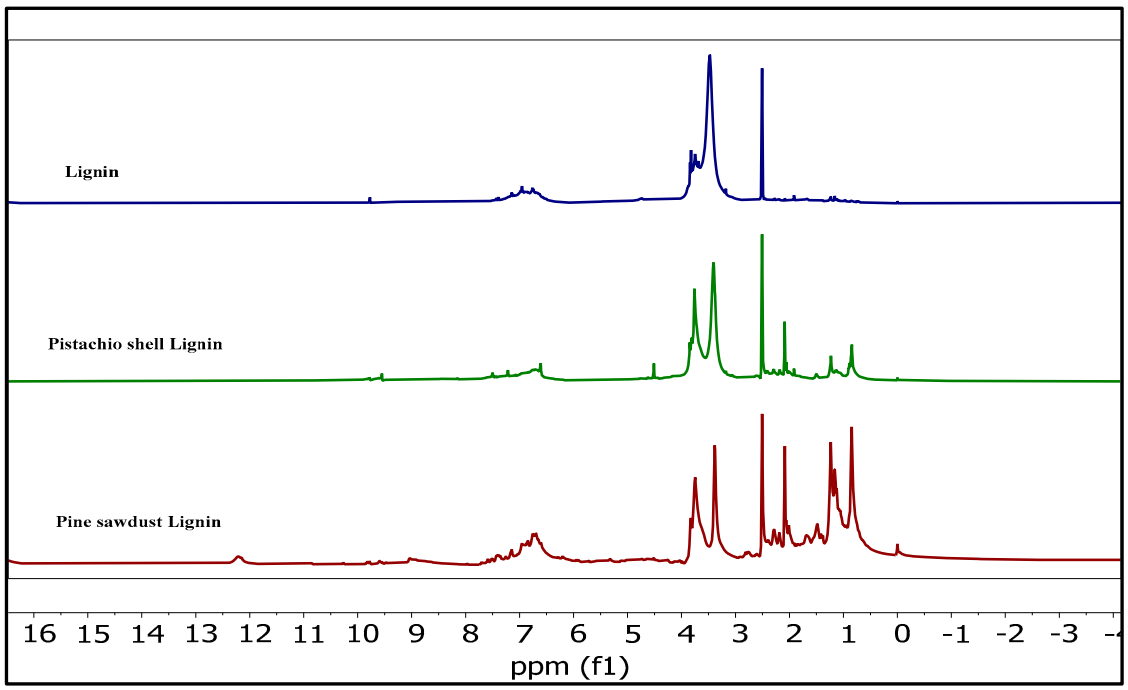

Figure 4. ^{1}H-NMR spectrum of extracted lignin from pine sawdust and pistachio shells compared with commercial lignin.

Table 2. ^{1}H NMR chemical shifts and functional groups of extracted lignin from pine sawdust and pistachio shells.

Chemical Shift (ppm)	Functional Group
6.5–7.0	Aromatic protons
5.75–6.25	H-α with α-O-Ac in β-O-4
3.95–4.50	H-γ in β-O-4, β-5, β-1, and β-β protons
3.0–4.0	-OCH_3 protons
2.50–3.55	H-β in β-1 and β-β protons
2.20–2.50	H-in Ar-OAc
1.50–2.20	H-in aliphatic-OAc and Ar-OAc in 5-5 units

4.2.3. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was used to determine the thermal stability and decomposition temperature of the extracted lignin from the pine sawdust and pistachio shells. TGA measurements were taken using a Seiko TG/DTA220 instrument operating under nitrogen. Samples for each measurement were maintained at 14 ± 5 mg, and scans were performed from 25 to 560 °C at 10 °C/min to observe the thermal degradation and stability of each lignin based on its source. TGA curves reveal the weight loss percentage with respect to the temperature of thermal degradation. The lignin structure is composed of mostly aromatic rings having various branches, leading to a wide range of degradation temperatures from 100 to 560 °C. Figure 5 shows TGA curves for the pine sawdust, pistachio shells, and commercial lignin. Degradation of the lignin samples was divided into three stages. In stage one, the initial weight loss step occurred at 30–120 °C due to the evaporation of absorbed water. Stage two took place around 180–350 °C and is attributed

to the degradation of carbohydrate components in the lignin samples. The final stage of the degradation occurred over a wide range of temperatures above 350 °C. During this stage, degraded volatile products derived from lignin, including phenolics and alcohols, are observed.

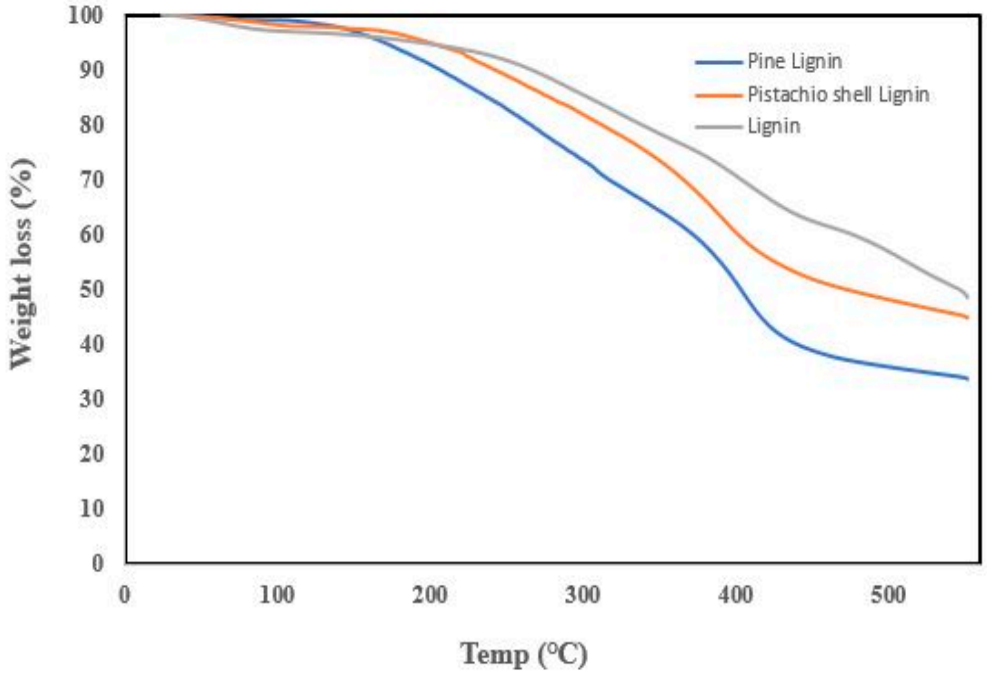

Figure 5. TGA plots of lignin from pistachio shells, pine sawdust, and commercial lignin obtained under nitrogen atmosphere at 10 °C/min.

4.2.4. Identification of Phenolic Monomers Using GC-MS

Phenolic monomers from the lignin samples were identified by using GC-MS. A 5977B MSD and 7890B GC system from Agilent Technologies was used for product analysis. The GC-MS was equipped with a 30 m × 250 µm id. (0.25-µm film) DB-5 MS capillary column. Hydrogen was employed as a carrier gas at a constant flow rate of 1.2 mL/min. The initial oven temperature was 50 °C and programmed to 200 °C at 12 °C/min, and held for one minute, and programmed to 300 °C at 20 °C/min, and held for one minute. The injection volume was 2 µL. The ion source was electron impact (EI). The compounds were identified by comparing the data with the NIST library. Figure 6 shows the GC-MS chromatogram of depolymerization products of the extracted lignin from the pine sawdust. Table 3 shows 12 identified phenolic monomers from the extracted lignin. The major phenolic monomers were identified as syringaldehyde, vanillin, and trimethoxy benzyl alcohol. Figure 7 shows the relative abundance of the phenolic monomers from the pine sawdust lignin.

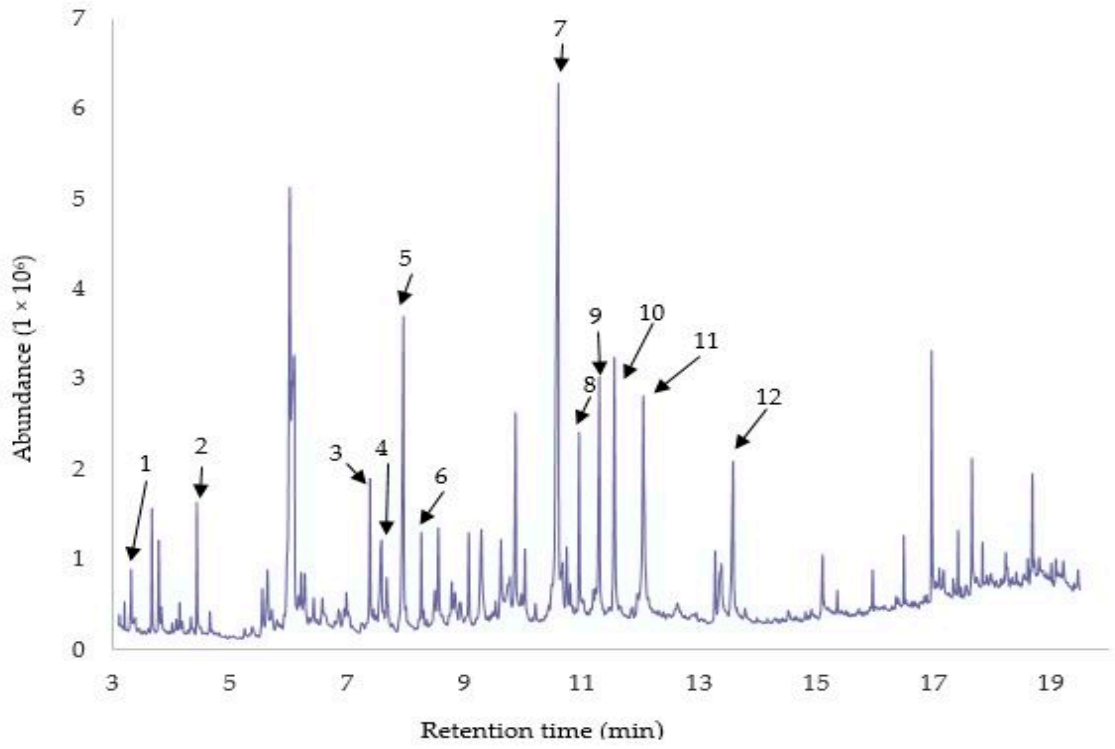

Figure 6. GC-MS total ion chromatogram of phenolic monomers from pine sawdust lignin.

Table 3. Identified phenolic monomers and retention time of Pine sawdust lignin.

No	Retention Time (min)	Phenolic Monomer	Abundance (%)
1	3.318	Phenol	0.63
2	4.429	Guaiacol	1.15
3	7.484	Syringol	2.02
4	7.674	m-Hydroxy benzaldehyde	2.23
5	7.948	Vanillin	5.52
6	8.548	Propyl guaiacol	1.95
7	10.584	Syrinzaldehyde	12.82
8	10.958	Methoxy eugenol	2.41
9	11.290	Coniferaldehyde	4.13
10	11.545	Synapyl alcohol	3.85
11	12.050	Trimethoxy benzyl alcohol	4.93
12	13.569	Synapaldehyde	3.51

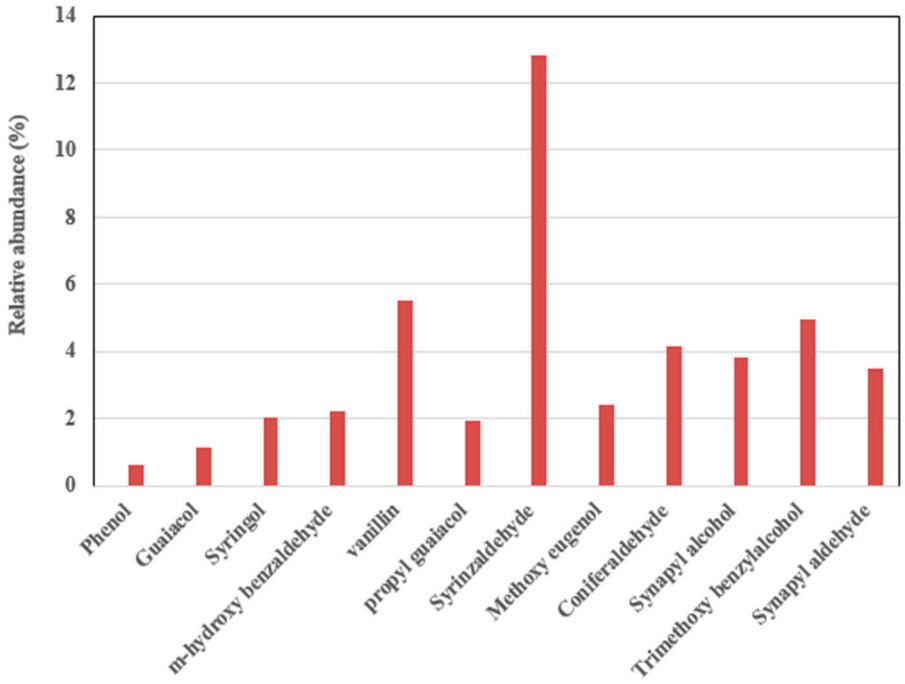

Figure 7. Relative abundance of phenolic monomers from pine sawdust lignin.

5. Conclusions

Lignin was extracted using accelerated solvents extraction (ASE) and depolymerized using subcritical water and a catalyst. Agricultural waste materials such as pine sawdust and pistachio shells were used for the extraction of lignin using methyl isobutyl ketone, ethanol, and 0.1 M H_2SO_4 as solvents. The extracted lignin yield was 15.78 $\pm$ 3.38% from pistachio shells and 18.86 $\pm$ 1.52% from the pine sawdust. The depolymerization of the extracted lignin was performed using subcritical water and a Ni-Graphene catalyst at 240 °C for ten minutes. The depolymerization products were analyzed using GC-MS. There were 12 different phenolic monomers identified from the depolymerized lignin. The major phenolic monomers are vanillin and syringaldehyde. Subcritical water was used as a green solvent for the depolymerization of the extracted lignin. This study demonstrated the conversion of biowaste materials into value-added chemicals using environmentally friendly techniques.

Author Contributions: Conceptualization, B.J. and D.E.R.; methodology, B.J., R.R. and D.E.R.; validation, B.J., R.R., M.S.R. and D.E.R.; formal analysis, B.J., R.R., M.S.R. and D.E.R.; investigation, B.J., R.R. and M.S.R.; data curation, B.J.; writing—original draft preparation, B.J.; writing—review and editing, B.J. and D.E.R.; supervision D.E.R.; project administration, D.E.R.; funding acquisition, D.E.R. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by the National Science Foundation EPSCoR Track II Dakota BioCon project for North and South Dakota (Grant Nos.IIA-1355466 and IIA-1330842).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Tursi, A. A review on biomass: Importance, chemistry, classification, and conversion. *Biofuel Res. J.* **2019**, *6*, 962. [CrossRef]
2. Nanda, S.; Mohammad, J.; Reddy, S.N.; Kozinski, J.A.; Dalai, A.K. Pathways of lignocellulosic biomass conversion to renewable fuels. *Biomass Convers. Biorefin.* **2014**, *4*, 157–191. [CrossRef]

3. Mosier, N.; Wyman, C.; Dale, B.; Elander, R.; Lee, Y.Y.; Holtzapple, M.; Ladisch, M. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresour. Technol.* **2005**, *96*, 673–686. [CrossRef] [PubMed]
4. Dhillon, R.; von Wuehlisch, G. Mitigation of global warming through renewable biomass. *Biomass Bioenergy* **2013**, *48*, 75–89. [CrossRef]
5. Lucas, M.; Macdonald, B.A.; Wagner, G.L.; Joyce, S.A.; Rector, K.D. Ionic Liquid Pretreatment of Poplar Wood at Room Temperature: Swelling and Incorporation of Nanoparticles. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2198–2205. [CrossRef] [PubMed]
6. Espinoza-Acosta, J.L.; Torres-Chávez, P.I.; Olmedo-Martínez, J.L.; Vega-Rios, A.; Flores-Gallardo, S.; Zaragoza-Contreras, E.A. Lignin in storage and renewable energy applications: A review. *J. Energy Chem.* **2018**, *27*, 1422–1438. [CrossRef]
7. Lu, Y.; Lu, Y.C.; Hu, H.Q.; Xie, F.J.; Wei, X.Y.; Fan, X. Structural characterization of lignin and its degradation products with spectroscopic methods. *J. Spectrosc.* **2017**, *2017*, 8951658. [CrossRef]
8. Thakur, V.K.; Thakur, M.K.; Raghavan, P.; Kessler, M.R. Progress in green polymer composites from lignin for multifunctional applications: A review. *ACS Sustain. Chem. Eng.* **2014**, *2*, 1072–1092. [CrossRef]
9. Pandey, M.P.; Kim, C.S. Lignin Depolymerization and Conversion: A Review of Thermochemical Methods. *Chem. Eng. Technol.* **2011**, *34*, 29–41. [CrossRef]
10. Deuss, P.J.; Scott, M.; Tran, F.; Westwood, N.J.; de Vries, J.G.; Barta, K. Aromatic Monomers by in Situ Conversion of Reactive Intermediates in the Acid-Catalyzed Depolymerization of Lignin. *J. Am. Chem. Soc.* **2015**, *137*, 7456–7467. [CrossRef]
11. Erdocia, X.; Prado, R.; Corcuera, M.A.; Labidi, J. Base catalyzed depolymerization of lignin: Influence of organosolv lignin nature. *Biomass Bioenergy* **2014**, *66*, 379–386. [CrossRef]
12. Gall, D.L.; Kontur, W.S.; Lan, W.; Kim, H.; Li, Y.; Ralph, J.; Donohue, T.J.; Noguera, D.R. In vitro enzymatic depolymerization of lignin with release of syringyl, guaiacyl, and tricin units. *Appl. Environ. Microbiol.* **2018**, *84*, e02076-17. [CrossRef] [PubMed]
13. Stärk, K.; Taccardi, N.; Bösmann, A.; Wasserscheid, P. Oxidative Depolymerization of Lignin in Ionic Liquids. *ChemSusChem* **2010**, *3*, 719–723. [CrossRef]
14. 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. [CrossRef]
15. Chio, C.; Sain, M.; Qin, W. Lignin utilization: A review of lignin depolymerization from various aspects. *Renew. Sustain. Energy Rev.* **2019**, *107*, 232–249. [CrossRef]
16. Jadhav, B.; Roy, R.; Rahman, S.; Amit, T.A.; Subedi, S.; Hummel, M.; Gu, Z.; Raynie, D.E. Enhancing the Efficacy of the Subcritical Water-Based Alkali Lignin Depolymerization by Optimizing the Reaction Conditions and Using Heterogeneous Catalysts. *Biomass* **2022**, *2*, 178–187. [CrossRef]
17. Muley, P.D.; Henkel, C.; Abdollahi, K.K.; Marculescu, C.; Boldor, D. A critical comparison of pyrolysis of cellulose, lignin, and pine sawdust using an induction heating reactor. *Energy Convers. Manag.* **2016**, *117*, 273–280. [CrossRef]
18. Stoffel, R.B.; Neves, P.V.; Felissia, F.E.; Ramos, L.P.; Gassa, L.M.; Area, M.C. Hemicellulose extraction from slash pine sawdust by steam explosion with sulfuric acid. *Biomass Bioenergy* **2017**, *107*, 93–101. [CrossRef]
19. Watkins, D.; Nuruddin, M.; Hosur, M.; Tcherbi-Narteh, A.; Jeelani, S. Extraction and characterization of lignin from different biomass resources. *J. Mater. Res. Technol.* **2015**, *4*, 26–32. [CrossRef]
20. FAOSTAT. Food and Agriculture Data. 2018. Available online: http://www.fao.org/faostat/en/#home (accessed on 1 September 2022).
21. Kasiri, N.; Fathi, M. Production of cellulose nanocrystals from pistachio shells and their application for stabilizing Pickering emulsions. *Int. J. Biol. Macromol.* **2018**, *106*, 1023–1031. [CrossRef]
22. Ghasemynasabparizi, M.; Ahmadi, A.; Mazloomi, S. A review on pistachio: Its composition and benefits regarding the prevention or treatment of diseases. *J. Occup. Health Epidemiol.* **2015**, *4*, 57–69. [CrossRef]
23. Li, X.; Liu, Y.; Hao, J.; Wang, W. Study of Almond Shell Characteristics. *Materials* **2018**, *11*, 1782. [CrossRef] [PubMed]
24. Achinivu, E.C. Protic Ionic Liquids for Lignin Extraction—A Lignin Characterization Study. *Int. J. Mol. Sci.* **2018**, *19*, 428. [CrossRef] [PubMed]
25. Obst, J.R.; Kirk, T.K. Isolation of lignin. In *Methods in Enzymology*; Elsevier: Amsterdam, The Netherlands, 1988; pp. 3–12.
26. Sun, R.; Tomkinson, J.; Jones, G.L. Fractional characterization of ash-AQ lignin by successive extraction with organic solvents from oil palm EFB fibre. *Polym. Degrad. Stab.* **2000**, *68*, 111–119. [CrossRef]
27. Rahman, M.S.; Roy, R.; Jadhav, B.; Hossain, M.N.; Halim, M.A.; Raynie, D.E. Formulation, structure, and applications of therapeutic and amino acid-based deep eutectic solvents: An overview. *J. Mol. Liq.* **2021**, *321*, 114745. [CrossRef]
28. Ma'Ruf, A.; Pramudono, B.; Aryanti, N. Lignin isolation process from rice husk by alkaline hydrogen peroxide: Lignin and silica extracted. *AIP Conf. Proc.* **2017**, *1823*, 020013.
29. Riyadi, R.; Masyithah, Z.; Hutagalung, A.; Haryanto, B. The effect of temperature and reaction time on lignin content of Imperata Cylindrica. *AIP Conf. Proc.* **2021**, *2342*, 090001.
30. Roy, R.; Jadhav, B.; Rahman, S.; Raynie, D.E. Characterization of residue from catalytic hydrothermal depolymerization of lignin. *Curr. Res. Green Sustain. Chem.* **2021**, *4*, 100052. [CrossRef]