




Article

Enhancing the Efficacy of the Subcritical Water-Based Alkali Lignin Depolymerization by Optimizing the Reaction Conditions and Using Heterogeneous Catalysts

Balawanthrao Jadhav ¹, Ranen Roy ¹, Md Sajjadur Rahman ¹, Tanvir A. Amit ¹, Shiksha Subedi ¹, Matthew Hummel ², Zhengrong Gu ² and Douglas E. Raynie ^{1,*}

¹ Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD 57007, USA

² Department of Agricultural and Biosystems Engineering, South Dakota State University, Brookings, SD 57007, USA

* Correspondence: douglas.raynie@sdstate.edu

Abstract: The catalytic depolymerization of alkali lignin into phenolic monomers was studied using subcritical water. In this study, subcritical water was used as the greener solvent with heterogeneous catalysts. The goal of this study was to screen for the best catalyst for the depolymerization, to optimize the reaction conditions, and to increase the yield of the phenolic monomers. The depolymerization reactions were performed at 200 and 240 °C for 5, 10, and 15 min, using subcritical water as the solvent with different catalysts. The treatment of the lignin sample with Ni-Graphene catalyst in subcritical water at 240 °C for 10 min resulted in the highest total yield of phenolic monomers, which was 41.16 ± 0.27 mg/g of alkali lignin. The catalysts also resulted the highest yield for each of the phenolic monomers guaiacol (G), vanillin (G), and homovanillic acid (G) compared to other catalysts studied. The optimized method proved to be an excellent approach to depolymerize alkali lignin.

Keywords: hydrothermal depolymerization; alkali lignin; subcritical water; catalysts; and phenolic monomers



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1. Introduction

In recent years, the consumption of fossil feedstocks, such as coal, natural gas, and crude oil, has been increasing due to the high demand for value-added chemicals and energy. Depleting fossil resources and increasing global warming have brought special attention to researchers throughout the world to find alternative sustainable and renewable sources for the demand. Lignocellulosic biomass is considered as a potential alternative source of fossil fuels to produce value-added chemicals and biofuels. It is a complex biopolymer which is abundantly available in the secondary cell wall of plants and is composed of three different polymers: cellulose, hemicellulose, and lignin [1]. Among them, the biorefinery and pulping industries use cellulose and hemicellulose to produce biofuels and value-added products, while lignin is treated as a waste material due to its low reactivity. Lignin is a complex organic biopolymer and the second most abundant biomass on earth. The percentages of lignin in lignocellulosic biomass varies from 10 to 30%, depending on the sources and environment [1]. Approximately 40–50 million tons of lignin have been produced from the pulp and paper industries per annum worldwide, but only 2% of them have been utilized for further industrial applications [2]. However, being polyaromatic in nature and having easy availability, lignin could be a promising source of various value-added aromatic chemicals [3].

Lignin is an amorphous copolymer of p-coumaryl (H), coniferyl (G), and sinapyl (S) alcohols bound together by C-C, C-O-C bonds, 5-5, β - β , β -5, β -1, α -O-4, 5-O-4, and β -O-4 ether linkages [1]. The high content of oxygen and lower heating value suggest development of effective technologies to convert them into the valuable phenolic monomers [4].

These monomers are being used in many industries, such as synthesis of resins, polymers, and additives for food products [5].

Researchers have been facing challenges to understand the mechanism of the depolymerization of lignin due to its complex and recalcitrant structure. Several conventional methods such as base-catalyzed, acid-catalyzed, fast pyrolysis, oxidation, microwave assisted, ionic liquid-based, deep eutectic solvent-based, and supercritical carbon dioxide-based depolymerization of lignin have been proposed [6,7].

The depolymerization of wheat straw lignin was reported using supercritical CO₂, acetone, and water fluid as a solvent the operating temperature was 300 °C at 100 bar, and the processing time was 3.5 h [8]. Stark et al. reported the depolymerization of organosolv lignin from beech using ionic liquids and depolymerization of lignin conducted at 100 °C for 24 h [9]. Jiang et al. studied the depolymerization of two lignins, an organosolv lignin from a mixture of hardwoods and lignin from the soda pulping of a mixture of wheat straw and Sarkanda grass, using pyrolysis temperature range from 400–800 °C, and maximum yield was found at 600 °C [10]. These methods require chemicals, high temperature, and processing time to achieve the desired phenolic compounds. This study reports the depolymerization of lignin using green, and environmentally friendly solvent (subcritical water), minimal reaction temperature (240 °C), and less processing time (10 min).

Subcritical water-based depolymerization is greener and requires fewer steps. Therefore, it would be wise to improve the efficiency of this method using another green approach, which is addition of catalyst to the reaction. Gas chromatography/mass spectrometry (GC-MS) is an excellent instrument to analyze the compounds achieved from the lignin [11]. Resources for lignin depolymerization and other bioconversion processes have recently been reviewed [12,13]. Catalytic hydrodeoxygenation of lignin materials in subcritical water has been subject to recent study [14–18]. These studies show that active metals, such as Mg, Al, Zn, and Fe supported on zeolites, are useful for the hydrothermal liquefaction of such biomass samples, but the catalytic performance, minimization of coke formation, selectivity of conversion products, and other performance factors are yet to be studied in detail. We propose a set of heterogeneous catalysts and mild reaction conditions to complement these previous studies, providing guidance for process optimization towards the formation of monoaromatic reaction products.

Catalytic liquefaction using subcritical water is an efficient greener method to convert complex lignin into the monomeric compounds [19]. This process requires lower temperatures (200–240 °C) compared to the traditional methods, greener solvents, and can improve the solubility of the lignin [20]. The lower temperature and pressure of this method prevents char formation and could increase the yield of aromatic compounds [21]. In this method, greener aspects, such as subcritical water and catalysts, could improve the yield and the quality of the products [22]. The protons released from the subcritical water reaction may attach on the surface of the catalysts and can increase the depolymerization on the active sites of catalysts [23]. Another green aspect of this method is that the zeolite-supported and carbon supported catalysts are easily recoverable compared to traditional catalysts [24].

Subcritical water exists in the liquid state between its natural boiling point (100 °C) and its critical temperature (374 °C) by applying pressure (Figure S1) [25]. Under subcritical conditions, the density and dielectric constant of water are lower due to lessening of the intermolecular hydrogen bonding [26]. The lower dielectric constant could help to increase the solubility of the less polar monomeric compounds [27]. Higher polarity, compared with organic solvents, of the subcritical water can increase the solubility of the solids, liquids, and gases [25]. The properties of ordinary water and subcritical water [28,29] are shown in Table S1.

Nagel and Zhang proposed the lignin depolymerization mechanism and cleavage of the β -O-4 bond using a lignin dimer [30]. The metal catalyst adsorbs the hydrogen transferred during in-situ in hydrothermal liquefaction. The free proton helps to cleave the β -O-4 linkage to obtain the phenolic monomers from the lignin. Figure 1 shows the possible pathways of lignin depolymerization in the presence of subcritical water and catalysts.

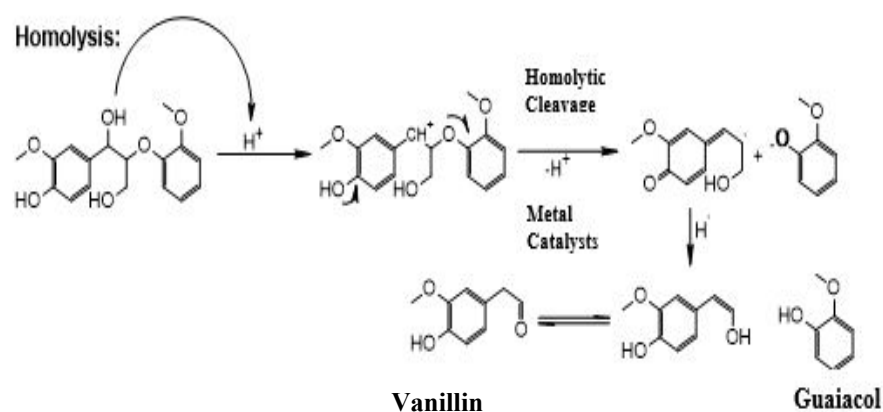
Mechanism:

Figure 1. The possible pathways of lignin depolymerization in the presence of subcritical water and catalyst [30].

Therefore, the main goal of this study was to determine a highly efficient, greener method for the depolymerization method of lignin based on subcritical water and catalytic approach. This study would help to understand the importance of finding optimum reaction temperature and time, and the role of catalyst to achieve the value-added chemicals.

2. Materials and Methods

2.1. Materials and Catalysts

Alkali lignin was purchased from Sigma Aldrich (St. Louis, MO, USA). The alkali-treated lignin is a low sulfur content (<4.0%) lignin and a product of a bioethanol production process. Characterization of the alkali lignin is reported in the literature [31]. The catalysts 5% V/Zelite, 1.7% V/ZrO₂ (Sulfate), 1.7% V/ZrO₂ (Neutral), Ni-Graphene, Ni-Zinc, 5% V/Ni-Graphene, and 1.7% V/Zelite were synthesized and characterized in house. Deionized water was used for the depolymerization of alkali lignin. Ethyl acetate (99.9%) and acetic acid (99.9%) were purchased from Fisher Scientific (Pittsburgh, PA, USA). *o*-Terphenyl was purchased from Sigma Aldrich (St. Louis, MO, USA) and was used as an internal standard for the quantification of phenolic monomers using GC-MS. Other standards (vanillin, homovanillic acid, acetovanillone, guaiacylacetone, and isoeugenol) were purchased from Sigma Aldrich (St. Louis, MO, USA). Guaiacol was purchased from Acros Organics (Morris Plains, NJ, USA).

2.2. Brunauer–Emmett–Teller (BET) Analysis for Heterogeneous Catalysts

V/Zelite catalysts were prepared by an impregnation method using aqueous vanadium oxynitrate, dried in air at 120 °C for four hours, then calcined in air at 550 °C for six hours. Nickel catalysts were prepared by impregnation with nickel (II) nitrate hexahydrate, oven dried at 120 °C for four hours, then calcined under nitrogen at 550 °C for five hours. An analysis method for quantifying surface acidic group was developed using NH₃ -temperature programmed desorption (TPD). Generally, the NH₃ desorption peak temperature indicates the strength, e.g., the type of acid sites, while the peak area of the TCD (thermo-conductive detector) signal at different desorption temperature is able to quantify amount/density of the specific surface acidic group. Increase of the desorption temperatures indicated significant increase of acidity active catalytic sites. The surface area of the catalysts was determined using a gas adsorption analyzer (Micromeritics Tristar 3000). ASAP 2020 Micropore Analyzer with liquid nitrogen was used to carry out the analysis of the physisorption of the catalysts at 77 K. The catalysts were dried overnight in the sample tubes to remove moisture before nitrogen isotherm analysis. The specific surface areas of the catalysts were calculated by the Brunauer–Emmett–Teller (BET) theory [32].

2.3. Catalytic Hydrothermal Depolymerization Reaction

Catalytic hydrothermal depolymerization reactions of lignin were conducted using an unmodified Helix subcritical water instrument engineered by Applied Separations (Allentown, PA, USA). A 24-mL stainless-steel vessel was loaded with 250 mg of alkali lignin and 25 mg of catalyst (a ratio of lignin/catalyst of 10:1), then the excess volume of the vessel was taken up with glass beads. Deionized water flowed into the vessel and the pressure was maintained between 15.0 to 21.5 MPa for all reactions, monitored by a pressure transducer placed between the reaction vessel and the exit valve of the supercritical reactor. The reaction was carried at 200 or 240 °C for 5, 10, or 15 min with constant stirring. The vessel was quickly cooled right after the completion of the reactions, and reaction mixture was collected at ice-water temperature. All reactions were conducted in triplicate and the absolute standard deviation of these results is shown. Figure 2 shows the stepwise process of the depolymerization of the alkali lignin.

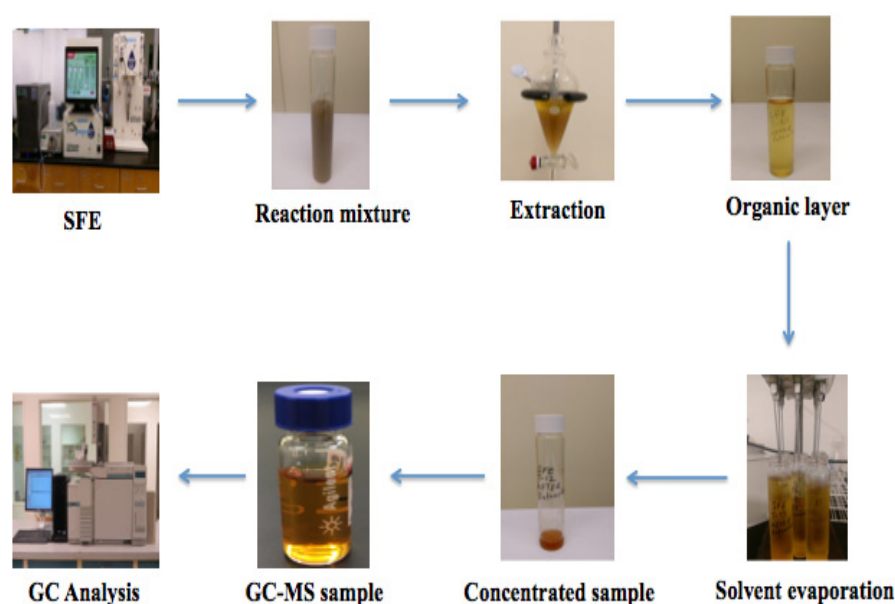


Figure 2. Stepwise process for the depolymerization of alkali lignin.

2.4. Extraction of Phenolic Monomers from Reaction Mixture

The liquid products and lignin residue were separated using vacuum filtration. Approximately 0.2 mL of acetic acid added to the liquid mixture for the protonation of phenoxide ions and ethyl acetate were used to extract the organic products from the aqueous medium. The organic layer was concentrated under N₂ gas. *o*-Terphenyl (100 µL) was added to 1.5 mL of sample as an internal standard for the quantification of phenolic monomers [33]. The product yield of phenolic monomers was calculated by the weight percentage of the products compared to the initial weight of the alkali lignin using the following equation:

$$Y_{\text{Phenolic monomer}} (\text{wt}\%) = \frac{\text{Wt of phenolic monomer}}{\text{Wt of alkali lignin}} \times 100 \% \quad (1)$$

where Y represents the % yield of the phenolic monomers and Wt is the weight of phenolic monomers and alkali lignin, respectively.

2.5. GC-MS Analysis

The phenolic monomers were identified and quantified a 7890B GC-MS system (Agilent Technologies) equipped with a 30 m × 250 µm i.d. DB-5 capillary column (0.25 µm film) with a model 5977B mass selective detector. Hydrogen gas was used as a carrier gas at a constant flow of 1.2 mL/min. The initial oven temperature was 50 °C and increased

to 200 °C at 20 °C/min and held for one minute. Finally, the temperature was increased to 300 °C at 40 °C/min and held for two minutes. Split injection of 2 µL was used at a split ratio of 10:1. Electron ionization (EI) was used, and compounds were identified by comparing the data with the NIST library and standards.

3. Results and Discussion

Table 1 shows the N₂ adsorption-desorption analysis and surface area of the heterogeneous catalysts used in this investigation. Ni-Graphene showed the largest surface area at 615.40 ± 13.60 m²/g and Ni-Zn showed the lowest surface area at 0.81 ± 0.20 m²/g.

Table 1. Surface area of the different types of catalysts.

Catalyst	S _{BET} (m ² /g)
5% V/Zeolite	374.53 ± 10.49
1.7% V/ZrO ₂ (Sulfate)	440.15 ± 1.27
1.7% V/ZrO ₂ (Neutral)	11.81 ± 1.33
Ni-Graphene	615.40 ± 13.60
Ni-Zn	0.81 ± 0.20
5% V/Ni-Graphene	281.96 ± 6.05
1.7% V/Zeolite	353.50 ± 3.64

3.1. Product Analysis and Quantification

The phenolic monomers collected from the depolymerization process of the alkali lignin in subcritical water with catalysts are identified by GC-MS. Figures S2–S4 show the resulting chromatograms. The cleavage of the C-O bond in the alkali lignin took place in the presence of subcritical water and catalysts. The main products were found to be monoaromatic oxygenates or phenolics. Twelve different phenolic monomers were identified from the alkali lignin, shown in Table S2. The heterogeneous catalysts studied enhanced the lignin depolymerization, reducing the reaction time and the formation of char, as shown in Table 2. The standard calibration curves of guaiacol, vanillin, isoeugenol, acetovanilone, guaiacylacetone, and homovanillic acid, provided in the supporting information catalysts, are linear over the calibration range ($R^2 > 0.9998$). Figure 3 shows the yield of total, combined phenolic monomers from the alkali lignin in the presence of subcritical water and the different heterogeneous catalysts at 240 °C for 10 min. The total yield of phenolic monomers is shown in Table 2. The table shows that the catalyzed reactions produce 25–70% more total monophenols than the reaction with no catalyst. The lowest results were obtained with the Ni-Zn and 1.7% V/ZrO₂ (Neutral) catalysts, which were identical to reactions performed under similar conditions without catalyst. The Ni-graphene catalyst produced the highest yield of phenolic compounds, 41.16 ± 0.27 mg/g, of the catalysts evaluated, perhaps due to the high surface area of the Ni-graphene. In terms of weight percent, 62% conversion to phenolic monomers is obtained in the presence of Ni-graphene catalyst and 38% of residue is left over from the reaction. No char formation is observed in the residue from the reaction because of the lower temperature used for the reaction [34]. The 5% V/Zeolite (33.28 ± 0.44 mg/g) and 1.7% V/ZrO₂ (sulfate) (34.46 ± 0.22 mg/g) catalysts showed similar conversions.

Table 2. Total yield of phenolic monomers in the presence of subcritical water and different types of catalyst.

No	Catalyst	Total Yield (mg/g of Lignin)
1	5% V/Zeolite	33.28 ± 0.44
2	1.7% V/ZrO ₂ (Sulfate)	34.46 ± 0.22
3	1.7% V/ZrO ₂ (Neutral)	24.97 ± 0.36
4	Ni-Graphene	41.16 ± 0.27
5	Ni-Zinc	24.57 ± 0.14
6	5% V/Ni-Graphene	31.21 ± 0.16
7	1.7% V/Zeolite	30.90 ± 0.40
8	No catalyst	24.06 ± 0.27

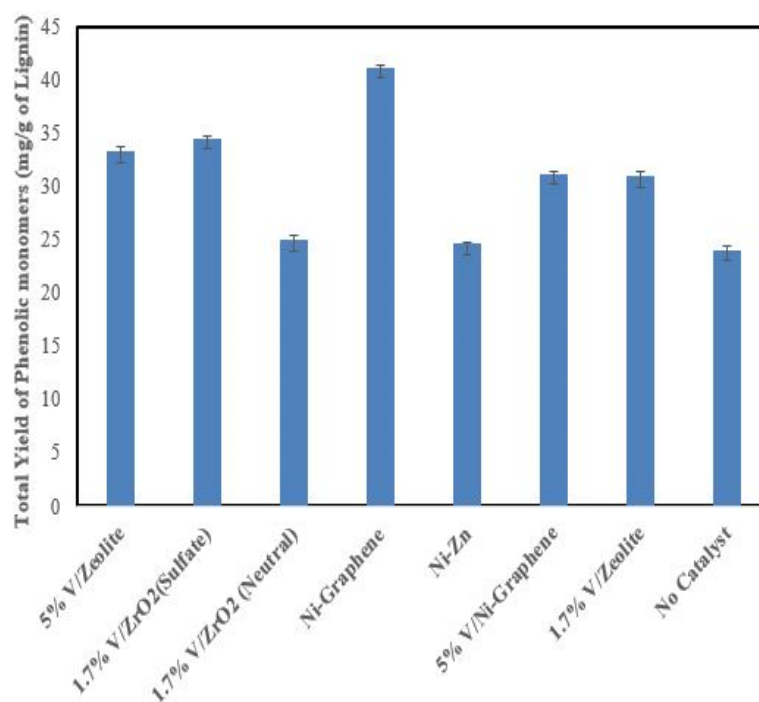
**Figure 3.** Total yield of phenolic monomers in the presence of subcritical water and different types of catalysts at 240 °C for 10 min reaction time.

Figure 4 shows the yield of individual monomers (guaiacol, vanillin, isoeugenol, acetovanilone, guaiacylacetone, and homovanillic acid) from these reactions. Homovanillic acid and vanillin were the phenolic monomers produced in the greatest amounts when no catalyst was used, or regardless of catalyst type. The relative amount of guaiacol and minor monomers (isoeugenol, acetovanilone, guaiacylacetone) produced was the most significant difference between catalysts, with Ni-graphene enhancing guaiacol formation, which was suppressed in 5% V/zeolite. In the presence of Ni-graphene, 14.96 ± 0.18 mg/g of homovanillic acid and 9.59 ± 0.34 mg/g of vanillin were obtained.

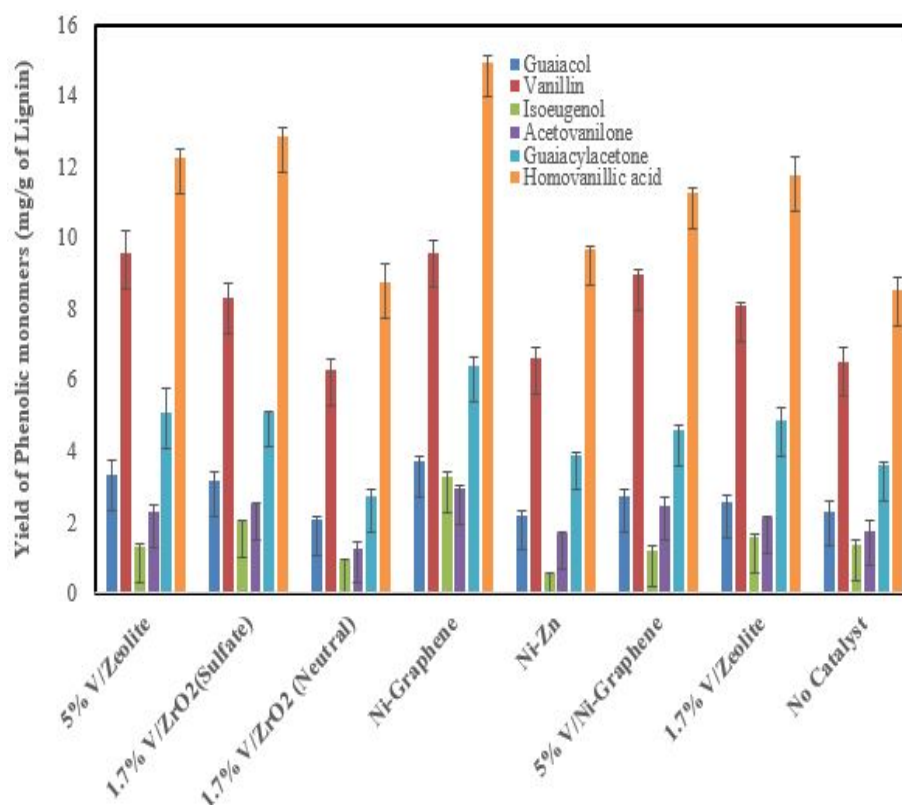


Figure 4. Yield of the major phenolic monomers from alkali lignin in presence of different type of catalysts at 240 °C for 10 min.

3.2. Effect of Reaction Time on Product Yield

Table 3 shows the effect of reaction time for the depolymerization of alkali lignin for the catalysts which provided the greatest yield of monomers. In the case of subcritical water with catalyst, among the reaction times examined, the 10-min treatment showed the highest yield, 41.16 ± 0.27 mg/g of phenolic monomers derived from alkali lignin in the presence of Ni-graphene catalyst, and decreased to 16.95 ± 0.11 mg/g at 15 min. Ten minutes consistently showed the highest conversion of lignin into phenolic monomers from the lignin, regardless of catalyst. Reasons for decreasing yield may be due to condensation polymerization between small radicals and secondary decomposition of products and converting into gases [35].

Table 3. Total Yield of phenolic monomers from the alkali lignin at 240 °C for 5, 10-, and 15-min reaction time.

Catalyst	Yield (mg/g of Lignin)		
	5 min	10 min	15 min
Ni-Graphene	11.89 ± 0.14	41.16 ± 0.27	16.95 ± 0.11
5% V/Zeolite	13.90 ± 0.07	33.28 ± 0.44	17.51 ± 0.12
1.7% V/ZrO ₂ (Sulfate)	13.36 ± 0.11	34.46 ± 0.22	26.96 ± 0.26

3.3. Effect of Temperature on Product Yield

Table 4 shows the effect of temperature for the depolymerization of alkali lignin for the top performing catalysts. The higher conversion of the lignin to phenolic monomers is found at 240 °C for each of these catalysts. The yield of monomers approximately doubled over this limited temperature range. The highest yield was found to be 41.16 ± 0.27 mg/g, 33.28 ± 0.44 mg/g, and 34.46 ± 0.22 mg/g in the presence of Ni-graphene, 5% V/Zeolite,

and 1.7% V/ZrO₂ at 240 °C for 10 min and pressures below 21.5 Mpa. Ni-Graphene showed twice the yield compared to when no catalyst was used at the same temperature and 5% V/Zeolite and 1.7% V/ZrO₂ was 1.5 times higher at that temperature. The yield of phenolic monomers was found to be 24.06 ± 0.27 mg/g of lignin when no catalyst was used (i.e., to establish baseline conditions). At the higher temperature, formation of residue decreased, and the monomer yield increased. Incomplete decomposition of lignin at lower temperature suppresses the yield of monomers. Table 5 shows the yield of each phenolic monomer in the presence of subcritical water and Ni-graphene catalyst. As a demonstration of reaction selectivity, with the Ni-graphene catalyst, three monomers (homovanillic acid, vanillin, and guaiacylacetone) accounted for just over 75% of the total conversion products.

Table 4. Total yield of phenolic monomers from the alkali lignin at 200 and 240 °C.

Catalyst	Yield (mg/g of Lignin)	
	200 °C	240 °C
Ni-Graphene	17.90 ± 0.19	41.16 ± 0.27
5% V/Zeolite	18.03 ± 0.13	33.28 ± 0.44
1.7% V/ZrO ₂ (Sulfate)	18.72 ± 0.11	34.46 ± 0.22

Table 5. Yield phenolic monomers in the presence of Ni-graphene catalyst at 240 °C with standard deviation of triplicate reactions.

Phenolic Monomer	Yield (mg Monomer/g Alkali Lignin)	Std. Dev.
Guaiacol	3.70	0.16
Vanillin	9.59	0.34
Isoeugenol	3.26	0.15
Acetovanillone	2.95	0.06
Guaiacylacetone	6.38	0.26
Homovanillic acid	14.96	0.18

4. Conclusions

In this study, depolymerization of alkali lignin was investigated using a subcritical water-based method and different catalysts to achieve high efficiency at relatively milder reaction conditions. The catalysts (Ni-Graphene, 5% V/Zeolite, and 1.7% V/ZrO₂ (Sulfate)) were shown to enhance reaction efficiency. The depolymerization of alkali lignin with subcritical and Ni-graphene catalyst suggests a potential method to produce the aromatic phenols. The reaction time (10 min) and temperature (240 °C) is lower than traditional methods [36]. Overall, this method is greener, eco-friendly, cheaper, and capable of being used on a large scale for the depolymerization of alkali lignin [37]. The catalysts were able to convert the lignin into low molecular weight monomers, such as vanillin, homovanillic acid, guaiacol, and syringaldehyde, in the presence of subcritical water. Further, our companion paper [34] shows that, in addition to promotion lignin depolymerization, this process suppresses recondensation of reaction products, as suggested in [13]. Among the catalysts studied, Ni-graphene showed the best performance in terms of phenolic monomer yield. Depolymerization of alkali lignin with the optimized subcritical water method and Ni-Graphene catalyst could be a highly potential method to obtain clean and value-added phenolic monomers.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/biomass2030011/s1>, Figure S1 shows the phase diagram of water representing sub- and supercritical region. GC-MS; Figures S2–S4 display the characterization of the depolymerization of alkali lignin in the presence of subcritical water and different types of heterogeneous catalysts. Figure S5 shows the calibration curves of phenolic monomers standards. A table for the properties of subcritical water and normal water, a table for the identified phenolic monomers, and a table for the total yield of phenolic monomers from the alkali lignin in the presence

of subcritical water and different types of catalysts are provided. Table S1. Properties of water and subcritical water; Table S2. Phenolic monomers and retention time.

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

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Data Availability Statement: Data found in Supplementary Information.

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

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