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Screening of Catalysts for the Subcritical Water Depolymerization of Lignin

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SCREENING OF CATALYSTS FOR THE SUBCRITICAL WATER DEPOLYMERIZATION OF LIGNIN

BY

BALAWANTHRAO JADHAV

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Doctor of Philosophy
Major in Chemistry
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2020

DISSERTATION ACCEPTANCE PAGE

Balawanthrao Jadhav

This dissertation is approved as a creditable and independent investigation by a candidate for the Doctor of Philosophy degree and is acceptable for meeting the dissertation requirements for this degree. Acceptance of this does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Douglas Raynie
Advisor Date

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TABLE OF CONTENT

ABBREVIATIONS

AL	Alkali Lignin
SCW	Subcritical Water
ASE	Accelerated Solvent Extraction
MIK	Methyl Isobutyl Ketone
TGA	Thermogravimetric Analysis
GC-MS	Gas Chromatography-Mass Spectrometry
FT-IR	Fourier Transformation Infrared Spectroscopy
([bmim][Cl])	1-butyl-3-methylimidazolium chloride
OPB	Oil Palm Biomass
$ScCO_2$	Supercritical Carbon dioxide
[MMIM]-[$MeSO_4$]	1,3-dimethylimidazolium methyl sulfate
DCM	Dichloromethane
BSA	Bovine Serum Albumin
LC-MS/MS	Liquid chromatography-tandem mass spectrometry
AA	Anhydrous Ammonia
CSS	Coriandrum Sativum Seeds
PS	Pistachio Shells
AADESs	Amino acid deep eutectic solvents
HDO	Hydrodeoxygenation
HTL	Hydrothermal Liquefaction
[BMIM]CF_3SO_3]	1-butyl-3-methylimidazolium trifluoromethanesulfonate

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ABSTRACT

SCREENING OF CATALYSTS FOR THE SUBCRITICAL WATER DEPOLYMERIZATION OF LIGNIN

BALAWANTHRAO JADHAV

2020

The current world population completely relies on non-renewable resources such as coal, fossils, and natural gas to get the energy, fuel, and value-added chemicals. The increasing demand for utilizing non-renewable resources leads to severe problems such as global warming, climate changes, and environmental pollution. The renewable resources such as wind, solar energy, and biomass are alternative source to overcome these problems and to save the environment. Lignocellulosic biomass is made up of cellulose, hemicellulose, and Lignin. Lignin is a copolymer of phenolic monomers and inexpensive naturally occurring complex material to produce value-added chemicals and various aromatics for industrial applications.

The first objective of this dissertation is, the catalytic depolymerization of alkali lignin (AL) into phenolic monomers were studied using green and eco-friendly solvent. In this study, subcritical water (SCW) was used as a green solvent with catalysts. The different types of heterogeneous catalysts were investigated for the depolymerization of alkali lignin in the presence of subcritical water. The goal of this study is to screen the best catalyst for the depolymerization of lignin in the presence of subcritical water. The depolymerization of alkali lignin was performed at 240°C for 10 minutes reaction time using subcritical water as a solvent and catalysts. The subcritical water and catalysts were used for the cleavage of the β-O-4 bond in the alkali lignin. The treatment of alkali lignin with Ni-Graphene catalyst in subcritical water resulted in the highest phenolic monomers yield of 40.84 ± 0.27 mg/ g of alkali lignin. This result shows that the Ni-Graphene catalyst with subcritical water is an efficient method for the depolymerization of lignin. The combination of the catalyst with subcritical water is beneficial for saving the reaction time and inhibition of repolymerization reaction. The most abundant phenolic monomers were guaiacol, vanillin, isoeugenol, acetovanillone, guaiacylacetone, and homovanillic acid identified using Gas Chromatography-Mass Spectrometry (GC-MS). This method is considered as the potential to produce a valuable chemical from the lignin under moderate conditions with 10 minutes reaction time.

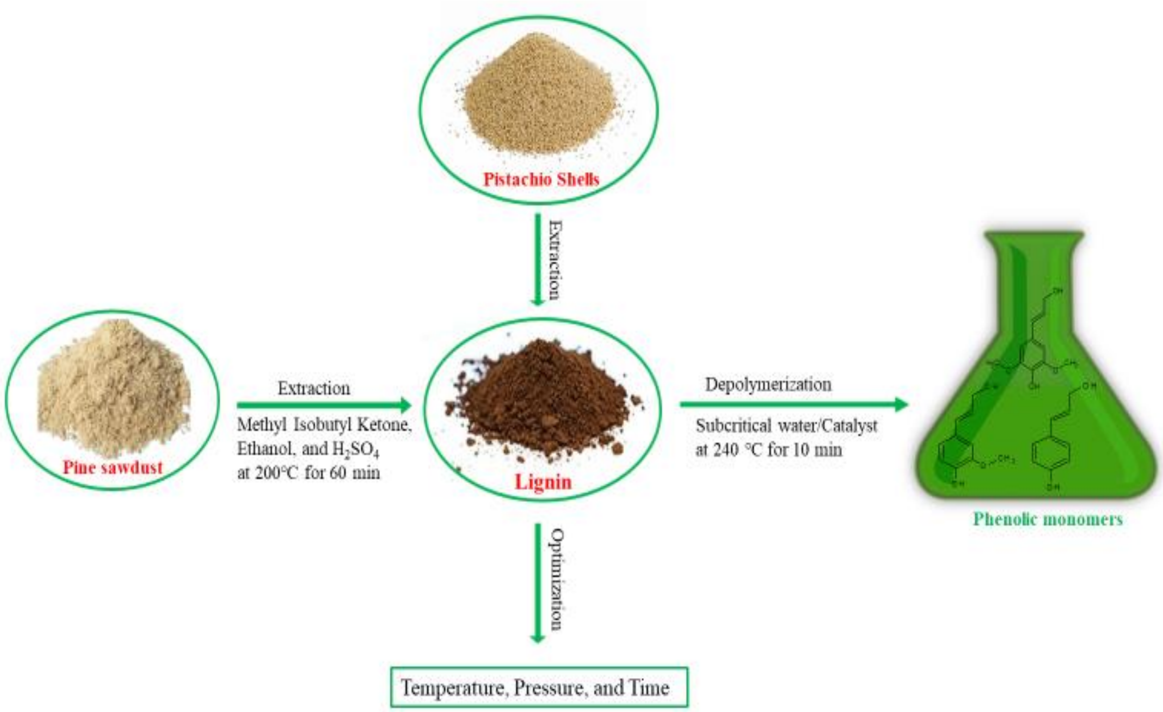
Secondly, optimized the reaction conditions for the depolymerization of alkali lignin in the presence of subcritical water. The depolymerization of lignin reaction was carried out at 200°C and 240°C for 5, 10, and 15 minutes reaction time. The highest conversion of phenolic monomers and selectivity of phenolic monomers was observed at 240°C for 10 minutes reaction time. The lowest yield was observed at 200°C and 5, 15 minutes reaction from the alkali lignin. The possible reason for the lowest yield was the repolymerization of lignin. The catalysts used for the optimization of conditions were Ni-Graphene, 5% V/Zeolite, and 1.7% V/ZrO_2 (Sulfate).

Finally, studied the extraction of lignin from the pine sawdust and pistachio shells biomass and performed the depolymerization reactions with extracted lignin using Ni-Graphene catalyst at 240°C for 10 minutes reaction time. The accelerated solvent extraction (ASE) and the mixture of methyl isobutyl ketone (MIK) and ethanol

(7:3) used as solvent A, and a mixture of water and 0.1 M H_2SO_4 used as a solvent B. The extraction of lignin was performed at 200℃ for 60 min with 1400-1530 psi pressure. The characterization of extracted lignin studied using TGA, FT-IR, and ^{1}H NMR. 12 different phenolic monomers were identified using GC-MS from the extracted lignin. The major identified phenolic monomers were Syringaldehyde, vanillin, coniferyl aldehyde, trimethoxy benzyl alcohol, and synapyl alcohol. The total conversion yield was found to be 45.2% from the pistachio shell extracted lignin. The total extraction of lignin was found to be 23.57±3.38% from the pistachio shells, and 22.86 ± 1.52% from the pine sawdust biomass.

The goal of this dissertation was, to develop the eco-friendly and viable technique for the depolymerization of lignin using green solvents and decreasing the harsh conditions such as temperature and pressure for breaking the bonds in the lignin. The conclusion of this dissertation was, Successfully, converted the lignin into phenolic monomers using minimal reaction conditions (temperature and pressure) in the presence of green solvent (subcritical water) and catalysts and also extracted the lignin from the waste biomaterials and applied the same optimized conditions and catalyst to get the phenolic monomers from the lignin in the presence of subcritical water. Finally, conclude that this approach is a green and environmentally friendly method for converting biomass into value-added chemicals.

Graphical Abstract:



CHAPTER ONE

INTRODUCTION AND BACKGROUND

1.1. Introduction

1.1.1. Biomass

The continuous growth of the world population every year significantly, and completely relies on nonrenewable resources such as coal, fossils, and natural gas for energy and food lead to the depletion of energy resources.[1-3] The utilization of nonrenewable resources increases global warming and environmental pollution.[4] To address these issues researchers are looking for alternative and renewable resources for replacing nonrenewable resources to produce energy, food, and chemicals for the future generations. Biomass is an excellent, promising, and alternative renewable source to overcome these issues, and for the production of energy and useful materials.[5] Biomass is a plant and animal-derived organic material.[6]

The main resources of biomass are:[7]

1. Forestry residues
2. Agricultural residues like wheat straw, rice straw, and corn stover
3. Wood from natural forests and woodlands
4. Sugarcane bagasse and rice husk from agricultural waste
5. Animal wastes
6. The black liquor from paper manufacturing industries
7. Sewage
8. Municipal solid wastes
9. Food processing wastes

Biomass is used to produce liquid fuels for transportation, to generate electricity by burning biomass, and converting the biomass into chemicals to make plastics and resins.[8] The advantages of using biomass is reduced global warming and replacement of fossil fuels.[9]

1.2. Lignocellulosic Biomass

1.2.1. Introduction

Lignocellulosic biomass is a plant-derived organic material and composed of three main components, cellulose, hemicellulose, and lignin.[10] Lignocellulosic biomass is a renewable and economical resource to produce biofuel, biomaterials, and value-added chemicals.[11] The lignocellulosic biomass consists of 40-45% cellulose, 25-35% hemicellulose, and 15-30% lignin.[12] Figure 1.1 shows the structure of lignocellulosic biomass in the plant cell wall.

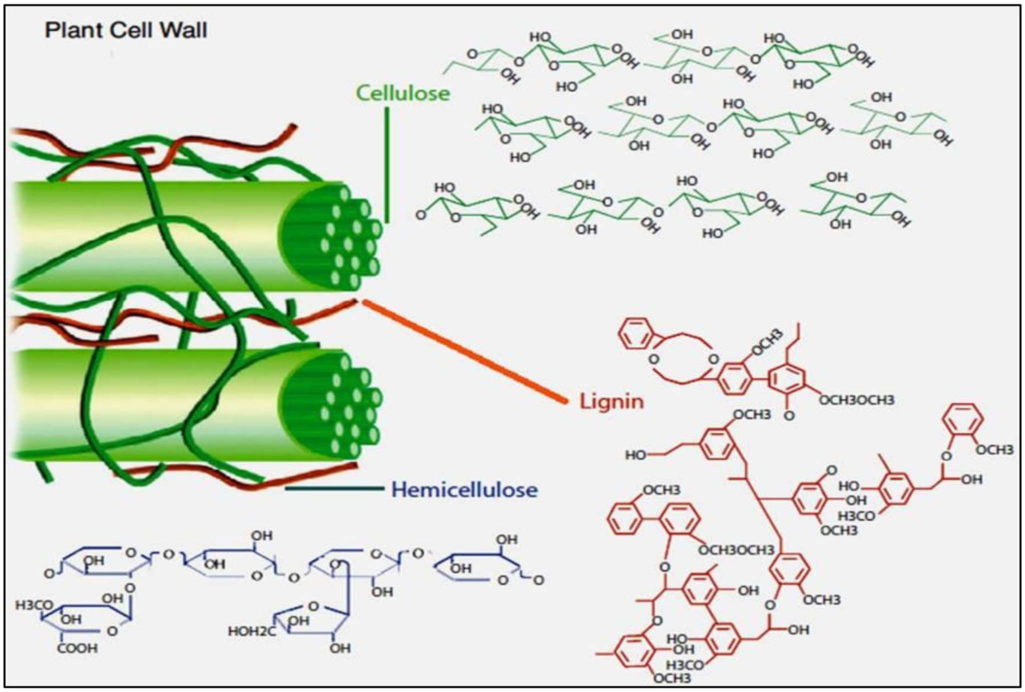


Figure 1.1. Structure of Lignocellulosic biomass and different types of components.[13]

1.3. Lignin

1.3.1. Introduction

Lignin is one of the major components in lignocellulosic biomass and the second most renewable source of producing bio-oil and value-added chemicals.[14, 15] Lignin is a source of aromatic Chemicals.[16] These value-added chemicals are platform chemicals for the pharmaceuticals, polymer, and pesticides industries.[17, 18] Lignin is derived from the plant material and consists of 15-30% of their weight and about 40% of the biomass energy content.[19] The main source of producing petroleum-based chemicals is fossils. The increasing demand for fuels and chemicals causes the decreasing fossil resources. The utilization of fossils for producing fuels increases environmental pollution as well as global warming.[4] It is very necessary to find the alternative and natural renewable source for the production of chemicals. Lignin is a promising biopolymer for replacing fossils to produce fossil-based chemicals and reducing the emission of CO_2.[20-22] The structure of lignin changes with the plant species.[23] Lignin is a complex and high molecular weight polymer.

1.3.2. Lignin Structure

Lignin is a highly complex organic biopolymer [24] and composed of phenylpropane units and bonded together by C-C and C-O bonds.[25] p-hydroxy-phenyl propanol, guaiacyl-propanol, and syringyl-propanol linked together by condensed linkages 5-5-biphenyl, β-β-resinol, β-5, and β-1-(1,2-diarylpropane) linkages, and ether linkages α-O-4, 5-O-4-diaryl ether, and more than 60% β-O-4-aryl ether.[26] Lignin is composed of the three major monolignols that are coniferyl alcohol (G), paracoumaryl alcohol (H-units), and sinapyl alcohol (S-units).[27] Figure 1.2 shows the complex structure of lignin and different types of chemical bonds and linkages.[28] Table 1.1 shows the percentage of chemical bonds and linkages in lignin in different biomass sources. The β-O-4 bond percentage is more than 50% present in all kinds of biomasses.

Table 1.1. Percentage of chemical bonds and linkages in lignin in different biomass.[29]

Bond	Linkages	Softwood lignin (%)	Hardwood lignin (%)	Gross lignin (%)
β-O-4	Ether	43-50	50-65	74-84
α-O-4	Ether	5-7	<1	ND
4-O-5	Ether	4	6-7	ND
5-5	C-C	5-7	<1	ND
β-5	C-C	9-12	3-11	5-1
β-1	C-C	1-9	1-7	ND
β-β	C-C	2-6	3-12	1-7

ND: Not Detected

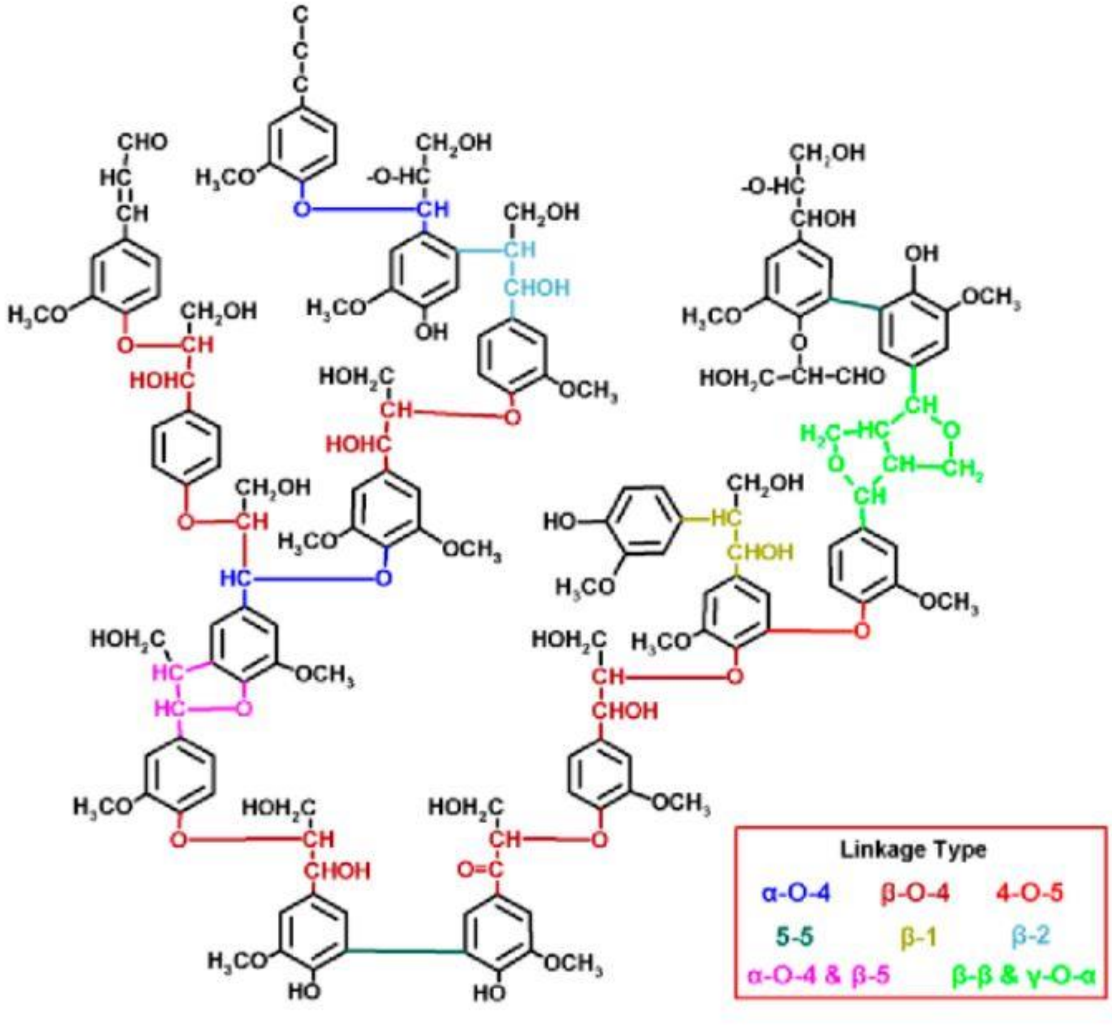


Figure 1.2. The Complex structure of lignin.[28]

1.3.3. Lignin Sources

Lignin is mainly produced in the pulp and paper industries. The annual production of lignin from the pulp and paper industry is around 50 million tons worldwide.[30] Table 1.2 shows the average organic constituents present in different biomass feedstock.[4] The main source of lignin is corn stover, wheat straw, rice straw, prairie cordgrass, switchgrass, pine sawdust, birch wood, and Pistachio shells. Utilization of these materials could help to reduce waste production, greenhouse gas emission and increase the revenue for the industries by converting them into valuable products.[31]

Table 1.2. Cellulose, Hemicellulose, and Lignin percent in the different feedstock.[31]

Feedstock	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Softwood	40-44	20-32	25-35
Hardwood	40-44	15-35	18-35
Switchgrass	37	29	19
Wheat straw	38	29	15
Corn stover	38	26	19
Miscanthus	43	24	19
Eucalyptus	49	21	18
Agave	78	6	13
Bagasse	49	31	19

1.4. Lignin monomers applications

Lignin is used as an alternative source to produce transportation biofuels, green chemicals, and used as a combustion fuel in pulp and paper mills. The lignin phenolic monomers such as coniferyl alcohol, coumaryl alcohol, and synapyl alcohol were used in the synthesis of resins[32, 33], aromatic polymers, additives in cement, the component in binders. Lignin is an attractive raw material to produce benzene, toluene, xylene, and phenol. The green chemicals produced from the lignin used as food additives, bio preservatives, pharmaceutical products, industrial products for phenolic resins, plastics, and jet fuel.

1.5. Lignin Extraction

Lignocellulosic biomass is the most abundant, low-cost, and renewable resource to produce valuable chemicals and biomaterial.[34] Lignocellulosic biomass constituents are cellulose, hemicellulose, and lignin.[35] 10-25% of lignin present in lignocellulosic biomass and second most abundant natural polymer.[14] The main sources of lignin are plant materials, agricultural wastes, and byproducts of pulp and paper industries. The main methods for the extraction of lignin were hydrothermal, acidic, alkaline, hydrogen peroxide, wet oxidation, ammonia fiber explosion, supercritical carbon dioxide, organosolv, ionic liquid pre-treatment methods, Soda-ethanol, ultrasound-assisted extraction, and microwave-assisted extraction.

The Ultrasound-Assisted extraction method was simple and more effective.[36] This method was improved economic efficiency and reduce environmental pollution.[37] The extraction of lignin from the rice straw was studied using Ultrasonic irradiation.[34] The reactive free radicals were produced after induces with ultrasonic irradiation at high temperature and pressure. The ultrasound irradiation increases the penetration of solvent and heat into the biomass and it improves the mass transfer.

The prairie cordgrass, switchgrass, and corn stover biomass were used for the extraction of lignin using the organosolv treatment method.[38] The main principle is that extraction is based on the solubility of the lignin in the organic solvent. Organosolv pretreatment cleaves the α-aryl ether bonds and β-aryl ether bonds.[39] The extracted lignin with this method was highly pure because low in carbohydrates, free of sulfur, and low in ash.[40] The main applications of organosolv lignin are the production of resins, limiting uses of toxic formaldehyde.[41] The solvents used for the extraction of lignin from the prairie cordgrass, switchgrass, and corn stover are ethyl acetate, water, and ethanol .[38] Sulfuric acid was added as a catalyst.

The extraction of lignin from the biomass was studied using high concentrations of acids and organic solvents.[42] The uses of these solvents are harmful to the environment and the cost of recycling is very high.[42] The scientists developed environmentally friendly solvents such as ionic liquids (IL) for the extraction of lignin from the biomass.[43] Because the ionic liquid has capable of dissolving biomass.[43] The extraction of lignin from oil palm biomass was studied using 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) ionic liquid. The dried oil palm biomass (OPB) was added to [bmim] [Cl] ionic liquid and heated at 110°C under an N_2 atmosphere for 8 h with high agitation.[44]

The supercritical CO_2 is used for the extraction of lignin from the corn stalks. Supercritical conditions are 31°C temperature and 1070 psi.[45] The environmentally friendly supercritical fluid used for the extraction of lignin from the biomass is carbon dioxide. The co-solvents such as ethanol or methanol added to the supercritical CO_2 to increase the solvating power of the liquid and diffusivity of the gas. Supercritical carbon dioxide has both properties liquid as well as gas and it is an extremely good solvent for a wide variety of chemicals, biological, and polymer extraction procedures. The main advantages of using this solvent including, easy to recover solvent, lower pressure drops, low cost, and exploited to control chemical reactivity.[45]

Lignin extracted in different pretreatment methods in the process of bio-ethanol production.[46] The pretreatment methods include sulphuric acid pretreatment, sodium hydroxide pretreatment, and steam explosion, etc. These extraction methods were operated at elevated temperature for several hours. These methods are not desirable because of high energy consumption, long reaction time, and unwanted reactions of lignin.[47] The microwave-assisted extraction is a technology used for the separation of compounds from the lignocellulosic biomass.[46] In this process it needs microwave energy and solvent. The main advantages of this method are the reduction of energy, uniform, and selective processing. The bamboo stem cut into small pieces and ground to 40-60 mesh particle size after an air dry. The conditions were used for the extraction of lignin from the bamboo was the temperature 90 and 109°C, time (0-120 min), and 700 W power applied to heat the material. The maximum extraction was found at 109°C for 60 min.[46] Other pretreatment of lignocellulosic biomass to extract the lignin is using Amino acid deep eutectic solvents (AADESs). Lignin is extracted using betaine: lysine and betaine: arginine DESs. These AADESs showed the highest solubility of lignin for the extraction. AADESs pretreatment is a green and sustainable process because AADESs are safer, nonvolatile, nonflammable, and nontoxic.[48]

The extraction of lignin from biomass using water or steam with high-pressure oxygen or air is called wet oxidation.[49] The oxygen, water, and elevated temperature were used for the extraction of lignin from the wheat straw.[50] The wet oxidation process was carried out in a specially designed loop-autoclave constructed at Riso National Laboratory.[51] Na_2CO_3 and water were used for the extraction of lignin from the wheat straw.

The anhydrous ammonia (AA) and NaOH were used for the extraction of lignin from the corn stover. The main benefit of using ammonia over other techniques is cost-effective. This method is economically more attractive than other techniques.[52] The liquid ammonia used for the swelling the biomass for altering the morphology.[52-54] This extraction involved two steps. In the first step biomass subjected to anhydrous ammonia and residue was treated with sodium hydroxide in the second step.[55] The main advantage of utilizing these two steps process is (1) increasing the recyclability of ammonia (2) performing solid-liquid separation under ambient conditions.[55] The AA treated corn stover showed the lignin removal was 70%, Cellulose 9%, and hemicellulose 35%.

Rye is one of the cereal crops and the straw was used for the extraction of lignin using alkaline hydrogen peroxide.[56] The main reason for using hydrogen peroxide is that reducing the production of chlorinated organic from the pulping and bleaching process.[57] Hydrogen peroxide with alkaline solution increased the extraction of lignin from lignocellulosic biomass.[58]

In this work, extracted the lignin from the pine sawdust and pistachio shells using methyl isobutyl ketone and ethanol organic solvents.

1.6. Depolymerization of Lignin

Lignin is a complex biopolymer and source of phenolic monomers.[59] Lignin conversion into phenolic monomers was reported using different techniques. The depolymerization of lignin was studied using acid catalyst, base catalyst, ionic liquid assisted depolymerization, pyrolysis, sub, and supercritical fluids, and metallic catalyzed depolymerization.

The depolymerization of lignin was reported using supercritical carbon dioxide, acetone, and water fluid.[60] The temperature of supercritical CO_2 ($ScCO_2$) was >31°C and pressure was >7.4 MPa.[61] The main advantage of this technique is that operating temperature is low comparative pyrolysis and gasification, and preventing the cross-linking reactions, and used non-toxic CO_2.[60] The acetone/water 8:2 v/v at 0.35 g/ml used for the dissolving lignin. The wheat straw lignin is used for producing phenolic monomers. The formic acid was added to the mixture because stabilizing alcohols and reduces the char formation. The temperature was 300°C and the pressure was 100 bar. The total processing time was 3.5 h.

The depolymerization of corn stover lignin was studied using base catalysts.[62] The two different types of NaOH concentration (2 and 4%) were used for the reaction.[62] The reaction temperatures were 270, 300, and 330°C used for 40 min.

The depolymerization of alkali lignin was reported using sub-and supercritical water.[24] The subcritical water means, water exist in a liquid state above its boiling point 100°C and below its critical temperature 647 K and pressure < 21.1 Mpa.[63] The temperatures were 553, 643, 653, and 663 K used for the reaction for 30, 60, 90, 120, and 240 min.[24] The reaction mixture was collected by washing the reactor vessel with methanol. The water-methanol soluble products were separated from the mixture by vacuum filtration. The qualitative analysis of water and methanol soluble products done by using GC-MS.[24]

The depolymerization of lignin was reported using an acid catalyst.[64] The 0.5 g of lignin dissolved in water and methanol (5:25 ml) solvent and 0.5g of SiO_2/Al_2O_3 solid catalyst loaded into the high temperature and pressure Parr autoclave reactor. The N_2 gas flushed into the reactor with 0.7 Mpa pressure.

The depolymerization of beech lignin was reported using the metal catalyst and ionic liquid.[65] The larger amount of lignin dissolved in ionic liquids comparative other solvents. The lignin dissolved in ionic liquids such as 1,3-dimethylimidazolium methyl sulfate [MMIM]-[$MeSO_4$] and 1-butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM]CF_3SO_3] and loaded into the 300 ml stainless steel autoclave reactor with Mn $(NO_3)_2$ catalyst.[65] The depolymerization of lignin was conducted at 100°C and 8 Mpa pressure for 24 h. The depolymerization products were extracted using dichloro methane (DCM) and identified using GC-MS.[65]

The depolymerization of lignin was reported using pyrolysis.[66] 1 mg of lignin sample was placed in a 20 mm quartz tube between quartz wool plugs. The sample placed in the Pyroprobe and pyrolyzed at a set point temperature. The temperature range was between 400 and 800°C. The ramp was 20°C/ms with a dwell time of 15 s in every case.[66] The phenolic compounds were identified using PyGC-MS. The maximum yield was found at 600°C.[66]

In this work, the depolymerization of lignin studied using subcritical water and catalysts.

1.7. Subcritical water

1.7.1. Introduction

Subcritical water means water exists in liquid at a higher temperature than its natural boiling point of 100℃ and below its critical temperature of 374℃ by applying pressure.[63] Figure 1.3 shows the sub and super-critical conditions of the water. Sub and supercritical water reactions involve applying temperature under pressure to achieve the reaction in the aqueous medium. Water at subcritical conditions acts as an acid and base catalyst.[67] The properties of water will change when it is in subcritical conditions. The density and dielectric constant will decrease by varying the temperature and pressure.[68] The decreasing the dielectric constant will increase the solubility of the small organic compounds.[69-74] The polarity of the subcritical water will increase the ability to dissolve the solids, liquids, and gases. Table 1.2 shows the properties of ordinary water and subcritical water.[74, 75] The ionic product of subcritical water is higher than normal water to increase the acid-base catalyzed reactions in biomass hydrolysis.[76]

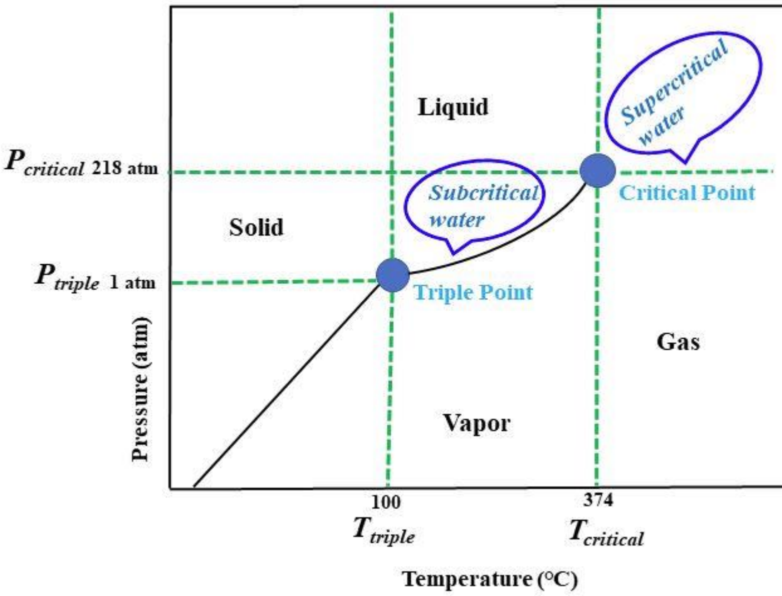


Figure 1.3. Phase diagram of water representing the sub-and supercritical region

Table 1.3. Properties of water and subcritical water.[74, 75]

Properties	Normal water	Subcritical water
Temperature (K)	298	523
Pressure (bar)	1	50
Density (g/m^3)	1	0.80
Dielectric constant	78.5	27.1
$p^{K}{}_{w}$	14.0	11.2
Heat capacity (Kj/Kg K)	4.2	4.86
Dynamic viscosity (mPa s)	0.89	0.11
Heat conductivity (mW/m K)	608	620

1.7.2. Applications of Subcritical water

Subcritical water is an alternative and greener solvent for the extraction of chemicals from various sources. Subcritical water is an emerging tool for the processing of bioorganic wastes including biomass conversion, hydrolysis of lignocellulose, carbohydrates, lipids, proteins, and extraction of bioactive compounds.[77-79] Subcritical water used to production of cellulose nanocrystals, and extraction of antioxidants, phenolic compound, and oils.

Hydrolysis of protein with subcritical water is an alternative method for enzymatic digestion.[80] This method was a potential and alternative to the traditional method for the hydrolysis of protein instead of using expensive acids or enzymes. The reaction was carried out in the temperature range of 200-300°C using subcritical water.[80] The glycine, alanine, serine, isoleucine, lysine, arginine, valine, proline, threonine, and histidine amino acids were identified after the hydrolysis of BSA in the presence of Subcritical condition.[80] The acetic acid, formic acid, pyruvic acid, maleic, malic, and fumaric acids were identified after the hydrolysis of BSA in the presence of subcritical water.[80]

The production of peptides from hemoglobin, bovine serum albumin (BSA), and β-casein were studied and compared the results with enzymatic digestion of proteins by trypsin.[81] BSA contains 17 disulfides bond, and β-casein contains five sites of phosphorylation. The liquid chromatography-tandem mass spectrometry (LC-MS/MS) was used for the analysis of the SCW hydrolysis products. The reaction tube was placed at 50°C for 10 minutes for equilibrium. The thermocouple is used to monitor the reaction temperature. The reactions were studied from 0 to 20 minutes using subcritical water. MS/MS (CID or ETD) scan used for the analysis. The Xcalibur software used the determine protein sequence.[81] The trypsin digestion of hemoglobin gave high sequence coverage for both the α-globin (88.9± 3.6%) and β-globin (92.7±4.0%). The hydrolysis of hemoglobin with subcritical water gave sequence coverage for both α-globin (91.5± 5.6%) and β-globin

(87.9±3.3%) at 160°C for 0 min. The sequence coverage increased with the increasing reaction time to 20 min. The sequence coverage was 97.4±3.9% for α-globin and 96.2±0.8% for β-globin. The peptide sequence coverage is higher with subcritical than the enzymatic digestion.[81]

Subcritical water is used to produce cellulose nanocrystals from the cellulose.[82] The traditional methods to produce cellulose nanocrystals were uses of concentrated solutions of strong acids.[83, 84] This method takes a long duration of washing steps and the nanocrystals are low resistance temperature because of acidic moieties. The ammonium persulfate[85, 86], and metaperiodate[87] is alternative technique to produce cellulose nanocrystals. These reagents were expensive, reactive, corrosive, and toxic. The subcritical water is an alternative greener solvent and environmentally friendly solvent to produce cellulose nanocrystals from the cellulose. The resulted cellulose nanocrystals from cellulose with the hydrolysis of subcritical water showed a high crystallinity index, rod-like shape, and higher thermal stability.[82] Cellulose is one of the main renewable components in the lignocellulosic biomass. The thermal stability of nanocrystals produced with subcritical water is higher than the nanocrystals produced with acid hydrolysis. The acid-treated nanocrystals degrade around 200°C and subcritical water treated nanocrystals degrade around 300°C. So, the production of cellulose nanocrystals from cellulose with subcritical water is more environmentally friendly, chemicals consumption reduction, and lower generation of chemical wastes comparative the acid treatment of cellulose.[82]

The depletion of fossil carbon reserves and increase the global warming led to the introduction of renewable biomass to produce fine chemicals, transportation fuels, and platform chemicals. Cellulose is the most abundant natural polymer.[88] Hydrolysis of cellulose studied using subcritical water.[88] They converted cellulose into glucose, fructose, and oligomers. The traditional methods were studied using acid catalyst, [89, 90] and enzyme catalyst hydrolysis.[91] The uses of subcritical water are environmentally friendly and green solvent for the hydrolysis of cellulose. The identified products were erythrose, dihydroxyacetone, fructose, glucose, glyceraldehyde, pyruvaldehyde, cellobiose, cellotriose, cellotetraose, cellopentaose, and cellohexaose. The hydrolysis of cellulose with subcritical water has reduced the uses of chemicals for the degradation of cellulose.[88]

The Coriandrum sativum seeds (CSS) and subcritical water are used for the extraction of antioxidants.[92] The coriander seeds contain linalool, limonene, camphor, and geraniol.[93] These compounds showed high stability than other oils.[94] The traditional methods for the extraction of antioxidants from the Coriandrum was using organic solvents and hydrodistillation.[95] The disadvantages of these methods were the use of organic solvents, more extraction time, and thermal degradation.[92] To overcome these issues scientists recently developed extraction techniques using subcritical water. This technique is more environmentally friendly.[96] The advantages of this technique over the conventional extraction techniques were shorter extraction time, higher quality of the extract, lower costs of the extracting agent, and environmentally compatibility. The extraction of antioxidants from CSS with subcritical water showed a significant improvement than conventional solid-liquid extraction, ultrasound-assisted, and microwave-assisted extraction. A linear correlation was observed between antioxidant (IC_{50} value) and total phenolic content (R^2 = 0.965), and total flavonoid content (R^2 =

0.709), which indicates that these groups of compounds are responsible for the antioxidant activity of Coriander sativum seeds.[92]

The extraction of pharmaceutical extracts such as volatile oil, tannins, flavonoids, anthraquinone, and lactone with subcritical water was studied.[97] The subcritical water extraction technique is widely used in the field of medicinal industries to bring huge economic benefits, environmental, and social benefits.[98] The 30 to 40 percent of medicines were used from the plant materials worldwide.[97] The plant medicines have incomparable advantages over relative chemical drugs. So, the extraction of medicines from plants is more important. The traditional techniques are using ultrasonic extraction, microwave extraction, membrane separation technologies, molecular distillation, and subcritical fluid extraction.[98] Among these techniques subcritical fluid extraction is the most prominent technique because this method is more feasible for heat-sensitive materials, no solvent residue, high extraction rate, and free of environmental pollution.[98] Another advantage of subcritical water is that the high temperature and pressure produce a high diffusion rate which promotes a very efficient extraction rate of the raw materials.[99, 100] The traditional methods for the extraction of essential oil from the plants were using steam distillation and organic solvent extraction, indicating more shortcomings, such as volatile compounds loss, low extraction efficiency, and need more heating.[97] The subcritical fluid technique developed for the extraction of volatile oil from the plant materials to overcome the disadvantage of traditional methods.[99] The organic compounds were more soluble under subcritical conditions. The Rosmarinus and subcritical water used to extract oxygenated fragrance flavor compounds.[99]

Steam distillation was performed for the extraction of volatile oil from the Rosemary leaves.[99] The total yield found to be using subcritical water was 0.494 mg/1 g of the sample at 150°C for 60 min. The total yield found to be using steam distillation was 0.249 mg/g of the sample at 150°C for 60 min.[99] The extraction of the volatile compounds from rosemary leaves with subcritical water showed a higher yield than steam distillation. The subcritical water is an effective way of extracting volatile oil from the plant materials comparative steam distillation and carbon dioxide extraction because of environmental advantages and low cost of water and energy.[99]

The extraction of anthraquinone from the roots of Morinda citrifolia was studied using subcritical water.[101] The anthraquinone has several therapeutic activities. They include antibacterial, antiviral, anticancer, and analgesic effects.[102] The conventional extraction method was using ethanol.[101] In this method final product contains ethanol, which is unacceptable for use on a human. The alternative solvent for the extraction of anthraquinone is subcritical water.[101] In subcritical condition water dielectric constant and polarity will decrease and increase the solvent power for organic compound dissolution. The total yield was found at 110°C was 20.8 mg/g dry root, at 170°C was 40.1 mg/g of the dry root, and at 220°C was 43.6 mg/g of dry root. The yield was increased with the increasing temperature because anthraquinone solubility increased with the increasing temperature of the water.[101]

The extraction of lactones from kava root was studied using subcritical water and compared with the Soxhlet extraction.[103] Kava roots were used as a beverage in Pacific island as a coffee or tea.[104] Kava roots were used as a phytomedicine. A number of studies have been carried out on the isolation and identification of kavalactones.[105-108] The different methods were proposed for the extraction of kavalactones using chloroform [109], methylene chloride [110], methanol [111], ethanol [112], and ethyl acetate [113] as a solvent.

The Soxhlet extraction was used for extracting kavalactones from kava roots. 0.5 g of ground kava was used for the extraction of kavalactones. Kavalactones were extracted for 6 h using 150 ml of water. The water extract was acidified with 2 M HCl and extracted using CH_2Cl_2. The residue in the Soxhlet extraction was sonicated for 18 h in 15 ml of acetone.[103]

The total yield of kavalactones with subcritical water was 104± 10 mg/g at 175°C for 20 minutes. The total yield of kavalactones in Soxhlet extraction was 48± 6 mg/g for 360 min.[103] The Soxhlet extraction was showed a nearly 50% lower recovery than the subcritical water extraction. The subcritical water extraction time was lesser than the Soxhlet extraction.[103]

The grape seeds and subcritical water used to extract the catechins and proanthocyanins and compared with the results of conventional extraction with methanol/water.[114] The grape seeds contain approximately 60% polyphenols and these extracts have antioxidant activity in vivo.[115] The total yield was found to be 292.7 mg/100 g of grape seeds powder with methanol/water extraction. The total yield was found to be 380.6mg/100 g of grape seeds powder with subcritical water extraction at 150°C. The subcritical water extraction method showed a higher yield than the methanol/water extraction. The subcritical water extraction is a selective and environmentally friendly technique for the extraction of different antioxidant activity compounds.[114]

Another active ingredient in the plant is phenolic compounds. These phenolic compounds are inhibiting tumor development in animals and humans, prevent cardiovascular disease, as well as anti-mutation, anti-virus, and anti-oxidation.[116] The extraction of phenolic compounds from the potato peels was studied.[117] The potato peels were considered as a waste generated from potato and it is a good source of phenolic compounds and fourth crop grown in the world.[118] Phenolic compounds from potato peels were preventing the oxidation of lipids.[119] Gallic acid (GAC) and Chlorogenic acid (CGA) are the major compounds in potato peels.[119] The conventional technique for the extraction of phenolic compounds from potato peel is solid-liquid extraction using organic solvents was reported.[120] The main drawbacks were long retention time and low yield of extraction. Subcritical water extraction is an alternative method for the extraction of phenolics from the potato peels is known as pressurized polarity water extraction. The intermolecular hydrogen bonds of water break down, and the dielectric constant decrease in subcritical conditions. The normal water dielectric constant was 79 and it is reduced to 27 in subcritical condition and which is equal to the ethanol dielectric constant.[121] The yield of phenolics with methanol was found to be 46.36 mg/100g and with ethanol was found to be 29.52 mg/100 g. The subcritical water extraction was carried out in a batch reactor. The total yield was found to be 81.83 mg/g with subcritical water at 180°C. The optimized time was 60 min. The conclusion of this study was subcritical water extraction showed higher recovery than the methanol extraction.[117]

The extraction of oil and water-soluble compounds such as proteins and carbohydrates from the sunflower seeds were studied using subcritical water.[122] The extraction of oils from oilseeds using an aqueous solvent is an alternative and greener process.[123] The extraction of oils with aqueous solvent from peanuts [124], coconuts [124], soybeans [125], and rapeseeds [126] were reported. They reported extraction yield was 93% and extraction carried out lower than 100°C but the main drawbacks were long agitation time, the formation of stable emulsions, and difficulty of separating phases as well as changing p^H of media. The main solution for the overcome above difficulties is that increasing temperature. The extraction rate will increase with increasing the temperature.[127] Subcritical water is a prominent solvent for the extraction of oil from the sunflower seeds.[127] Subcritical water means, water heated under pressure from its boiling temperature to its critical temperature. In subcritical conditions water polarity, viscosity, and surface tension will decrease and increase the diffusion rate.[128] The Soxhlet extraction was used for the oil extraction from sunflower seeds. The total oil yield with subcritical water was 44.3±0.3% after 30 min at 130°C. The total yield in the Soxhlet extraction was 46.2± 0.7% after 4 h. The extraction time was lesser with subcritical water than Soxhlet extraction.[122]

Biomass is one of the most abundant renewable sources and an important sustainable energy system. The conversion of biomass into liquid energy is the most popular and it will replace the decline of fossil fuels and reducing global warming. The conventional methods are direct pyrolysis, gasification, and liquefaction.[129-131] The hydrothermal liquefaction is carried out between 280-370°C.[132] The plant biomass consists of cellulose, hemicellulose, and lignin.[133] The production of bio-oil from biomass with subcritical was studied.[133] Woody biomass, grass, agricultural wastes, and micro-and macroalgae, etc. considered as biomass. The production of bio-oil from Oil palm biomass was studied using subcritical water.[133] These Oil palm wastes are utilizing to produce bio-oil using subcritical water. The yield of bio-oil increased when temperature increased from

360 to 390°C. However, increasing the temperature to 450°C decreased the yield of bio-oil. The higher temperature causes secondary decomposition of biomass and recombination of some free radicals, leading to form gas and char formation.[133]

The production of bio-oil from the biomass studied using subcritical water.[134] The production of food waste from processing animals, fruits, vegetables, dairy, and grain was nearly 36 million tons of food waste per year in the USA.[135] The decomposition of food waste generates the greenhouse gases such as methane and carbon dioxide. Food waste material is also an excellent renewable and sustainable source to produce liquid transportation fuels.[136, 137] A large number of food wastes such as peels, shells, seeds, and bagasse are used to produce sugars, fibers, fatty acids, and phenolic compounds.[138] Hydrothermal liquefaction (HTL) is applied to convert biomass into useful chemicals. HTL is used for converting lignocellulosic biomass into smaller molecules. The maximum oil yield was found to be 50 ± 3.18 wt% from starch biomass at 250°C for 60 min. The lowest yield was found to be 31± 3.4 wt% from starch at 250°C for 20 min. The yield of oil was increased with increasing time. The production of oil change takes place because of changing the polarity of feedstock.[139] The highly thermal stability fatty acids can be degraded under subcritical conditions to produce long-chain hydrocarbons, which have good fuel properties.[140] The subcritical water is used for the conversion of bio-oil from biomass

The production of bio-oil from microalgae with subcritical water was studied.[141] The production of bio-oil from fossils leading to an increase in the greenhouse and declining the fossils. Biomass is an alternative renewable source to produce bio-oil. Biomass is a promising, most abundant, and cheap feedstock to produce bio-oil.[142]

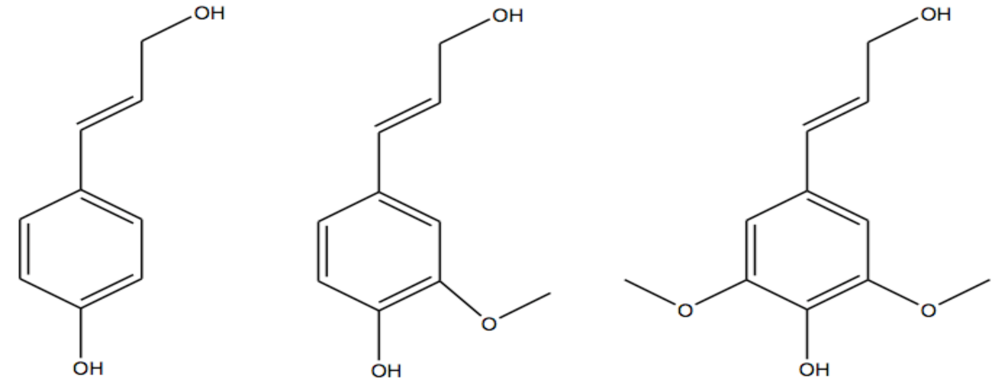
Microalgae biofuels are having a much lower impact on the environment and it has high caloric value, low viscosity, and low density.[143] These properties make microalgae more suitable for biofuel than lignocelluloses materials.[143] The conventional methods for the conversion of biomass to bio-oil were either biochemical or thermochemical methods.[144] These techniques need high temperature and pressure. The hydrothermal process is a promising method for converting bio-oil from biomass. Biomass is heated in water at mild temperature and pressure. In hydrothermal liquefaction (HTL) biomass converted into bio-oil using water at the subcritical conditions. The main advantage of this process is that no need for the drying process for biomass. The production of bio-oil with subcritical water has zero SO_X emission.[145] Water has several advantages over chemicals such as an ecologically safe, non-toxic, cheap, readily available, and environmentally benign solvent.[141] The bio-oil yield was showed higher at 300°C. The bio-oil production was decreased after 300°C because decomposition of bio-oil occurred.[146, 147] The conversion of algal biomass to bio-oil increases during the first phase of liquefaction until approximately 300°C. The bio-oil yield was decreased after 300°C because of breaking the secondary bonds in bio-oil.[148] The bio-oil yield also depends on the ratio of biomass and water. Solvents play an important role in the solvation and breaking the chemical bonds. The excess amount of water concentrations easily splits algal macromolecules into small gas molecules and decreases the bio-oil yield. The different categories of chemical compositions such as phenolics, nitrogenated compounds, oxygenates, hydrocarbons, and organic acids were observed in GC-MS analysis.[141] The subcritical water is the green and environmentally friendly solvent to produce bio-oil from the algae biomass.

CHAPTER TWO

CATALYST SCREENING FOR THE DEPOLYMERIZATON OF ALKALI LIGNIN INTO PHENOLIC MONOMERS IN THE PRESENCE OF SUBCRITICAL WATER

2.1. 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 petro-based chemicals, fuels, and energies. The depletion of fossil resources and increasing global warming brought special attention to using sustainable, alternative, and renewable resources like lignocellulosic biomass. Lignocellulosic biomass is mainly consisting of cellulose, hemicellulose, and lignin [149-152]. Lignin is an organic complex biopolymer and the second most abundant biomass on earth [41] and 10-20% of lignin present in the lignocellulosic biomass [153]. The lignin is an amorphous copolymer of p-coumaryl (H), coniferyl (G), and sinapyl (S) alcohols. Figure 2.1 shows the phenolic monomers of the lignin. These alcoholic units are bonded together by C-C and C-O-C bonds [154]. These phenolic monomers mainly linked together by 5-5, β-β, β-5, and β-1 condensed linkages and α-O-4, 5-O-4, and β-O-4 ether linkages [155]. The main sources of lignin are wood, plants, wheat straw, corn stover, and pine straw [156].



p-coumaryl alcohol *coniferyl alcohol* *sinapyl alcohol*

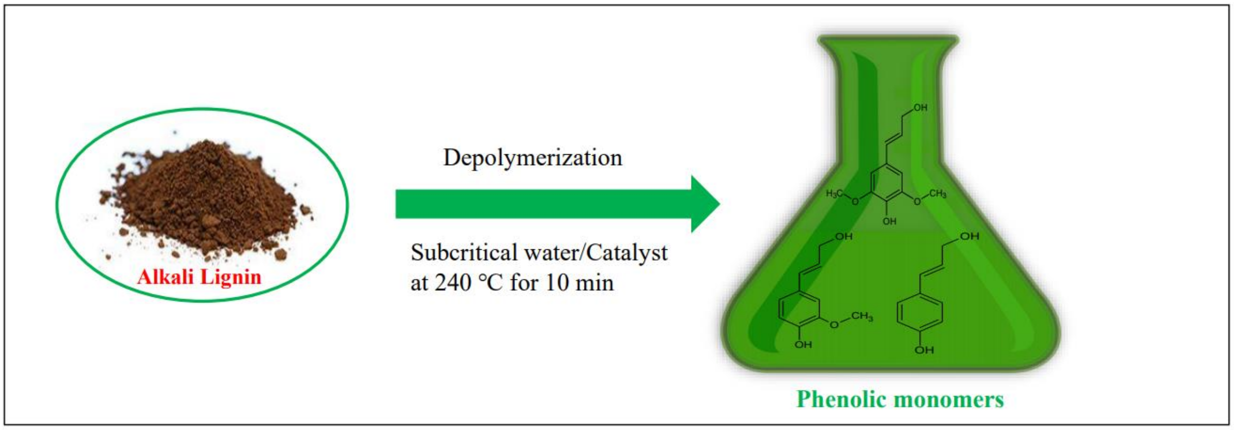
Figure 2.1. Phenolic monomers of the Lignin

Lignin is one of the renewable, and promising alternative source for producing fuel and aromatic phenolic monomers [157]. 40-50 million tons of lignin was produced from the pulp and paper industries per annum worldwide but only 2% of lignin was used for industrial applications [26]. The highest content of oxygen and lower heating values, indicating to develop the effective technologies for the usage of lignin resources to produce the value-added chemicals [158]. Lignin phenolic monomers are used for the synthesis of resins and polymers. Phenolic monomers from the lignin were used for the synthesis of cyanate ester resins, epoxy resins, polyesters, polyacetals, polycarbonates, polyanhydrides, polyoxalates, and vinyl ester resins [159].

The researchers are still facing challenges to understand the depolymerization of lignin due to the complex and recalcitrant structure of lignin [160-162]. Several methods were proposed for the depolymerization of lignin, such as base-catalyzed [62, 163, 164], acid-catalyzed [165-168], fast pyrolysis [169-173], oxidation [174, 175], microwave-assisted depolymerization [176, 177], ionic liquid depolymerization [178, 179], and supercritical carbon dioxide depolymerization of lignin using ethanol, methanol, and acetone as a cosolvent [60, 180, 181]. These methods showed low selectivity and need severe reaction conditions (high temperature and pressure) for the depolymerization of lignin. Ionic liquid assisted depolymerization method showed high selectivity, but the cost of ionic liquids and recycling is more. The uses of organic solvents for this process become very toxic to the environment.[182] To overcome these issues and minimize the usage of hazardous conditions and chemicals need an appropriate and suitable depolymerization method.

The main goal of this study is to convert the complex lignin into small chemicals or oligomers by using green solvent and minimizing the hazardous reaction conditions. In this study, developed the method which is an environmentally friendly and green approach for the depolymerization of alkali lignin in the presence of sub-critical water and different types of catalysts. The subcritical water and catalysts were used for the depolymerization of alkali lignin. The depolymerization of alkali lignin was performed at 240 ℃ for 10 minutes reaction time with different types of heterogeneous catalysts.[183] The Ni-Graphene catalyst at 240 ℃ for 10 minutes reaction time showed the highest conversion yield from the alkali lignin. The used operating conditions (temperature, time, and pressure) for the depolymerization of lignin were lesser than traditional methods. Under the subcritical condition's alkali lignin produced a smaller molecular weight value-added chemical. The 12 different phenolic monomers were identified, and six phenolic monomers were quantified from the alkali lignin using GC-MS.

Graphical Abstract:



2.2. Experimental section

2.2.1. Materials and Catalysts

Alkali Lignin was purchased from the Sigma Aldrich (St. Louis, MO). The Catalysts 5% V/Zeolite, 1.7% V/ZrO2 (Sulfate), 10% V-Ni/Zinc, 1.7% V/ZrO2 (Neutral), Ni-Graphene, Ni-Zinc, 5% V/Ni-Graphene, 1.7% V/Zeolite, Carbon supported (CoO, MoO, and LaO), and Zeolite supported (CoO, MoO, and LaO) were obtained from the Agriculture and Bio-system Engineering department (Dr. Gu), SDSU. The deionized water was used for the depolymerization of alkali lignin. Ethyl acetate (99.9%) was purchased from Fisher Scientific Store for the extraction of phenolic monomers. O-Terphenyl was purchased from the Sigma Aldrich (St. Louis, MO) used as an analytical internal standard for the quantification of phenolic monomers. Other standards such as vanillin, homovanillic acid, acetovanillone, guaiacylacetone, and isoeugenol purchased from Sigma Aldrich (St. Louis, MO). Guaiacol was purchased from Acros Organics (New Jersey, USA). Acetic acid (99.9%) was purchased from the Sigma Aldrich (St. Louis, MO) for the protonation of phenolic compounds.

2.2.2. Hydrothermal Conversion Process

The lignin depolymerization reactions were conducted in Helix sub-critical H_2O instrument from Applied separation (Allentown, PA). The de-ionized water is used as a hydrogen donor and solvent during the depolymerization process.[184] The 24 ml of stainless-steel vessel was loaded with 250 mg of alkali lignin and 25 mg of catalyst (The ratio of lignin/catalyst is 10:1). The 21 ml of deionized water passed through the reservoir into the vessel. The subcritical water depolymerization of lignin was carried under settled reaction temperature 240℃ for 10 minutes reaction time with a constant stirring. The pressure increased with increasing reaction temperature. The pressure of the reaction was 15.0 to 21.5 MPa. The vessel was quickly cooled down using ice-water. The gas-outlet valve was opened to reduce the pressure from the gas level to the atmospheric level. Figure 2.2 shows the stepwise process for the depolymerization of alkali lignin in the presence of subcritical water and catalyst.

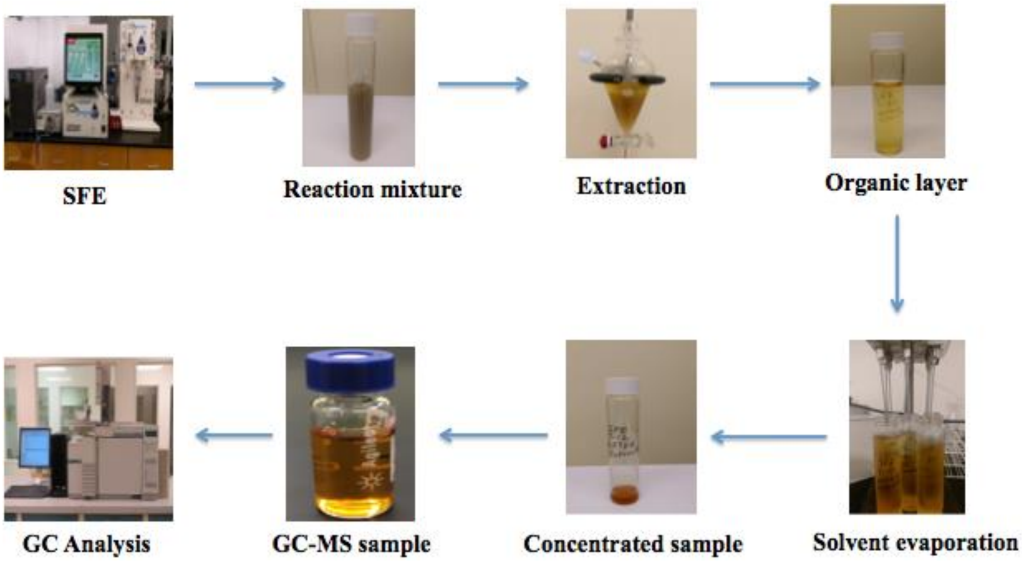


Figure 2.2. Stepwise process for the depolymerization of alkali lignin in the presence of subcritical water and different types of catalysts.

2.2.3. Separation and Extraction of Phenolic monomers

The liquid phenolic products and unreacted lignin residue separated through the vacuum filtration. 0.2 ml of acetic acid added to the liquid mixture for the deprotonation of phenoxide ions. The ethyl acetate is used for separating organic products from the aqueous medium. The organic layer is concentrated under N_2 gas. The 1.5 ml of concentrated sample was used for the GC-MS analysis.

2.2.4. GC-MS Analysis

Phenolic monomers from the alkali lignin were identified and quantified by using 5977B MSD and 7890B GC system from the Agilent Technologies (Wilmington, DE). This GC-MS was equipped with a 30m*250µm*0.25µm film thickness DB-5 MS capillary column. Hydrogen was employed as a carrier gas at a constant flow rate of 1.2 ml/min. The initial temperature of the oven was 50°C held for 0 min and then programmed from 50°C to 200°C at 20°C/min with an isothermal hold for 1 min and from 200°C to 300°C at 40°C/min hold for 2 min. The injection volume was 2µl. The ion source was electron impact (EI) and total ion chromatogram (TIC) used in GC-MS.[185] The compounds were identified by comparing the data with the NIST library.

2.3. Results and Discussion

2.3.1. Product Analysis and Quantification

The cleavage of the C-O bond of the alkali lignin took place in the presence of subcritical water and catalysts. The main products were mono aromatics oxygenates (Phenolics). The standard calibration curves of guaiacol, vanillin, isoeugenol, acetovanilone, guaiacylacetone, and homovanillic acid were used for the quantification of phenolic monomers. Figure 2.3 shows the standard calibration curves of major phenolic monomers.

These calibration curves showed R^2 >0.9998. O-Terphenyl was used as an internal standard for the quantification of phenolic monomers[186]. Figure 2.4 shows the GC-MS chromatogram of phenolic products from the alkali lignin in the presence of (a) 5% V/Zeolite, (b) 1.7% V/ZrO_2 (Sulfate), and (c) 10% V-Ni/Zn catalysts. The signal peaks are related to the various volatile phenolic monomers. The twelve different phenolic monomers were identified from the alkali lignin based on the total ion chromatogram, and the result is shown in Table 2.1. All these monomers were obtained at 240°C for 10 minutes reaction time. The catalysts enhance the depolymerization of alkali lignin and reduce the reaction time. The relative concentration of the phenolic monomers identified by the relative abundance of peak area.

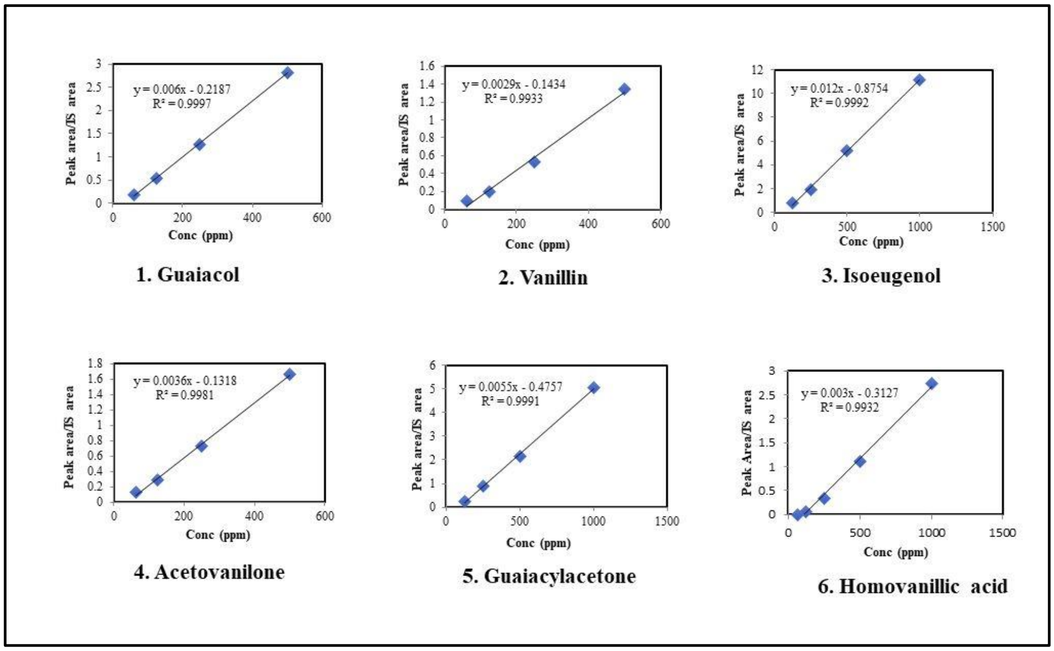


Figure 2.3. Standard calibration curves of phenolic monomers.

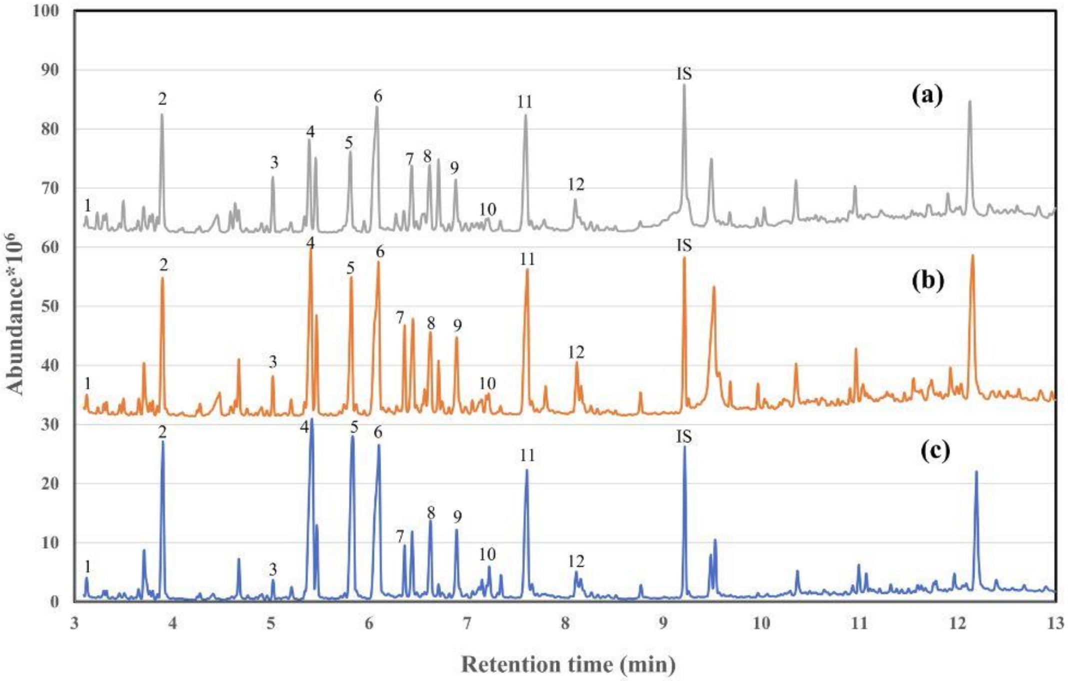


Figure 2.4. GC-MS chromatogram of phenolic monomers from the alkali lignin in the presence of subcritical water and (a) 5% V/Zeolite (b) 1.7% V/ZrO_2 (Sulfate) and (c) 10% V-Ni/Zn catalysts.

Table 2.1. Identified phenolic monomers and retention time in the presence of 5% V/Zeolite catalyst

No	Retention time (min)	Phenolic monomer	Molecular weight	Moiety
1	3.121	Phenol	94	H
2	3.899	Guaiacol	124	G
3	5.024	Ethyl guaiacol	152	G
4	5.467	Vinyl guaiacol	150	G
5	5.831	Propyl guaiacol	166	G
6	6.095	Vanillin	152	G
7	6.365	Isoeugenol	164	G
8	6.627	Acetovanillone	166	G
9	6.895	Guaiacylacetone	180	G
10	7.226	Butyrovanillone	194	G
11	7.607	Homovanillic acid	182	G
12	8.155	Coniferyl aldehyde	178	G

Figure 2.5 shows the yield of phenolic monomers in the presence of subcritical water and 5%V/Zeolite catalyst. The total yield was found to be 33.76 ± 0.44 mg/g of alkali lignin in the presence of a 5% V/Zeolite catalyst. Table 2.2 shows the yield of phenolic monomers in the presence of a 5% v/Zeolite catalyst.

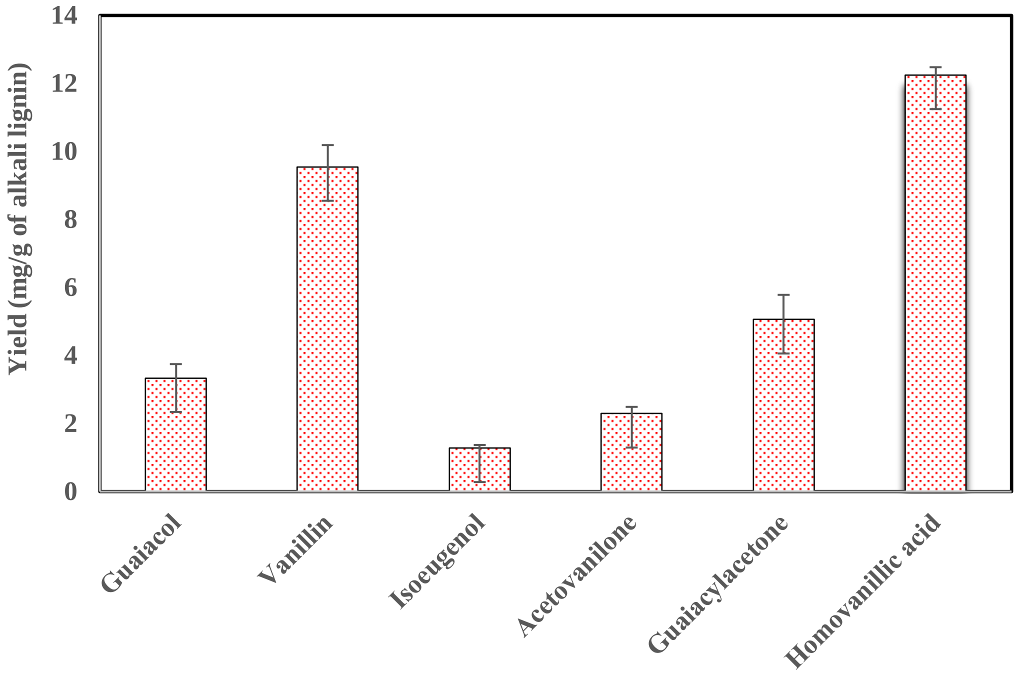


Figure 2.5. quantification results of phenolic monomers in the presence of subcritical water and 5%V/Zeolite catalyst.

Table 2.2. The yield of phenolic monomers, standard deviation, and % RSD in the presence of 5% V/Zeolite catalyst.

Phenolic monomer	Yield (mg/g of alkali lignin)	STD	% RSD
Guaiacol	3.34	0.40	12.15
Vanillin	9.55	0.63	6.67
Isoeugenol	1.28	0.09	7.07
Acetovanillone	2.29	0.09	8.54
Guaiacylacetone	5.06	0.72	14.31
Homovanillic acid	12.5	0.23	1.90

Figure 2.6 shows the yield of phenolic monomers from the alkali lignin in the presence of 1.7 % V/ZrO_2 (Sulfate) catalyst. The total yield was found to be 33.96 ± 0.22 mg/g of alkali

lignin in the presence of a 1.7 % V/Zeolite (Sulfate) catalyst. Table 2.3 shows the yield of phenolic monomers.

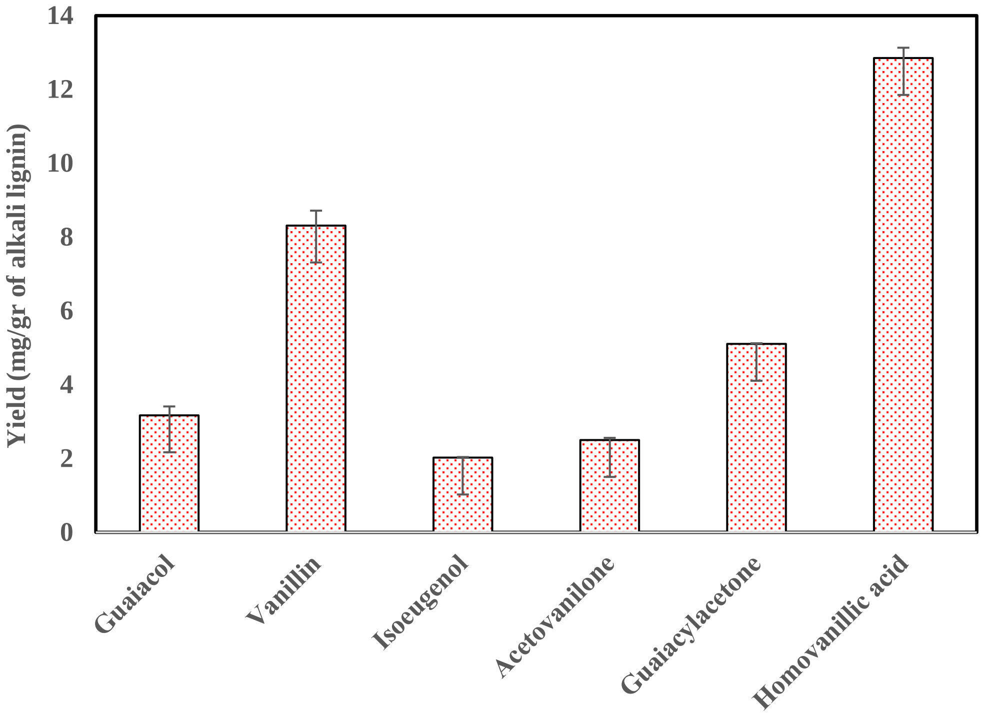


Figure 2.6. quantification results of phenolic monomers in the presence of subcritical water and 1.7% V/ZrO$_2$ (Sulfate) catalyst.

Table 2.3. Yield of phenolic monomer, standard deviation, and % RSD in the presence of 1.7% V/ZrO$_2$ (Sulfate) Catalyst.

Phenolic monomer	Yield (mg/g of alkali lignin)	STD	% RSD
Guaiacol	3.16	0.24	7.6
Vanillin	8.31	0.40	4.8
Isoeugenol	2.03	0.01	0.77
Acetovanillone	2.50	0.05	2.4
Guaiacylacetone	5.10	0.01	0.34
Homovanillic acid	12.85	0.26	2.17

Figure 2.7 shows the yield of phenolic monomers for the depolymerization alkali lignin in the presence of 10% V-Ni/Zinc catalyst. The total yield was found to be 17.42 ± 0.37 mg /g of alkali lignin in the presence of 10% V-Ni/Zinc catalyst. The major phenolic monomers were identified as vanillin and homovanillic acid in the presence of these three types of catalysts. Table 2.4 shows the yield of phenolic monomers, standard deviation, and % RSD in the presence of a 10% V/Ni-Zn catalyst.

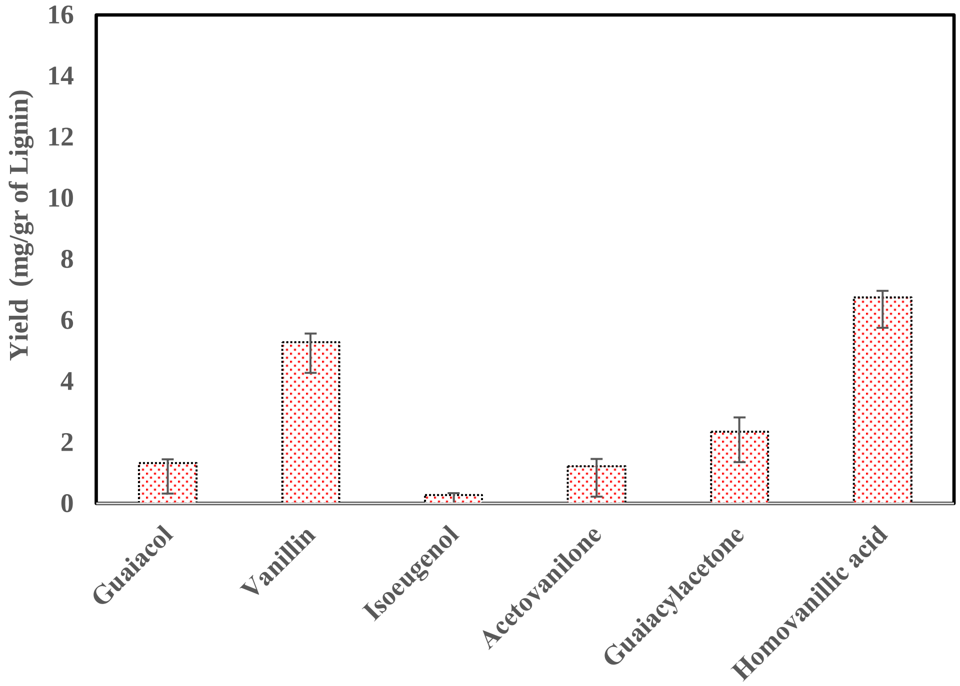


Figure 2.7. Quantification of phenolic monomers from the alkali lignin in the presence of subcritical water and 10% V/Ni-Zn catalyst.

Table 2.4. The yield of phenolic monomer, standard deviation, and % RSD in the presence of 10% V/Ni-Zn catalyst.

Phenolic monomer	Yield (mg/g of alkali lignin)	STD	% RSD
Guaiacol	1.31	0.12	9.1
Vanillin	5.27	0.28	5.4
Isoeugenol	0.27	0.06	23.9
Acetovanillone	1.22	0.23	19.1
Guaiacylacetone	2.35	0.46	19.7
Homovanillic acid	6.75	0.21	3.1

Figure 2.8 shows the GCMS chromatogram of phenolic monomers for the depolymerization of alkali lignin in the presence of subcritical water and (a) 1. 7% V/ZrO$_2$ (Neutral) (b) Ni-Graphene and (c) Ni-Zinc catalyst. Table 2.5 shows the twelve different phenolic monomers identified by using GC-MS.

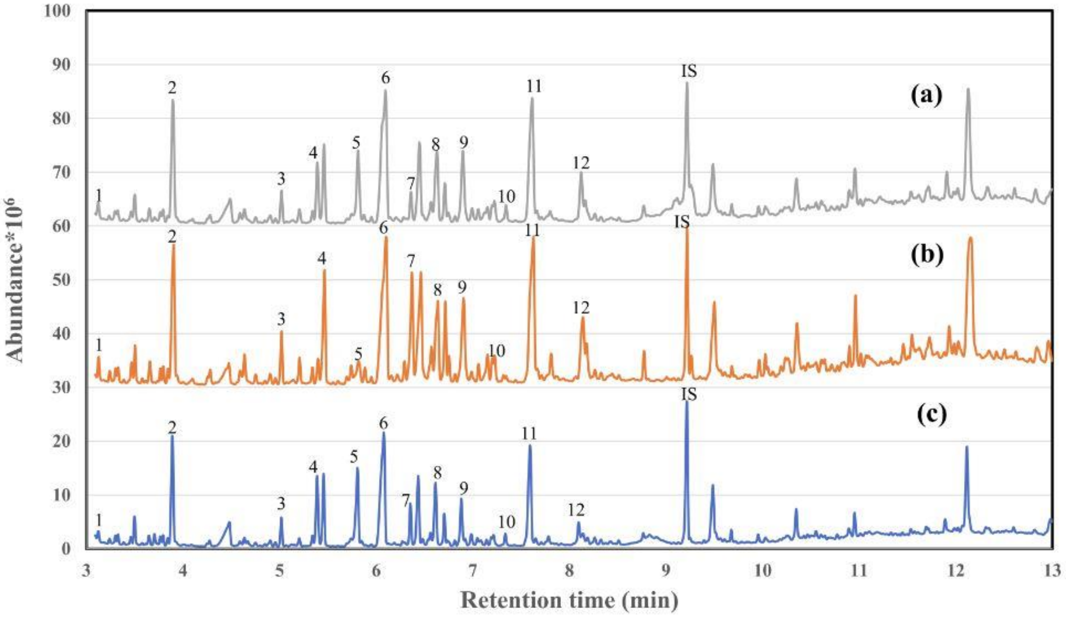


Figure 2.8. GC-MS chromatogram of phenolic monomers from the alkali lignin in the presence of subcritical water and (a) 1.7% V/ZrO$_2$ (Neutral) (b) Ni-Graphene and (c) Ni-Zn catalysts

Table 2.5. Identified phenolic monomers and retention time.

No	Retention time (min)	Phenolic monomer	Molecular weight	Moiety
1	3.125	Phenol	94	H
2	3.892	Guaiacol	124	G
3	5.012	Ethyl guaiacol	152	G
4	5.458	Vinyl guaiacol	150	G
5	5.807	Propyl guaiacol	166	G
6	6.077	Vanillin	152	G
7	6.356	Isoeugenol	164	G
8	6.615	Acetovanillone	166	G
9	6.883	Guaiacylacetone	180	G
10	7.214	Butyrovanillone	194	G
11	7.593	Homovanillic acid	182	G
12	8.140	Coniferyl aldehyde	178	G

Figure 2.9 shows the yield of six major phenolic monomers from the alkali lignin. The total yield was found to be 21.97 ± 0.36 mg/g of alkali lignin in the presence of 1.7 % V/ZrO_2 (Neutral) catalyst. Table 2.6 shows the yield of each phenolic monomers, standard deviation, and % RSD in the presence of 1.7% V/ZrO_2 (Neutral) catalyst.

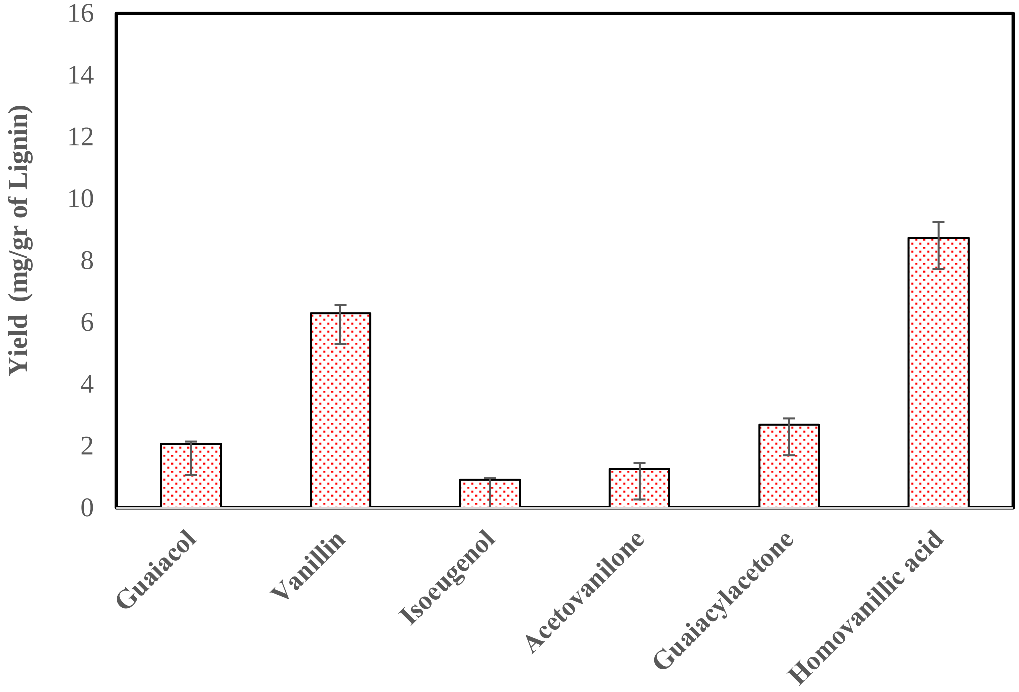


Figure 2.9. Quantification results of phenolic monomers from the alkali lignin in the presence of subcritical water and 1.7% V/ZrO_2 (Neutral) catalyst.

Table 2.6. The yield of phenolic monomer, standard deviation, and % RSD in the presence of 1.7% V/ZrO_2 (Neutral) catalyst.

Phenolic monomer	Yield (mg/g of alkali lignin)	STD	% RSD
Guaiacol	2.07	0.07	3.6
Vanillin	6.30	0.26	4.2
Isoeugenol	0.90	0.04	5.4
Acetovanillone	1.27	0.17	13.7
Guaiacylacetone	2.70	0.19	7.1
Homovanillic acid	8.73	0.51	5.8

Figure 2.10 shows the yield of phenolic monomers from the alkali lignin in the presence of Ni-Graphene catalyst. The total yield was found to be 40.84 ± 0.27 mg/g of alkali lignin in the presence of Ni-Graphene catalyst. Table 2.7 shows the yield of depolymerized compounds from the alkali lignin.

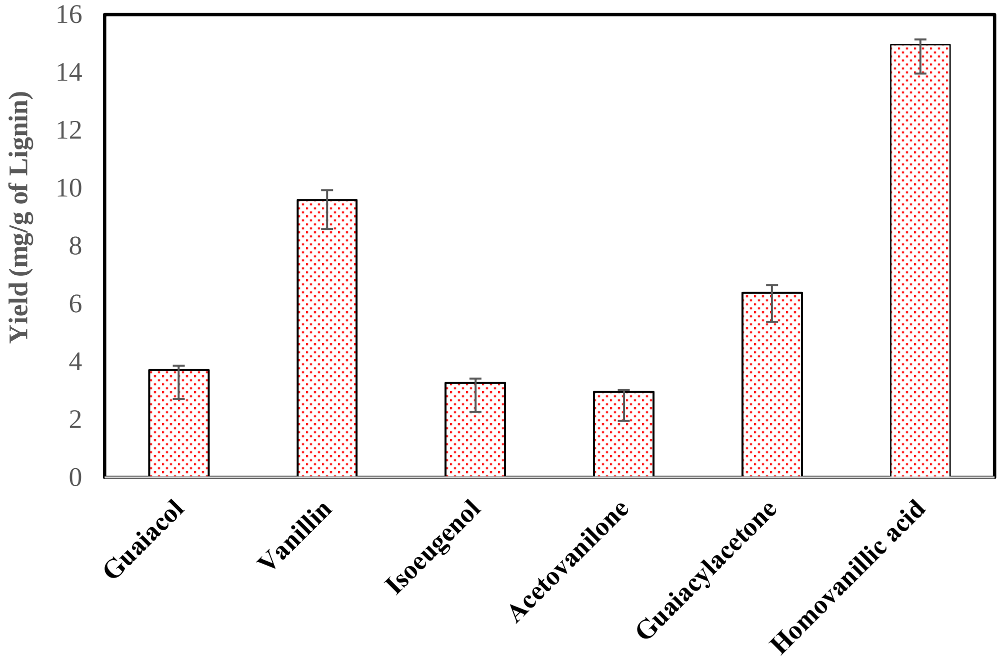


Figure 2.10. Quantification of results of phenolic monomers from the alkali lignin in the presence of subcritical water and Ni-Graphene catalyst.

Table 2.7. The yield of phenolic monomers, standard deviation, and % RSD in the presence of Ni-Graphene catalyst.

Phenolic monomer	Yield (mg/g of alkali lignin)	STD	% RSD
Guaiacol	3.70	0.16	4.3
Vanillin	9.59	0.34	3.5
Isoeugenol	3.26	0.15	4.8
Acetovanillone	2.95	0.06	2.1
Guaiacylacetone	6.38	0.26	4.1
Homovanillic acid	14.96	0.18	1.2

Figure 2.11 shows the yield of phenolic monomers from the alkali lignin in the presence of Ni-Zinc catalyst. The total yield was found to be 24.57 ± 0.14 mg/g of alkali lignin in the presence of Ni-Zn catalyst. Table 2.8 shows the yield of depolymerized compounds from the alkali lignin.

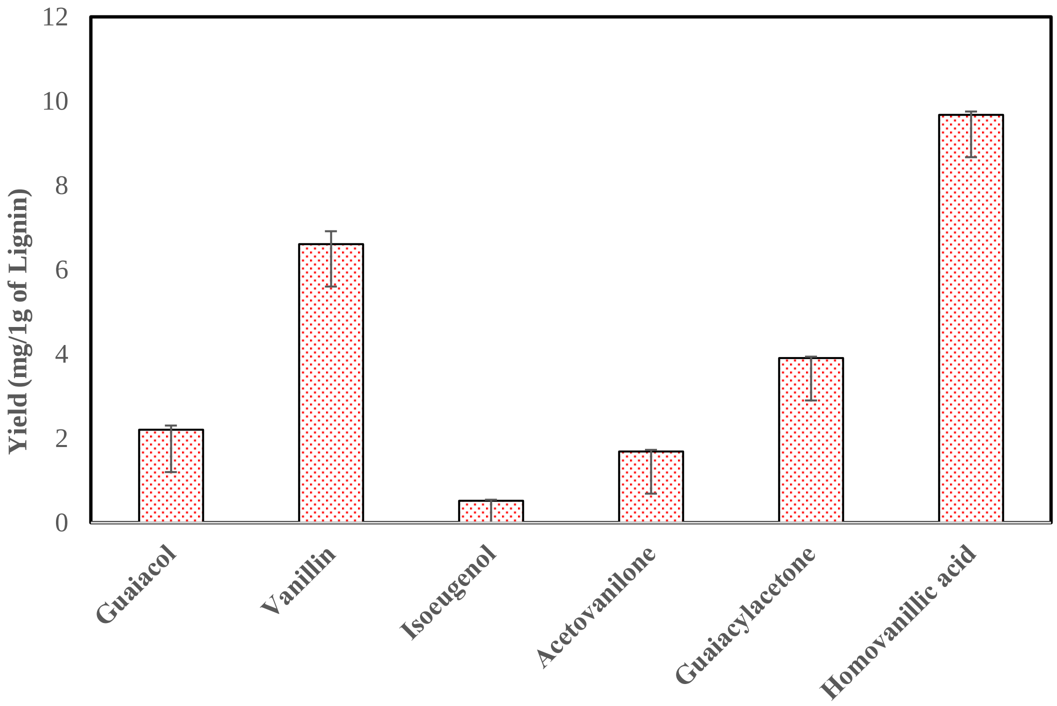


Figure 2.11. Quantification results of phenolic monomers from the alkali lignin in the presence of subcritical water and Ni-Zinc catalyst.

Table 2.8. The yield of phenolic monomers, standard deviation, and % RSD in the presence of Ni-Zn catalyst.

Phenolic monomer	Yield (mg/g of alkali lignin)	STD	% RSD
Guaiacol	2.20	0.10	4.7
Vanillin	6.60	0.31	4.8
Isoeugenol	0.51	0.02	5.8
Acetovanillone	1.69	0.04	2.3
Guaiacylacetone	3.90	0.04	1.0
Homovanillic acid	9.67	0.08	0.8

Figure 2.12 shows the GCMS chromatogram of phenolic monomers for the depolymerization of alkali lignin in the presence of subcritical water and (a) 5% V/Ni-Graphene (b) 1.7% V/Zeolite and (c) No catalyst. Table 2.9 shows the twelve different phenolic monomers identified by using GC-MS.

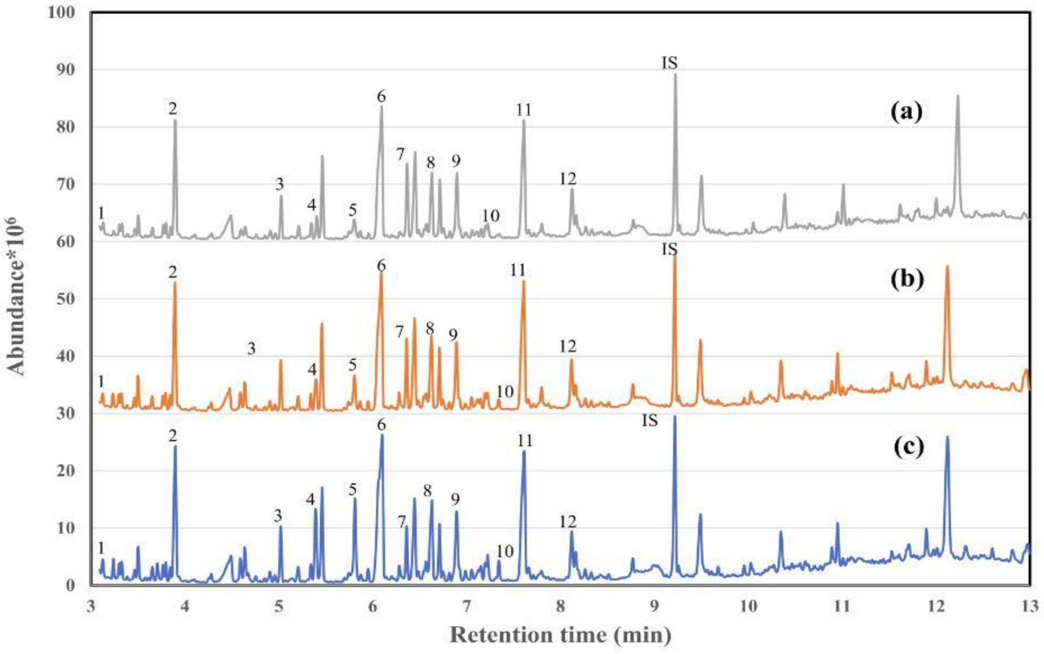


Figure 2.12. GC-MS chromatogram of phenolic monomers from the alkali lignin in the presence of subcritical water and (a) 5% V/Ni-Graphene (b) 1.7% V/Zeolite and (c) No catalysts.

Table 2.9. Identified phenolic monomers and retention time in the presence of 5% V/Ni-Graphene catalyst.

No	Retention time (min)	Phenolic monomer	Molecular weight	Moiety
1	3.127	Phenol	94	H
2	3.898	Guaiacol	124	G
3	5.023	Ethyl guaiacol	152	G
4	5.609	Vinyl guaiacol	150	G
5	5.813	Propyl guaiacol	166	G
6	6.098	Vanillin	152	G
7	6.363	Isoeugenol	164	G
8	6.629	Acetovanillone	166	G
9	6.896	Guaiacylacetone	180	G
10	7.226	Butyrovanillone	194	G
11	7.612	Homovanillic acid	182	G
12	8.164	Coniferyl aldehyde	178	G

Figure 2.13 shows the yield of six major phenolic monomers from the alkali lignin in the presence of a 5% V/Ni-Graphene catalyst. The total yield was found to be 31.21 ± 0.16 mg/g of alkali lignin in the presence of a 5% V-Ni-Graphene catalyst. Table 2.10 shows the yield of each phenolic monomer, standard deviation, and %RSD.

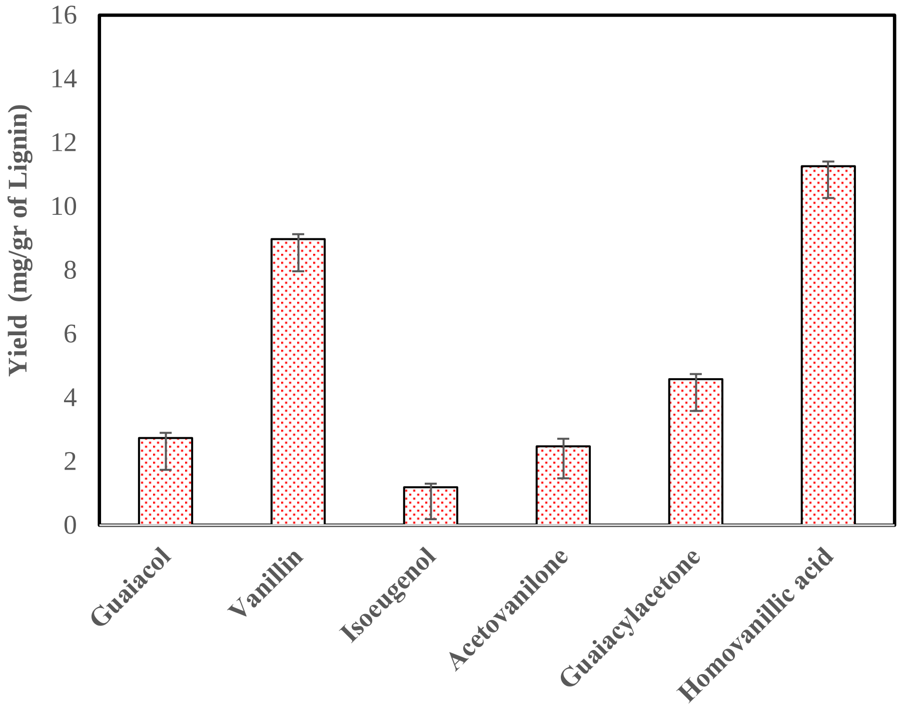


Figure 2.13. Quantification results of phenolic monomers from the alkali lignin in the presence of subcritical water and 5% V/Ni-Graphene catalyst.

Table 2.10. The yield of phenolic monomers, STD, and % RSD in the presence of 5% V/Ni-Graphene catalyst.

Phenolic monomer	Yield (mg/g of alkali lignin)	STD	% RSD
Guaiacol	2.73	0.16	5.9
Vanillin	8.97	0.17	1.8
Isoeugenol	1.19	0.11	9.5
Acetovanillone	2.47	0.24	9.7
Guaiacylacetone	4.58	0.16	3.4
Homovanillic acid	11.26	0.14	1.3

Figure 2.14 shows the yield of six major phenolic monomers from the alkali lignin in the presence of 1.7% V/Zeolite catalyst. The total yield was found to be 30.90 ± 0.40 mg/g of alkali lignin in the presence of 1.7% V/Zeolite catalyst. Table 2.11 shows the yield of each phenolic monomers, standard deviation, and %RSD in the presence of 1.7% V/Zeolite catalyst.

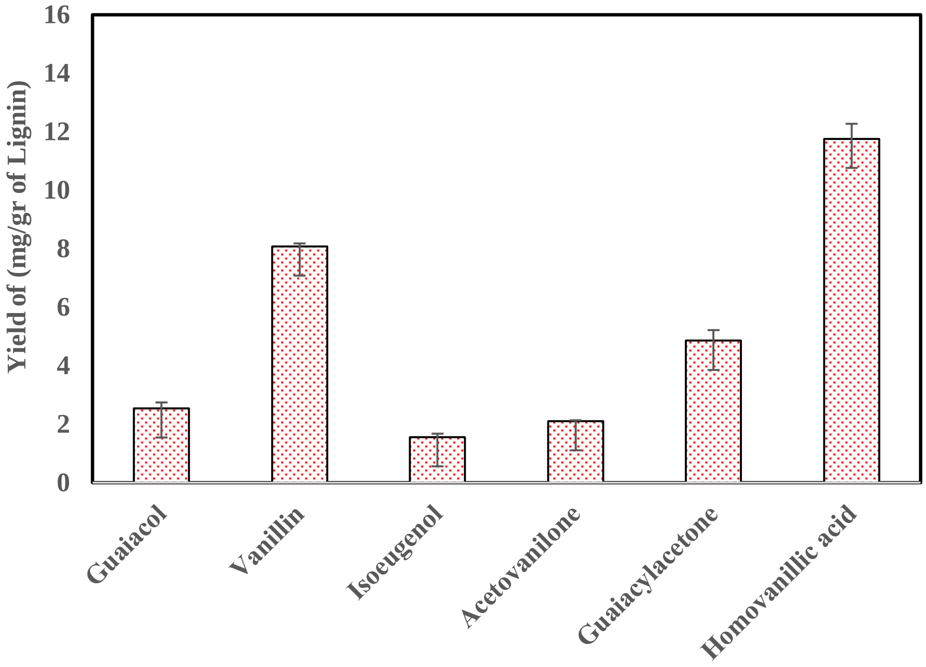


Figure 2.14. Quantification results of phenolic monomers from the alkali lignin in the presence of subcritical water and 1.7% V/Zeolite catalyst.

Table 2.11. The yield of phenolic monomers, standard deviation, and % RSD in the presence of 1.7% V/Zeolite catalyst.

Phenolic monomer	Yield (mg/g of alkali lignin)	STD	% RSD
Guaiacol	2.54	0.20	7.8
Vanillin	8.07	0.10	1.2
Isoeugenol	1.55	0.11	7.4
Acetovanillone	2.10	0.02	1.3
Guaiacylacetone	4.85	0.36	7.4
Homovanillic acid	11.56	0.50	4.3

Figure 2.15 shows the yield of six major phenolic monomers from the alkali lignin without catalyst. The total yield was found to be 24.06 ± 0.27 mg/g of alkali lignin without catalyst. Table 2.12 shows the yield of each phenolic monomers, STD, and %RSD without catalyst.

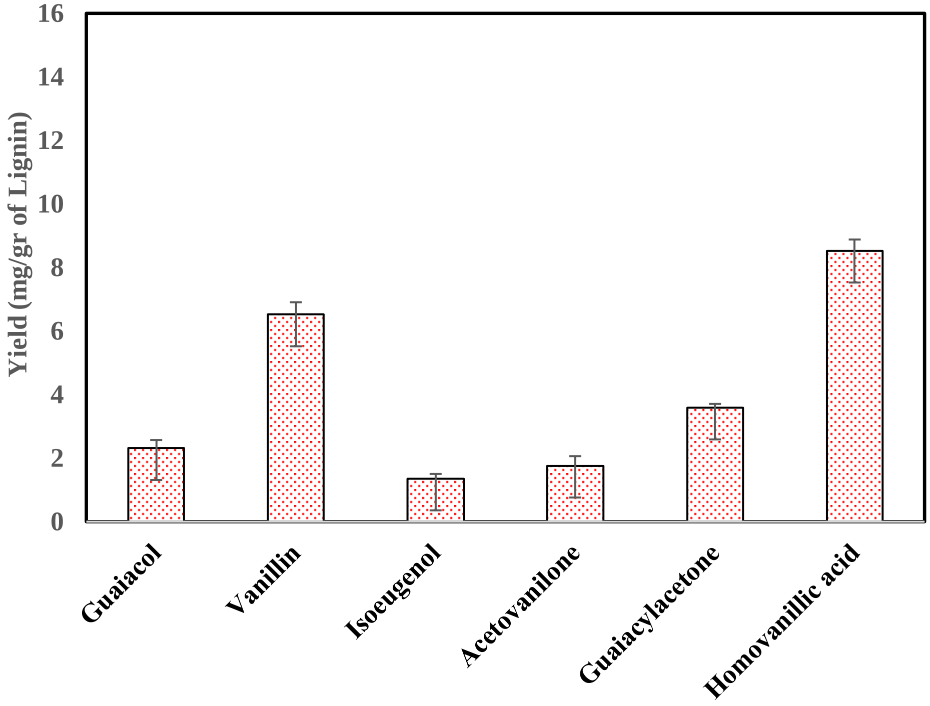


Figure 2.15. Quantification results of phenolic monomers from the alkali lignin in the presence of subcritical water and without catalyst.

Table 2.12. The yield of phenolic monomers, standard deviation, and % RSD without catalyst.

Phenolic monomer	Yield (mg/g of alkali lignin)	STD	% RSD
Guaiacol	2.31	0.25	11.2
Vanillin	6.52	0.38	5.9
Isoeugenol	1.35	0.14	10.7
Acetovanillone	1.76	0.30	17.1
Guaiacylacetone	3.58	0.11	3.3
Homovanillic acid	8.52	0.35	4.2

Figure 2.16 shows the GCMS chromatogram of phenolic monomers for the depolymerization of alkali lignin in the presence of subcritical water and carbon-supported (a) CoO (b) LaO and (c) MoO catalyst. Table 2.13 shows the 9 different phenolic monomers identified by using GC-MS.

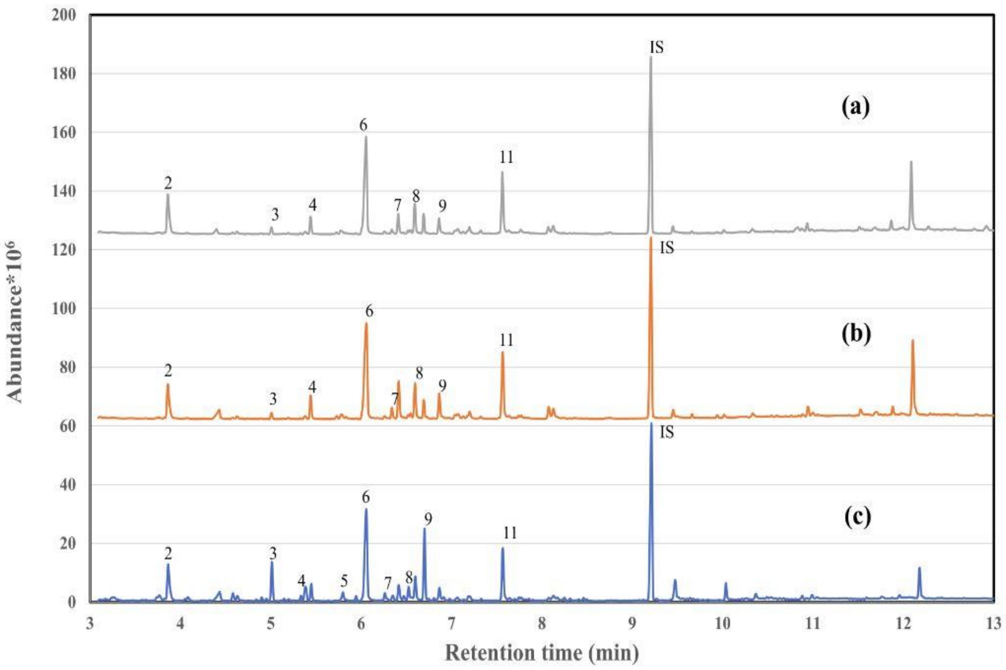


Figure 2.16. GC-MS chromatogram of phenolic monomers from the alkali lignin in the presence of subcritical water and Carbon supported (a) CoO (b) LaO and (c) MoO catalysts

Table 2.13. Identified phenolic monomers and retention time in the presence of carbon supported CoO catalyst.

No	Retention time (min)	Phenolic monomer	Molecular weight	Moiety
2	3.892	Guaiacol	124	G
3	5.012	Ethyl guaiacol	152	G
4	5.458	Vinyl guaiacol	150	G
5	5.807	Propyl guaiacol	166	G
6	6.077	Vanillin	152	G
7	6.356	Isoeugenol	164	G
8	6.615	Acetovanillone	166	G
9	6.883	Guaiacylacetone	180	G
11	7.593	Homovanillic acid	182	G

Figure 2.17 shows the yield of six major phenolic monomers from the alkali lignin in the presence of a CoO catalyst. The total yield was found to be 7.19 ± 0.08 mg/g of alkali lignin in the presence of a CoO catalyst. Table 2.14 shows the yield of each phenolic monomers, STD, and % RSD in the presence of carbon-supported CoO catalyst.

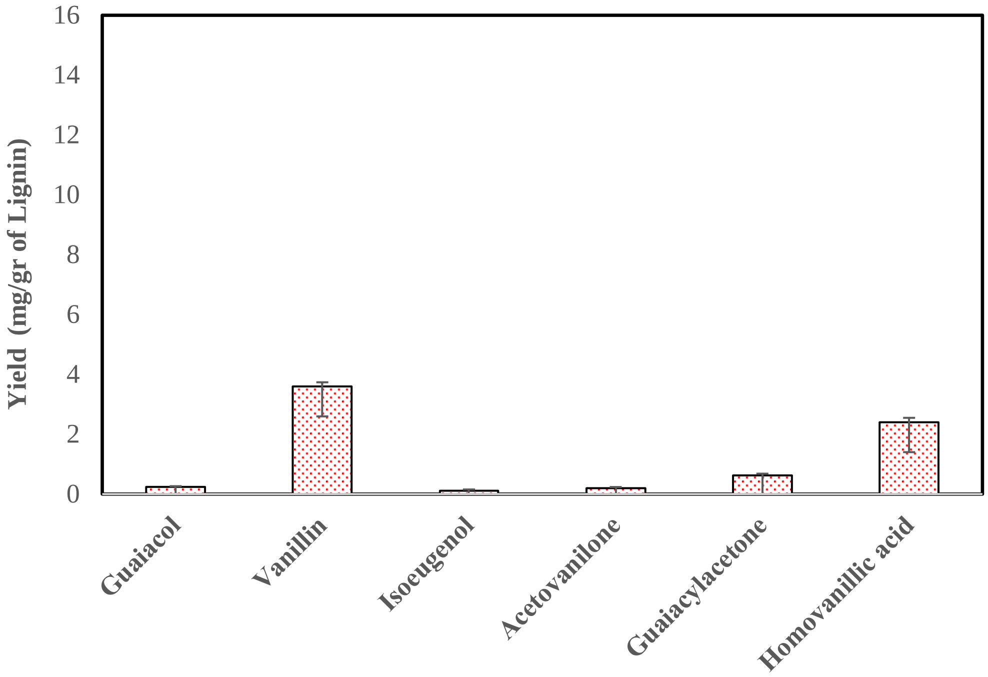


Figure 2.17. Quantification results of phenolic monomers from the alkali lignin in the presence of subcritical water and carbon supported CoO catalyst.

Table 2.14. Yield of phenolic monomers, standard deviation, and % RSD in the presence of carbon-supported CoO catalyst.

Phenolic monomer	Yield (mg/g of alkali lignin)	STD	% RSD
Guaiacol	0.25	0.01	5.76
Vanillin	3.59	0.13	3.86
Isoeugenol	0.06	0.01	18.81
Acetovanillone	0.20	0.03	14.12
Guaiacylacetone	0.62	0.05	8.76
Homovanillic acid	2.40	0.15	6.1

Figure 2.18 shows the yield of six major phenolic monomers from the alkali lignin in the presence of LaO catalyst. The total yield was found to be 9.01 ± 0.21 mg/g of alkali lignin

in the presence of LaO catalyst. Table 2.15 shows the yield of each phenolic monomer, standard deviation, and % RSD in the presence of carbon supported LaO catalyst.

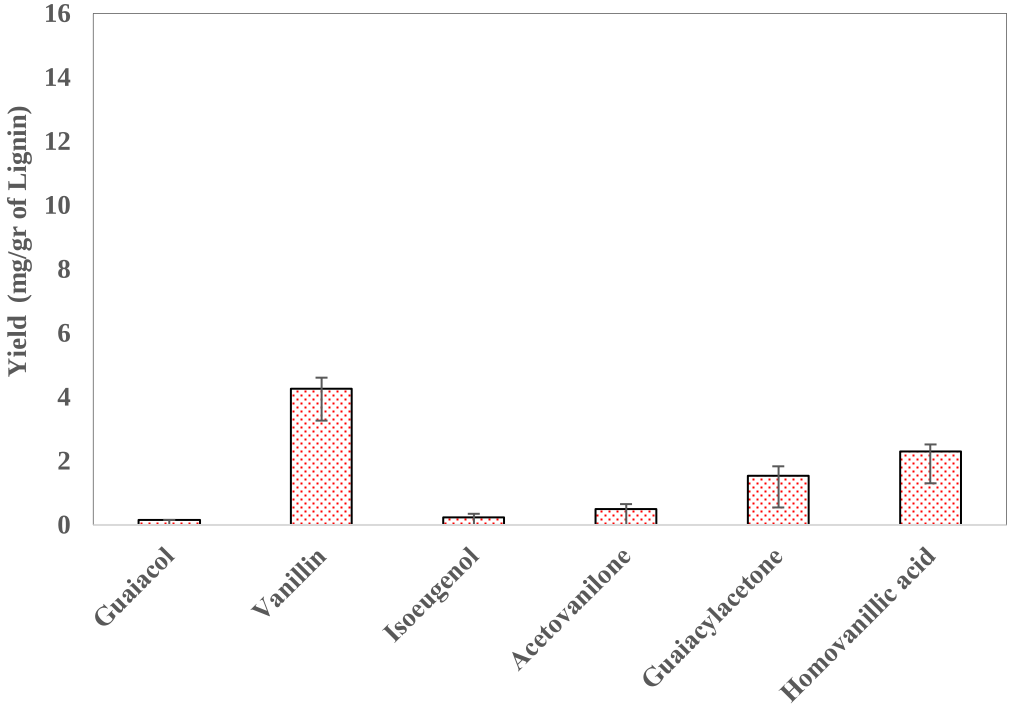


Figure 2.18. Quantification of the phenolic monomers from the alkali lignin in the presence of subcritical water and carbon supported LaO Catalyst.

Table 2.15. The yield of phenolic monomers, standard deviation, and % RSD in the presence of carbon supported LaO catalyst.

Phenolic monomer	Yield (mg/g of alkali lignin)	STD	% RSD
Guaiacol	0.15	0.06	4.1
Vanillin	4.26	0.34	8.0
Isoeugenol	0.24	0.10	4.6
Acetovanillone	0.50	0.15	7.1
Guaiacylacetone	1.55	0.28	3.5
Homovanillic acid	2.30	0.21	9.3

Figure 2.19 shows the yield of six major phenolic monomers from the alkali lignin in the presence of MoO catalyst. The total yield was found to be 8.46 ± 0.17 mg/g of alkali lignin in the presence of MoO catalyst. Table 2.16 shows the yield of each phenolic monomer, standard deviation and % RSD in the presence of carbon supported MoO catalyst.

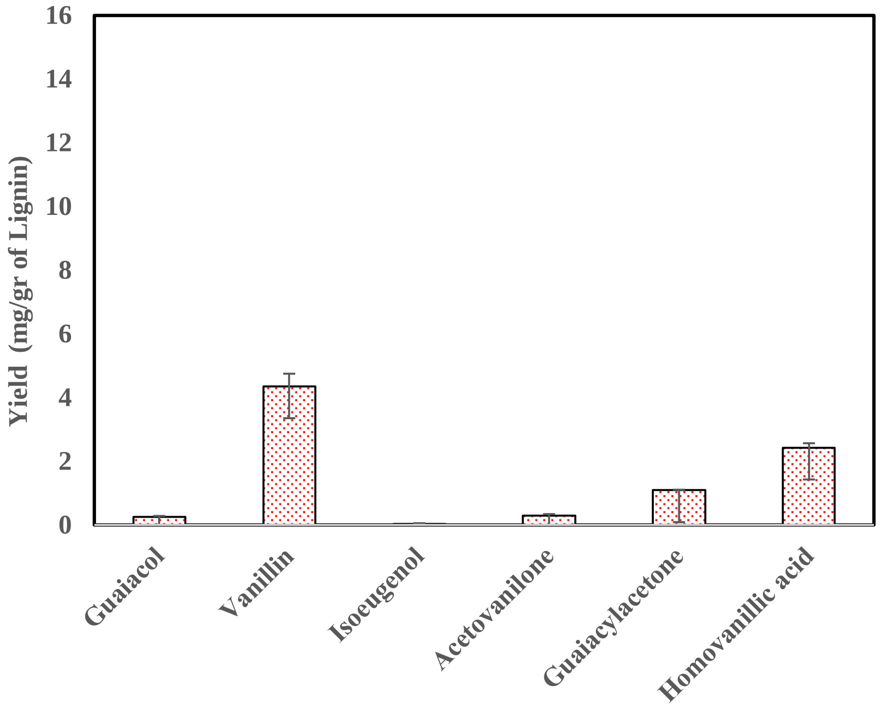


Figure 2.19. Quantification of phenolic monomers from the alkali lignin in the presence of subcritical water and carbon supported MoO catalyst.

Table 2.16. The yield of phenolic monomers, standard deviation, and % RSD in the presence of carbon supported MoO catalyst.

Phenolic monomer	Yield (mg/g of alkali lignin)	STD	% RSD
Guaiacol	0.27	0.02	8.5
Vanillin	4.35	0.39	9.1
Isoeugenol	0.04	0.01	16.3
Acetovanillone	0.29	0.04	14.8
Guaiacylacetone	1.08	0.01	1.6
Homovanillic acid	2.43	0.13	5.6

The depolymerization of alkali lignin performed using subcritical water and zeolite supported catalysts.[187] Figure 2.20 shows the GCMS chromatogram of phenolic monomers for the depolymerization of alkali lignin in the presence of subcritical water and zeolite supported (a) LaO (b) MoO and (c) CoO catalyst. Table 2.17 shows the 9 different phenolic monomers identified by using GC-MS.

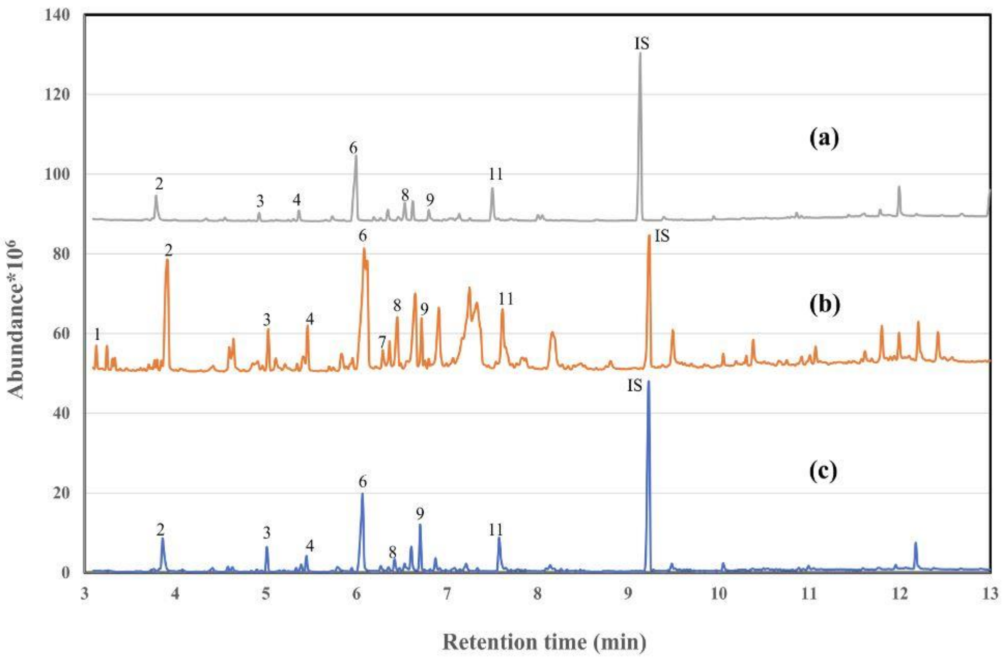


Figure 2.20. GC-MS chromatogram of phenolic monomers from the alkali lignin in the presence of subcritical water and Zeolite supported (a) LaO (b) MoO and (c) CoO catalysts.

Table 2.17. Identified phenolic monomers and retention time in the presence of zeolite supported catalysts

No	Retention time (min)	Phenolic monomer	Molecular weight	Moiety
1	3.125	Phenol	94	H
2	3.892	Guaiacol	124	G
3	5.012	Ethyl guaiacol	152	G
4	5.458	Vinyl guaiacol	150	G
6	6.077	Vanillin	152	G
7	6.356	Isoeugenol	164	G
8	6.615	Acetovanillone	166	G
9	6.883	Guaiacylacetone	180	G
11	7.593	Homovanillic acid	182	G

Figure 2.21 shows the yield of six major phenolic monomers from the alkali lignin in the presence of LaO catalyst. The total yield was found to be 7.95 ± 0.13 mg/g of alkali lignin in the presence of LaO catalyst. Table 2.18 shows the yield of each phenolic monomer, standard deviation and % RSD in the presence of zeolite supported LaO catalyst.

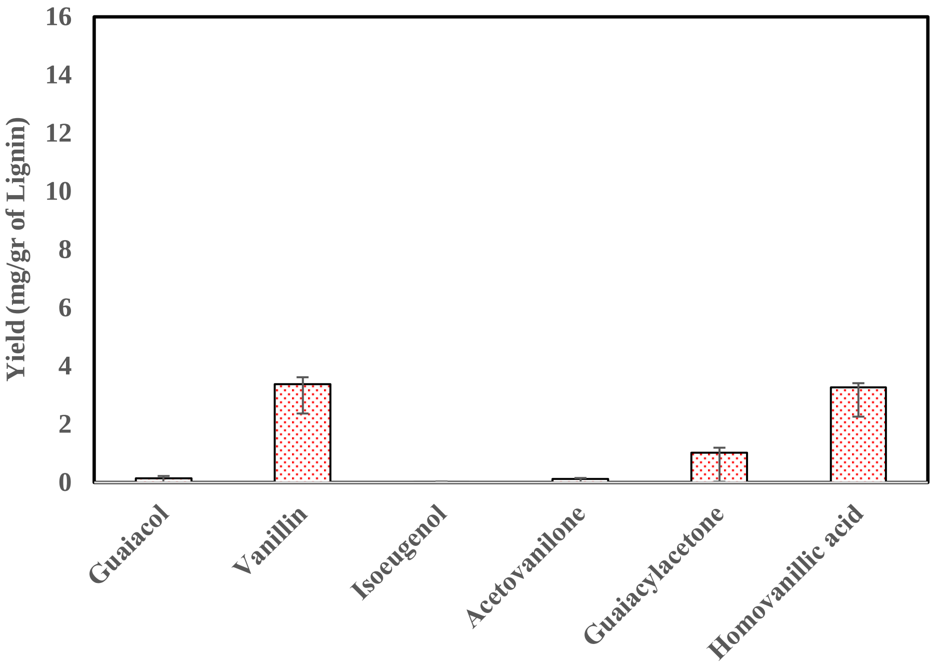


Figure 2.21. Quantification results of phenolic monomers from the alkali lignin in the presence of subcritical water and zeolite supported LaO catalyst.

Table 2.18. The yield of phenolic monomers, standard deviation, and % RSD in the presence of zeolite supported LaO catalyst.

Phenolic monomer	Yield (mg/g of alkali lignin)	STD	% RSD
Guaiacol	0.14	0.07	6.8
Vanillin	3.37	0.24	7.2
Isoeugenol	0.01	0.01	19.8
Acetovanillone	0.13	0.02	17.5
Guaiacylacetone	1.02	0.16	16.3
Homovanillic acid	3.26	0.14	4.5

Figure 2.22 shows the yield of six major phenolic monomers from the alkali lignin in the presence of MoO catalyst. The total yield was found to be 8.02 ± 0.07 mg/g of alkali lignin

in the presence of MoO catalyst. Table 2.19 shows the yield of each phenolic monomer, standard deviation, and % RSD in the presence of zeolite supported MoO catalyst.

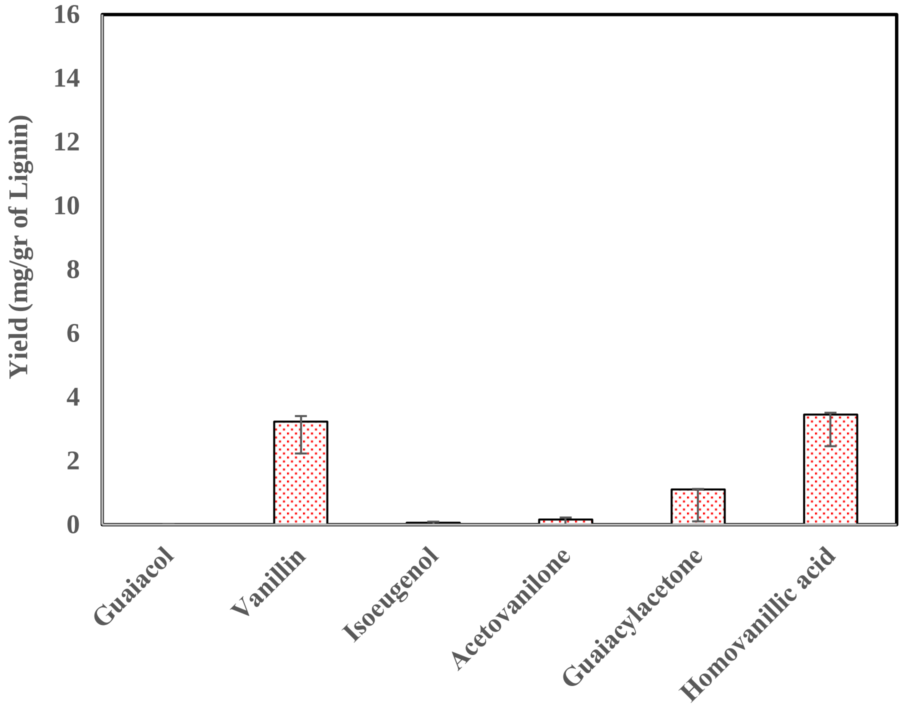


Figure 2.22. Quantification results of phenolic monomers from the alkali lignin in the presence of subcritical water and zeolite supported MoO catalyst.

Table 2.19. The yield of phenolic monomers, standard deviation, and % RSD in the presence of zeolite supported MoO catalyst.

Phenolic monomer	Yield (mg/g of alkali lignin)	STD	% RSD
Guaiacol	0.004	0.003	5.2
Vanillin	3.23	0.17	5.3
Isoeugenol	0.06	0.03	7.2
Acetovanillone	0.16	0.05	7.1
Guaiacylacetone	1.10	0.01	1.5
Homovanillic acid	3.46	0.04	1.3

Figure 2.23 shows the yield of six major phenolic monomers from the alkali lignin in the presence of a CoO catalyst. The total yield was found to be 8.03 ± 0.10 mg/g of alkali lignin in the presence of a CoO catalyst. Table 2.20 shows the yield of each phenolic monomers, standard deviation and % RSD in the presence of zeolite supported CoO catalyst.

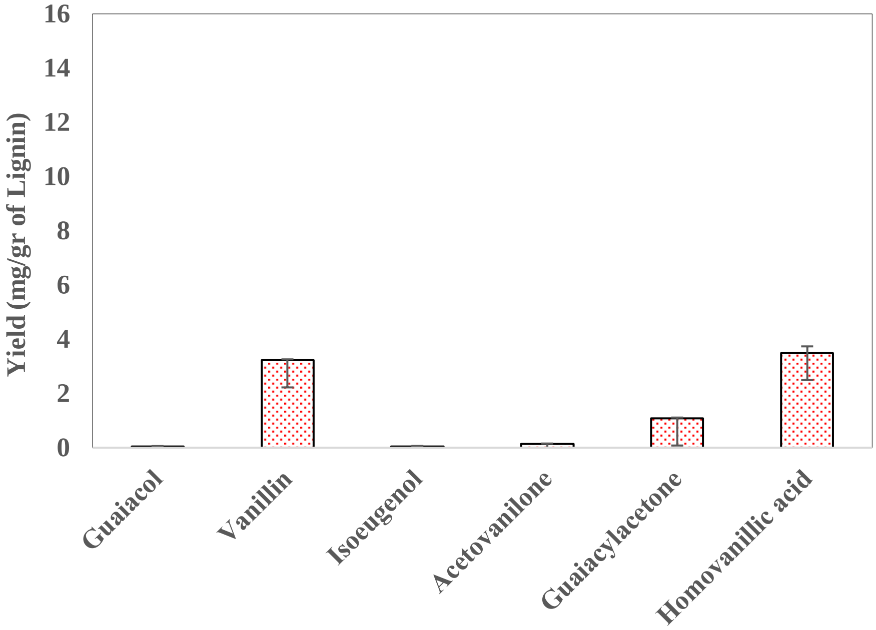


Figure 2.23. Quantification results of phenolic monomers from the alkali lignin in the presence of subcritical water and zeolite supported CoO catalyst.

Table 2.20. The yield of phenolic monomers, standard deviation, and % RSD in the presence of zeolite supported CoO catalyst.

Phenolic monomer	Yield (mg/g of alkali lignin)	STD	% RSD
Guaiacol	0.03	0.02	18.6
Vanillin	3.22	0.03	1.2
Isoeugenol	0.04	0.02	14.8
Acetovanillone	0.15	0.005	3.7
Guaiacylacetone	1.08	0.03	2.8
Homovanillic acid	3.49	0.24	7.0

Figure 2.24 shows the yield of six major phenolic monomers from the alkali lignin in the presence of different types of catalysts. The vanillin and homovanillic acid showed the highest conversion yield in the presence of subcritical water and different types of catalysts.

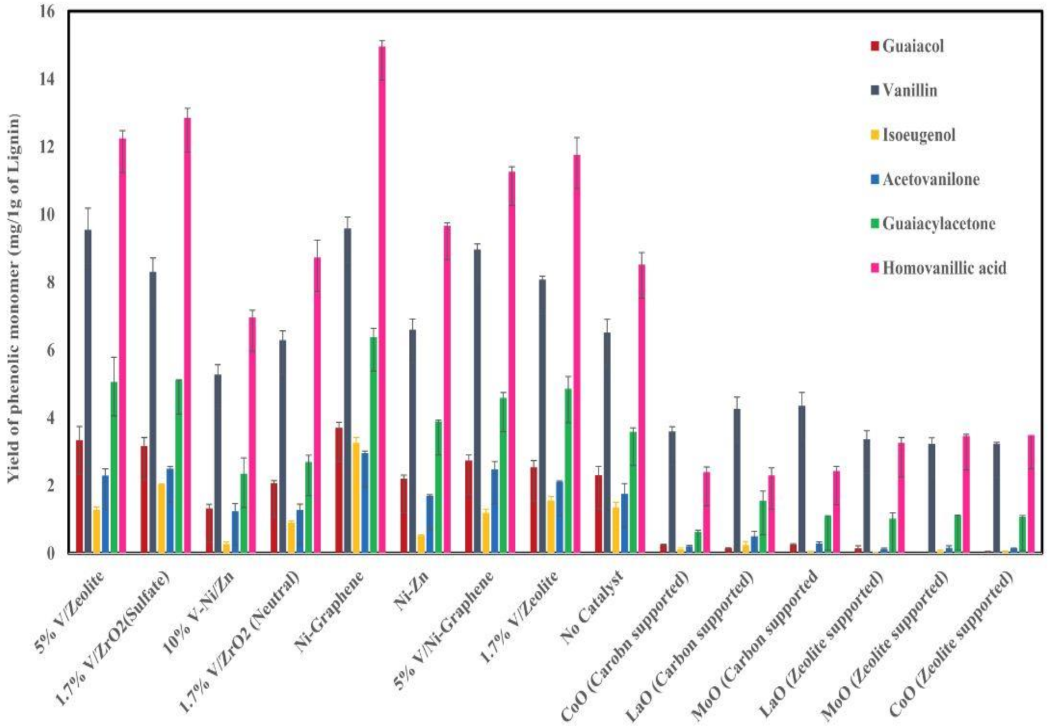


Figure 2.24. The yield of major phenolic monomers for the depolymerization of alkali lignin in the presence of subcritical water and different types of catalysts.

Figure 2.25 shows the total yield of phenolic monomers for the depolymerization of alkali lignin in the presence of subcritical water and catalyst. The Ni-Graphene showed the highest conversion yield in the presence of subcritical water. Table 2.21 shows the total yield of phenolic monomers from the alkali lignin in the presence of different catalysts.

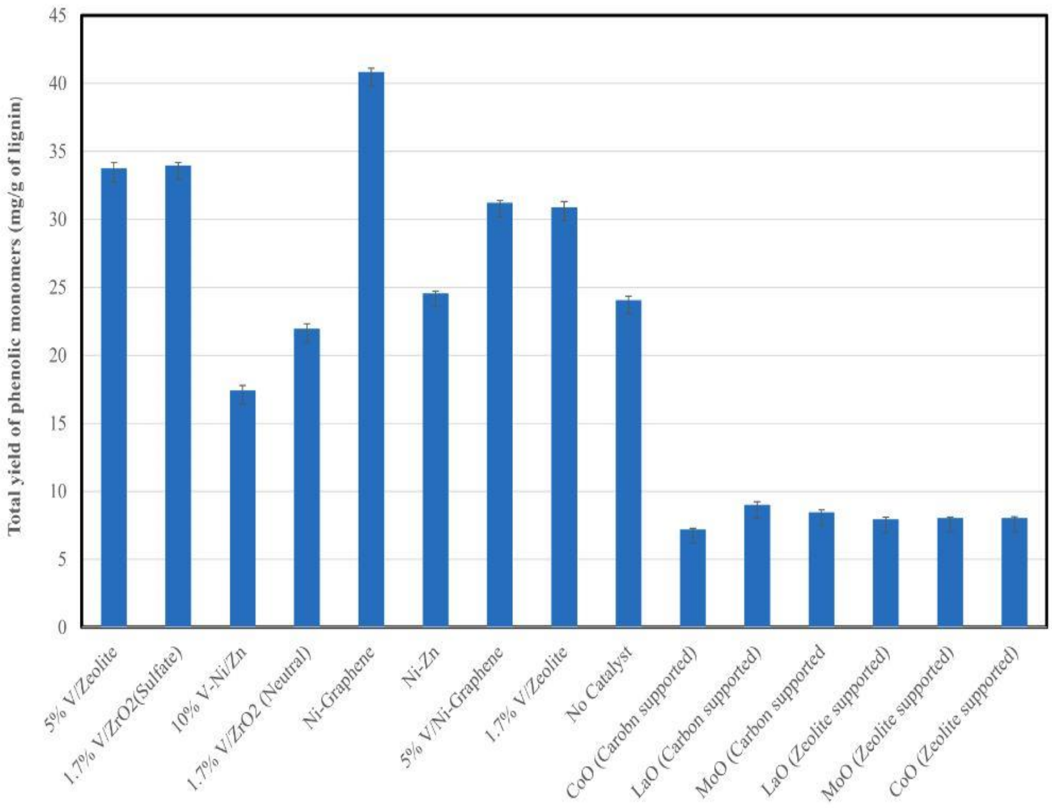


Figure 2.25. The total yield of phenolic monomers for the depolymerization of alkali lignin in the presence of subcritical water and catalysts.

Table 2.21. The total yield of phenolic monomers from the alkali lignin in the presence of a different catalysts.

No	Name of Catalyst	Total Yield (mg/g of alkali Lignin)
1	5% V/Zeolite	33.76 ± 0.44
2	1.7% V/ZrO_2 (Sulfate)	33.96 ± 0.22
3	10% V-Ni/Zinc	17.42 ± 0.37
4	1.7% V/ZrO_2 (Neutral)	21.97 ± 0.36
5	Ni-Graphene	40.84 ± 0.27
6	Ni-Zinc	24.57 ± 0.14
7	5% V/Ni-Graphene	31.21 ± 0.16
8	1.7% V/Zeolite	30.90 ± 0.40
9	CoO (carbon supported)	7.19 ± 0.08
10	LaO (carbon supported)	9.01 ± 0.21
11	MoO (carbon supported)	8.46 ± 0.17
12	LaO (zeolite supported)	7.95 ± 0.13
13	MoO (zeolite supported)	8.02 ± 0.07
14	CoO (zeolite supported)	8.03 ± 0.10
15	No Catalyst	24.06 ± 0.27

2.4. Role of Subcritical water and Catalysts in depolymerization of alkali lignin

The unique properties of subcritical water behave like an acid and base catalyst. The solubility of the lignin increases in subcritical conditions because of decreasing density and viscosity. The rate of diffusion will increase with the combination of subcritical water and catalyst. The depolymerization reactions at higher temperature lead to the formation of char, corrosion of the reaction vessel, damage the catalysts, and increase the repolymerization.[188] The catalysts prevent the formation of char and repolymerization reaction.

Zeolite (HZSM-5, Si/Al ratio was 30/1) and carbon supported catalysts play an important role in the depolymerization of lignin. Zeolite supported metal catalyst used for this study helps to control the reaction in the mixture to achieve the more stable products and increase the product yield because of acidic sites as well as pores. The acidic sites are responsible for breaking down the cross-linkages to get the desired products. The volume created by the pores helps to prevent the repolymerization reactions.[189] Metals used for generating hydrogen, and metal oxide through the metal hydrolysis reactions. This hydrogen helps in reductive depolymerization of lignin when using supported metal catalysts during hydrothermal liquefaction. The hydrogen breakdown to produce a hydrogen atom and a radical. The hydrogen radicals help to break the ether linkages to get the monomers and hydrogen atom used for the stabilizing phenoxide ion to get the stable products. In the hydrothermal liquefaction process, the hydrogen gas is produced *in-situ* and absorbed by the surfaces of the supported-metal catalysts which causes the dissociation of the hydrogen gas into atom and radical.[188] Hydrogen can be produced from the cheap and available water via metal hydrolysis.[190] The generation of hydrogen at high-temperature increase and promote the hydrodeoxygenation (HDO).[191]

The acid and alkali catalysts such as sulfuric acid, hydrochloric acid, phosphoric acid, Na_2CO_3, K_2CO_3, KOH, NaOH, and $Ca(OH)_2$ were widely used in the depolymerization of lignin.[192] However, the uses of homogeneous acid and alkali catalysts had a corrosion effect on liquefaction equipment,[193] need additional separation steps and require high cost for recovery of the catalysts.[194] The heterogeneous catalysts used for this study were hydrothermally stable at high temperature, environmentally friendly, easy to recover, and safe to dispose of. [193]

2.5. The possible pathways and mechanism of Alkali lignin in the presence of subcritical water and catalysts

The complete detailed mechanism for the depolymerization of alkali lignin still unclear. There are few literatures showed the possible pathways for the depolymerization of lignin in the presence of base and acid catalyst. The lignin depolymerization mechanism and cleavage of the β-O-4 bond were studied by using a lignin dimer.[195] The subcritical water source of proton and OH^-. β-O-4 dimer forms the α-carbon cation in the presence of acid followed by loss of formaldehyde via cleavage of C-C bond to form the vinyl ether. Vinyl ether undergoes hydrolysis to form the aldehyde and guaiacol. β-O-4 dimer in the presence of base undergoes E2 elimination at β, γ carbons to form the enol product which can be tautomerized into an aldehyde, and guaiacol.[195] The aldehyde undergoes hydrolysis to form the vanillin. Another possible way is hydrogen gas produced *in-situ* in hydrothermal liquefaction and adsorbed by the metal catalysts. Hydrogen gas dissociates into hydrogen atom and hydrogen radical at subcritical water condition. Hydrogen radical helps to cleave the β-O-4 linkage to get the phenolic monomers from the lignin.[188] Hydrogen atom helps to stabilize the phenoxide ion. Figure 2.26 shows the possible pathways of lignin depolymerization in the presence of subcritical water and catalysts.

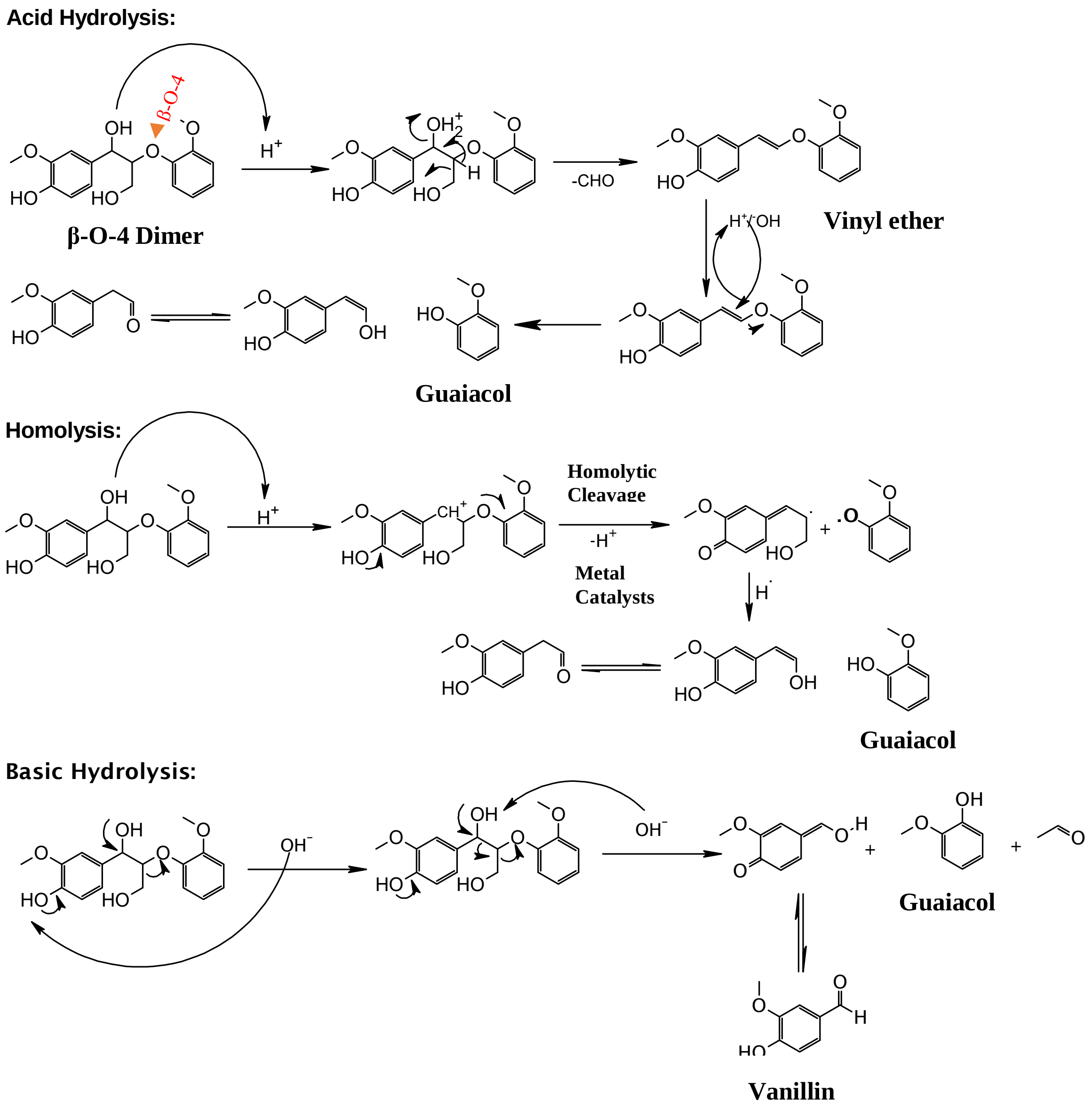


Figure 2.26. The possible pathways of lignin depolymerization in the presence of subcritical water and catalyst.

2.6. Summary

Product yield was calculated according to the following equation.

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

Y represents the yield of phenolic monomers and W is the weight of phenolic monomers and alkali lignin.

The Ni-Graphene catalyst showed the highest yield 41.16 ± 0.27 mg/g. The possible explanation for showing the highest yield is the high surface area of the Ni-Graphene. The total weight percent was calculated by using equation 1 and found to be 62% conversion in the presence of Ni-Graphene catalyst. The 10 % V-Ni/Zinc showed the lowest conversion yield than the without catalyst treatment because of the lowest surface area. The 5 % V/Zeolite (33.28 ± 0.44 mg/g) and 1.7% V/ZrO_2 (sulfate) (34.46±0.22 mg/g) catalysts showed the almost same conversion yield for the depolymerization of alkali lignin. The possible reason for the lowest yield at 15 minutes reaction time is, repolymerization of lignin and secondary decomposition of products.

In the hydrothermal liquefaction (HTL) process with subcritical water hydrogen, is helps in reductive depolymerization of lignin with supported catalysts. The in-situ hydrogen breaks down to produce the hydrogen radical and atom. The hydrogen radical initiates the depolymerization of lignin in the reaction and the hydrogen atom stabilizes the intermediate phenolic moiety in the reaction solution. A small amount of acetic acid was added at the stage of extraction and used as hydrogen donating solvent to stabilize the phenoxide ion in the depolymerization reaction [196].

In the HTL, process the hydrogen gas adsorbed by supported-metal catalysts surfaces and generates the hydrogen radical and atom. The hydrogen radical attacks the ether cross-linkages within the lignin polymer and cleaves the ether bonds results in the production of phenolic monomers from the lignin polymer.

The depolymerization of alkali lignin with subcritical water and Ni-Graphene catalyst is a potential method to produce the aromatic phenols from the alkali lignin. The performed reaction time (10 min) and reaction temperature (240℃) is lesser than other traditional methods [197]. The main advantage of this method was the usage of the green and most environmentally friendly, cheap, and universal solvent (subcritical water) for the depolymerization of alkali lignin instead of hazardous chemicals [198]. These reaction conditions and solvent prevent the repolymerization reaction, secondary decomposition, and formation of char in the reaction.

2.7. Conclusion

In this study, depolymerization of alkali lignin was investigated with subcritical water and different types of catalysts in relatively mild reaction conditions (240 ℃ for 10 minutes). The cleavage of β-O-4 bond promoted by the catalysts (Ni-Graphene, 5% V/Zeolite, and 1.7% V/ZrO_2 (Sulfate). The catalysts were able to convert the high molecular weight lignin into low molecular weight monomers in the presence of subcritical water. Among all the catalysts Ni-Graphene catalyst showed the best performance in terms of phenolic monomers yield. Ni-Graphene showed the 62% conversion of phenolic monomers from the alkali lignin. The treatment of alkali lignin with subcritical water and catalysts is green and eco-friendly to produce the greener chemical such as guaiacol, vanillin, acetovanillone, guaiacylacetone, and homovanillic acid. This study revealed that the reaction temperature, time, and solvent (subcritical water) played an important role in the lignin conversion and the production of phenolic monomers. To conclude, that the depolymerization of alkali lignin with subcritical water and Ni-Graphene catalyst is a great potential method to obtain the value-added phenolic monomers.

CHAPTER THREE

OPTIMIZATION OF REACTION CONDITIONS FOR THE DEPOLYMERIZATION OF ALKALI LIGNIN IN THE PRESENCE OF SUBCRITICAL WATER AND CATALYST

3.1. Introduction

Biomass is an organic material derived from living matter. Biomass is a renewable and alternative source for the production of chemicals.[199] The production of bio-waste materials from agriculture and industries is a main cause of pollution. There are few technologies developed for the destruction of these wastes into harmless and useful chemicals.[200] Lignocellulose is a plant-derived biomass and it consists of three types of components cellulose, hemicellulose, and lignin. Lignin is a complex biopolymer and building blocks of different aromatic phenols. Lignin is one of the raw materials for the production of aromatic chemicals.[60] Lignin is an effective source of biofuel and specialty chemicals such as phenolic monomers including phenols, guaiacols, syringol, and catechols.[201] These are well-known “green chemicals” that can be used as food additives and bio preservatives, pharmaceutical products, and industrial products for resins and plastics.[201] Lignin contain hydroxyphenyl propane units such as p-coumaryl, coniferyl, and sinapyl alcohols are connected with ether and carbon-carbon bonds.[154] It contains many oxygen functional groups phenolic compounds, hydroxyl, carbonyl group, carboxyl, ester, and ether bonds. β-O-4 linkage is a dominant bond in the lignin structure. So, the main strategy is breaking the β-O-4 linkage in the lignin.[202] Phenolic chemicals can be obtained from the lignin by chemical decomposition processes. These phenolic monomers are used for the synthesis of resins. Phenolic resins are used for the preparation of laboratory countertops, electric circuit boards, and adhesives. Approximately 50 million tons of lignin was produced every year worldwide as a by-product of the paper industry.[203] The industrial application of lignin is to substitute petroleum-derived phenol for the synthesis of phenol-formaldehyde (PF) resin.[26]

In recent years, many literatures on lignin liquefaction were studied using the aqueous-based solution or an organic solvent as the reaction medium.[25, 204, 205] The depolymerization of lignin in sub/supercritical fluids such as methanol [206, 207], and ethanol [208] has been studied by many researchers to obtain bio-oil products or phenolic chemicals with low molecular weights. The depolymerization of switchgrass lignin was studied using formic acid as a hydrogen source overnight at 350 °C in a sand bath.[209] The lignin degradation including hydrolysis, lignin catalytic cracking, lignin reduction, and oxidation have been reported and studied the utilization of lignin in the future.[4, 210, 211] All these methods require a high temperature, high pressure, longer reaction time, and chemicals for the depolymerization of lignin.

In this study, the lignin conversion was carried out in the presence of subcritical water and catalysts. Optimized the reaction conditions such as temperature, time, and pressure using the catalysts. The water in the liquefaction process could be an alternative reaction medium that serves as the reagent, solvent, and catalyst due to its unique properties under sub-and supercritical conditions. The density and dielectric constant of water decreases at the subcritical condition and it is influences the yield of phenolic monomers and promotes the degradation of lignin.[212] Subcritical water can hydrolyze many of the organic compounds that are catalyzed by enhanced ionic-water products and can achieve the water-molecule hydrothermal cleavage while providing a homogeneous phase for the organic-substance dissolution reactions.[213] From the previous objective of this study, selected the best catalysts (Ni-Graphene, 1.7% V/ZrO_2 (Sulfate) and 5% V/Zeolite) for the depolymerization of alkali lignin in the presence of subcritical water. The optimized reaction temperature was 240°C, time was 10 min and pressure was <21.5Mpa. This reaction temperature, pressure, and time were lesser than reported literatures.

3.2. Experimental procedure

3.2.1. Materials

Alkali Lignin was purchased from Sigma Aldrich (St. Louis, MO). Catalysts for this study was obtained from Dr. Gu, Department of Agriculture and Bio-system Engineering. Acetic acid for the protonation was purchased from Sigma Aldrich (St. Louis, MO). Ethyl acetate (99.9%) was purchased from the Fisher Scientific store for the extraction of phenolic monomers. O-Terphenyl internal standard purchased from Sigma Aldrich (St. Louis, MO). Deionized water is used as a solvent for the lignin depolymerization reactions.

3.2.2. Method

The depolymerization of alkali lignin reaction was conducted using the Subcritical Helix H_2O instrument from Applied Separation (Allentown, PA). 24ml of stainless-steel vessel used for the loading catalyst and alkali lignin. 250mg of alkali lignin and 25mg of catalyst were loaded into the vessel and passed 21ml of distilled water through the reservoir. The temperature conditions were 200^0C and 240^0C and allowed the reaction at these temperatures for 5,10 and 15 minutes. The reaction mixture was collected into the glass vial after the reaction time and filtered under a vacuum. 0.2 ml of acetic acid was added for the protonation of phenoxide ion. Ethyl acetate was used for the liquid-liquid extraction. The organic layer was collected from the aqueous layer and concentrated under N_2 gas. 1.5 ml of sample was collected into the GC vial for the GC-MS analysis. 100μl of O-Terphenyl was added as an internal standard for the quantification.

3.2.3. GC-MS Analysis

Phenolic monomers from the alkali lignin were identified and quantified by GC-MS. 5977B MSD and 7890B GC system from Agilent Technologies (Wilmington, DE) used for the product analysis. This GC-MS was equipped with a 30m*250μm*0.25μm film thickness DB-5 MS capillary column. Hydrogen gas is used as a carrier gas at a constant flow rate of 1.2 ml/min. The initial temperature of the oven was 50°C held for 0 min and then programmed from 50°C to 200°C at 20°C/min with an isothermal held for 1 min and from 200°C to 300°C at 40°C/min held for 2 min. The injection volume was 2μl. The ion source was electron impact (EI) and total ion chromatogram (TIC) used in GC-MS. The compounds were identified by comparing the data with the NIST library.

3.3. Results and Discussion

3.3.1. Identification of Products and Quantification

The optimization of reaction conditions for the depolymerization of alkali lignin was studied using three different types of catalysts and subcritical water. The catalysts were used for this study were Ni-Graphene, 1.7% V/ZrO_2 (Sulfate), and 5% V/Zeolite. The depolymerization of alkali lignin was studied at 200°C and 240°C for 5-, 10-, and 15-minutes reaction time. 12 different phenolic monomers were identified from the alkali lignin using Gas Chromatography-Mass Spectrometry (GC-MS). The quantification of major phenolic monomers was studied using their standard calibration curves. The quantified phenolic monomers were guaiacol, vanillin, acetovanillone, guaiacylacetone, isoeugenol, and homovanillic acid. Figure 3.1 shows the GC-MS chromatogram of phenolic monomers from the alkali lignin in the presence of subcritical water and Ni-Graphene catalyst at (a) 5 (b) 10 and (c) 15 minutes reaction time. Figure 3.2 shows the quantification results of phenolic monomers at 5,10-, and 15-minutes reaction time. Figure 3.3 shows the yield of phenolic monomers at 200°C and 240°C in the presence of Ni-Graphene catalyst. From figure 3.2 quantification data, 10 minutes reaction time showed the highest conversion of phenolic monomers from the alkali lignin.

From figure 3.3 quantification data 240°C showed the highest conversion yield from the alkali lignin. So, the optimized reaction temperature was 240°C, and the reaction time was 10 minutes. The optimized pressure was <21.5 Mpa.

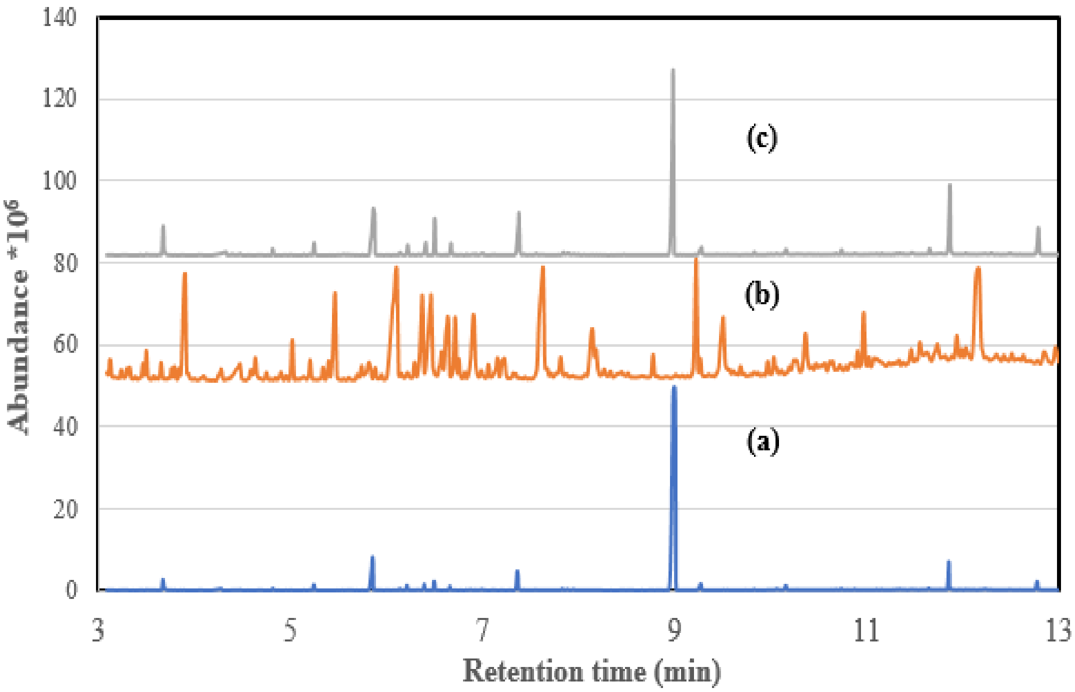


Figure 3.1. GC-MS chromatogram of phenolic monomers from the alkali lignin in the presence of subcritical water and Ni-Graphene catalyst for (a) 5 (b) 10 and (c) 15 minutes reaction time.

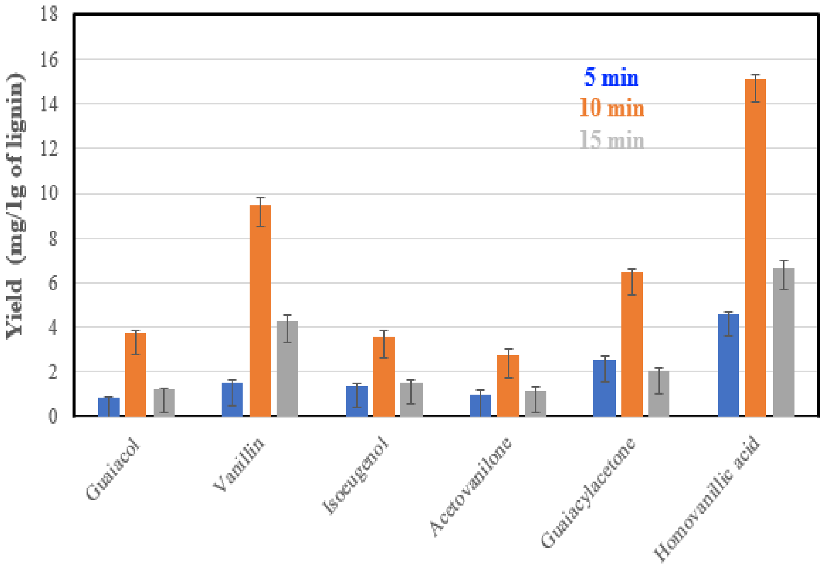


Figure 3.2. The yield of phenolic monomers in the presence of subcritical water and Ni-Graphene catalyst for 5, 10, and 15 minutes reaction time.

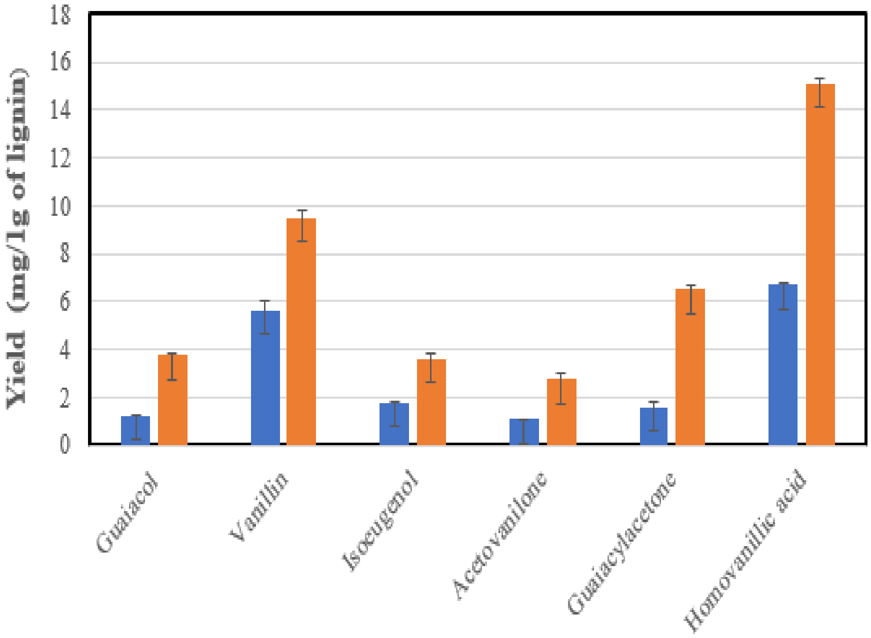


Figure 3.3. The yield of phenolic monomers for the depolymerization of alkali lignin in the presence of subcritical water and Ni-Graphene catalyst at 200 °C (blue) and 240 °C (Orange).

Figure 3.4 shows the GC-MS chromatogram of phenolic monomers from the alkali lignin in the presence of subcritical water and 1.7% V/ZrO_2 (Sulfate) catalyst for 5-, 10-, and 15-minutes reaction time. Figure 3.5 shows the yield of phenolic monomers at 5,10-, and 15-minutes reaction time. Figure 3.6 shows the quantification results of phenolic monomers at 200°C and 240°C. From the figure 3.5 quantification data, the 10 minutes reaction time was showed the highest conversion of phenolic monomers from the alkali lignin. From the figure 3.6 quantification data 240°C showed the highest conversion of phenolic monomers from the alkali lignin. So, the optimized reaction temperature was 240°C, and the reaction time was 10 minutes. The optimized pressure was <21.5 Mpa.

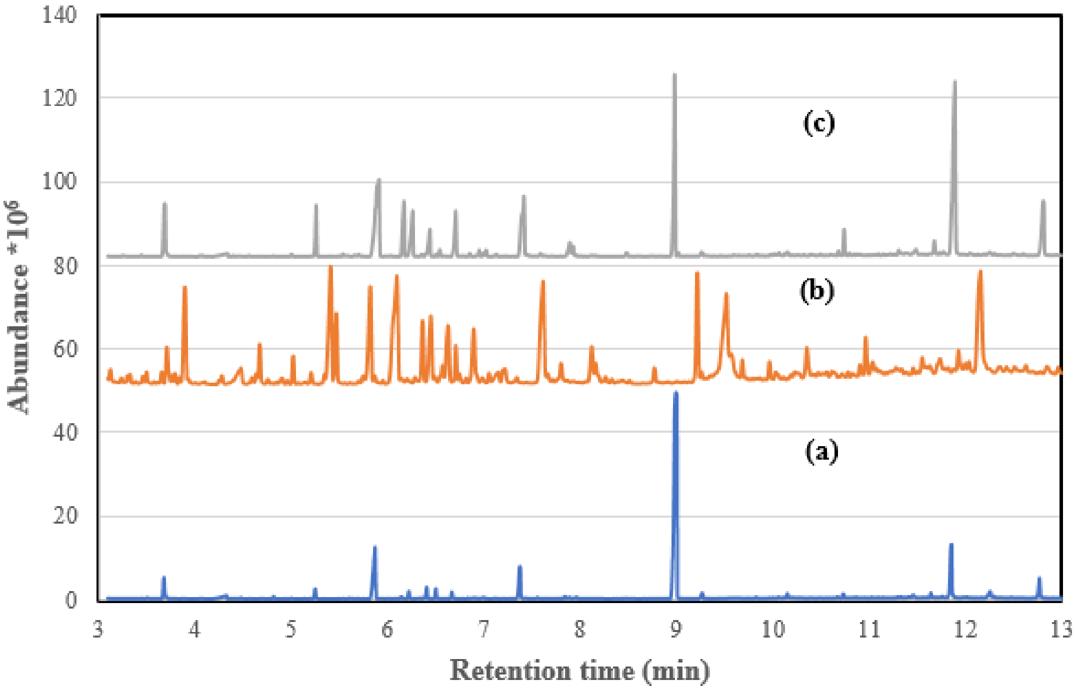


Figure 3.4. GC-MS chromatogram of phenolic monomers from the alkali lignin in the presence of subcritical water and 1.7% V/ZrO_2 (Sulfate) catalyst for (a) 5 (b) 10 and (c) 15 minutes reaction time.

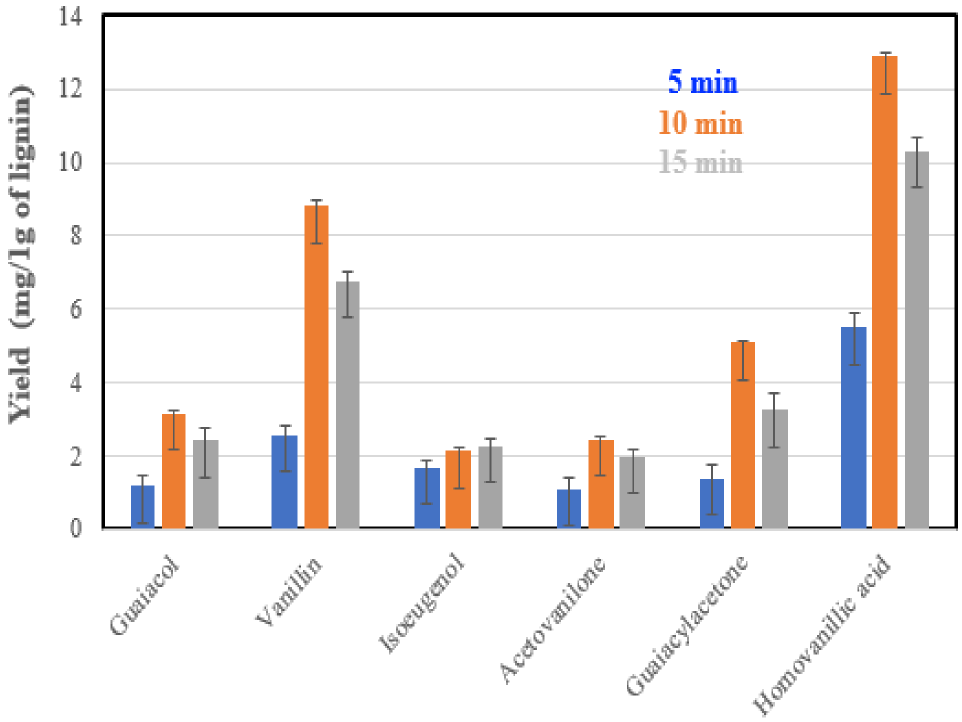


Figure 3.5. Yield of phenolic monomers in the presence of subcritical water and 1.7% V/ZrO$_2$ (Sulfate) catalyst for 5-, 10-, and 15-minutes reaction time.

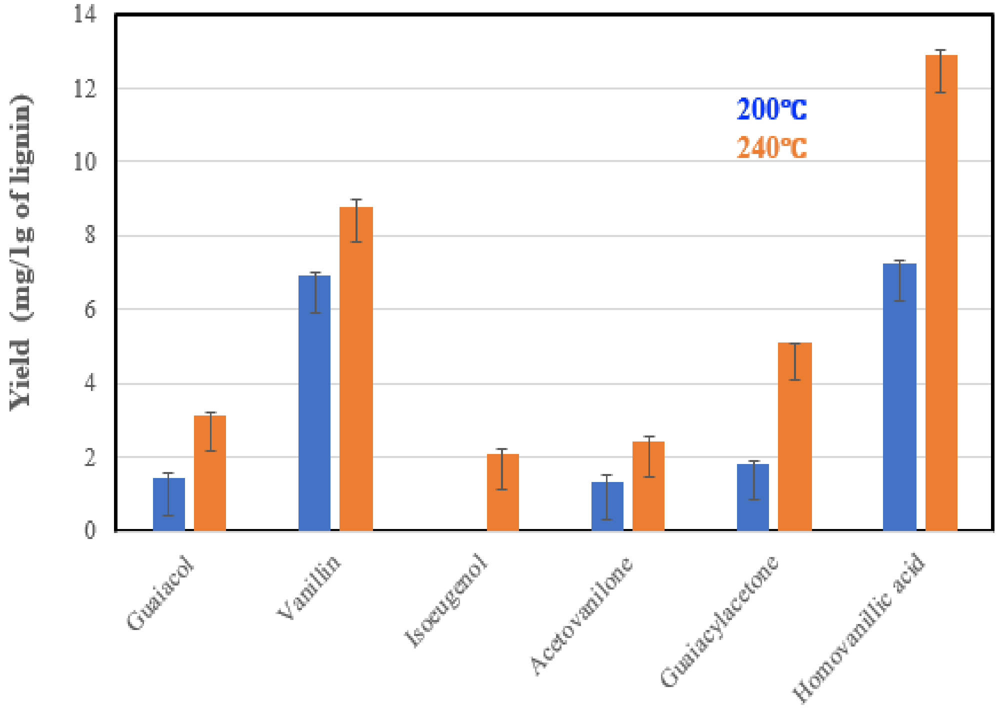


Figure 3.6. The yield of phenolic monomers for the depolymerization of alkali lignin in the presence of subcritical water and 1.7 % V/ZrO_2 (Sulfate) catalyst at 200 °C and 240 °C.

Figure 3.7 shows the GC-MS chromatogram of phenolic monomers from the alkali lignin in the presence of subcritical water and 5% V/Zeolite catalyst at 5-, 10-, and 15-minutes reaction time. Figure 3.8 shows the quantification results of phenolic monomers at 5,10-, and 15-minutes reaction time. Figure 3.9 shows the quantification results of phenolic monomers at 200°C and 240°C. From the figure 3.8 quantification data the 10 minutes reaction time was showed the highest conversion of phenolic monomers from the alkali lignin. From the figure 3.9 quantification data 240°C showed the highest conversion of phenolic monomers from the alkali lignin. So, the optimized reaction temperature was 240°C, and the reaction time was 10 minutes. The optimized pressure was <21.5 Mpa.

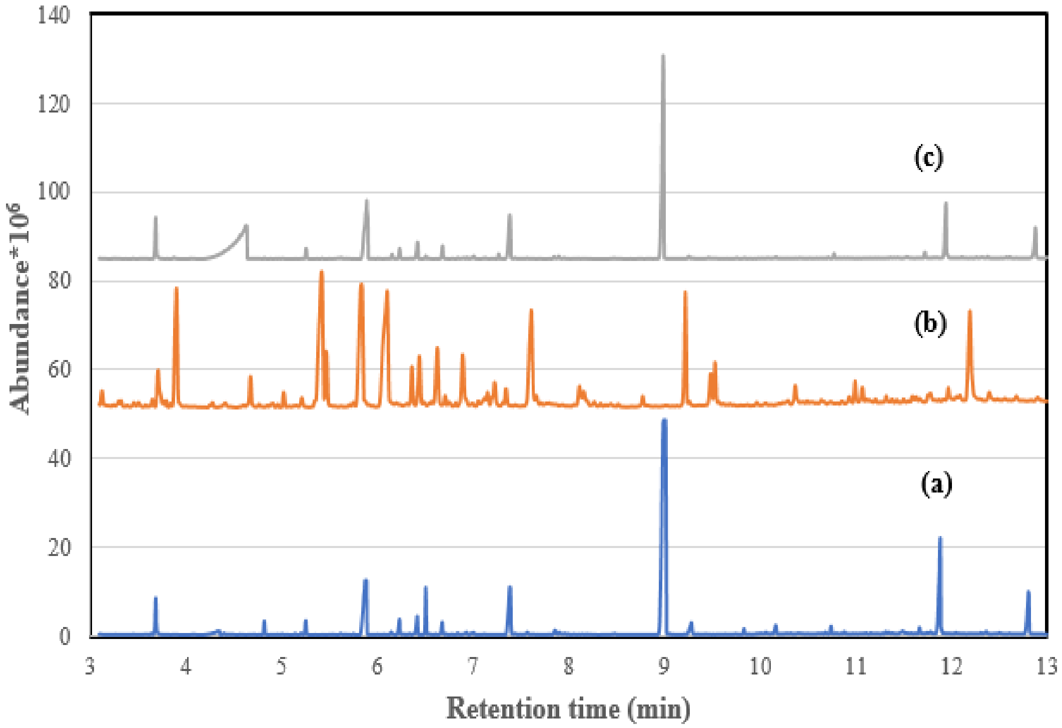


Figure 3.7. GC-MS chromatogram of phenolic monomers from the alkali lignin in the presence of subcritical water 5% V/Zeolite catalyst for (a) 5 (b) 10 and (c) 15 minutes reaction time

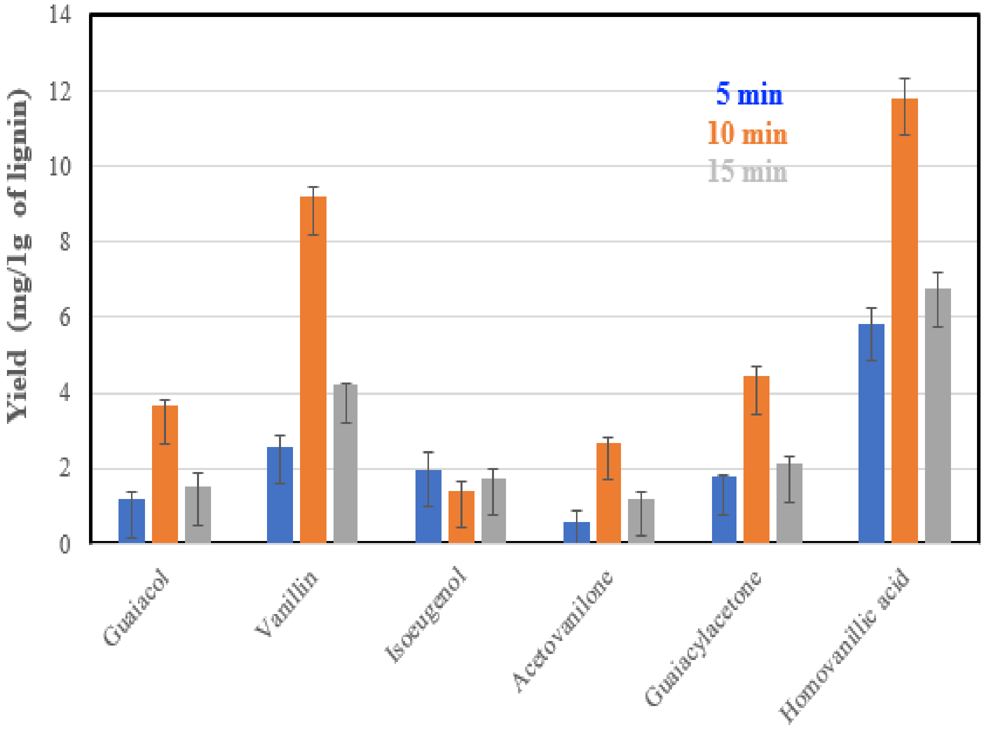


Figure 3.8. The yield of phenolic monomers for the depolymerization of alkali lignin in the presence of subcritical water and 5% V/Zeolite catalyst for 5, 10, and 15 minutes reaction time.

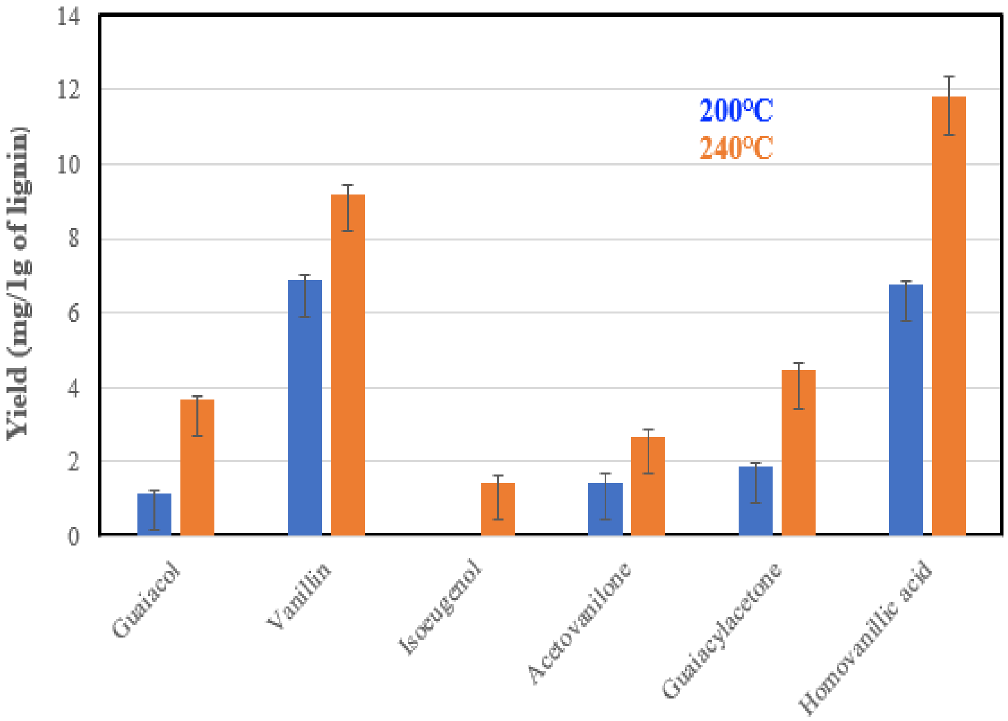


Figure 3.9. The yield of phenolic monomers for the depolymerization of alkali lignin in the presence of subcritical water 5% V/Zeolite catalyst at 200 °C and 240 °C.

3.4. Summary

Table 3.1 shows the total yield of phenolic monomers for the depolymerization of alkali lignin in the presence of subcritical water and three types of catalysts for 5, 10, and 15 reaction time. The 10 minutes reaction time showed the highest conversion yield from the lignin comparative 5 and 15 minutes reaction time. GC-MS chromatogram concludes that the 10 minutes reaction time showed the highest selectivity comparative 5 and 15 minutes reaction time. The possible reason for the low yield at 15 minutes reaction time is, repolymerization of lignin and secondary decomposition of products. Table 3.2 shows the total yield of phenolic monomers at 200°C and 240°C in the presence of three types of catalysts. The 240°C reaction temperature showed the highest yield in the presence of three catalysts. The temperature and reaction time plays an important role in the depolymerization of alkali lignin. The major phenolic monomers obtained by cleavage of β-O-4 bond in the presence of subcritical water and catalyst are vanillin and homovanillic acid.

Table 3.1. The total yield of phenolic monomers from the alkali lignin at 240°C for 5-, 10-, and 15-minutes reaction time.

	Yield (mg/g of lignin)		
Catalyst	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

Table 3.2. The total yield of phenolic monomers from the alkali lignin at 200 and 240°C

	Yield (mg/g of lignin)	
Catalyst	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

3.5. Conclusion

Optimized the reaction conditions for the depolymerization of alkali lignin in the presence of subcritical water and three different types of selected catalysts. Studied the depolymerization reactions at 200°C and 240°C for 5, 10- and 15-min reaction time and conclude that the 240°C reaction temperature and 10 min reaction time was the selective conditions for the depolymerization of alkali lignin. The optimized pressure was <21.5 MPa. These reaction times, temperatures, and pressure were lesser than reported literatures. This approach is a low cost, green, and environmentally friendly.

CHAPTER FOUR

EXTRACTION AND DEPOLYMERIZATION OF LIGNIN FROM THE PINE SAWDUST AND PISTACHIO SHELLS BIOMASS

4.1. Introduction

Lignocellulosic biomass is the world's most abundant renewable resource to produce biofuels, biomaterials, and chemicals.[214] The main components of biomass are cellulose, hemicellulose, and lignin.[215] Biomass is an alternative source to replace fossil fuels and reduce global warming.[216] Biomass include food crops, grassy and woody plants, residues from agriculture or forestry, oil-rich algae, and organic component of municipal and industrial wastes.[217]

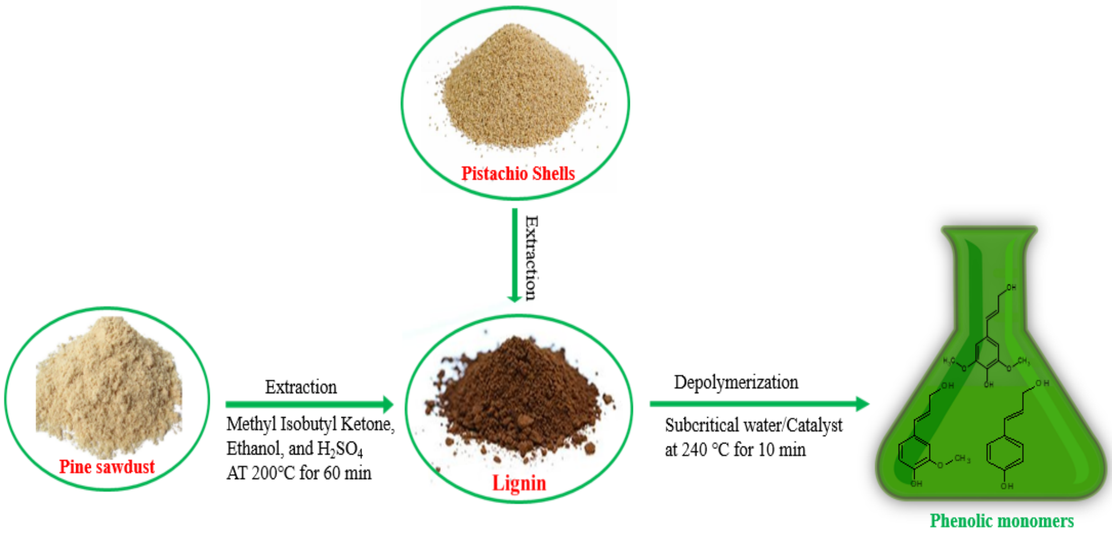
Pine sawdust, a common waste material from many forestry and industrial sectors.[218] Pine sawdust is an excellent raw material for biorefinery.[219] Pistachio shells (PS) is a potential alternative lignocellulosic biomass and generated in considerable amounts, as the annual production of pistachios in the last 10 years is between 800 to 900 ktones.[220] Pistachios is cultivated in Iran, the Middle East, the United States, and Mediterranean countries.[221] Iran is the largest pistachio producer in the world, yielding about 40% of the global production in the year of 2009.[222] The U.S. is the second-largest country and produces 27% of the total global production.[222] Pistachio shells are mostly used for animal feed or wood fuel.[221] This lignocellulosic biomass is an alternative source of 25.2% of Lignin.[223] Pistachio shells are used for the production of activated carbon by pyrolysis and gasification.[221]

Lignin is a naturally available biomass and aromatic polymer.[224] Lignin has a 3-D amorphous structure consisting of methoxylated phenylpropane units. Lignin is bonded together by C-C, β-β, β-1, β-5, and β-O-4 linkages.[225] Lignin is a source of phenolic monomers, which is widely used in the preparation of resins and polymers. Lignin can be used in binders and additives in cement. Lignin is applicable in many areas such as emulsifiers, dyes, synthetic flooring, dispersal agents, and paints.[226]

There are several techniques used for the extraction of lignin from the biomass such as using ionic liquids, acids, alkaline solutions, organic solvents, and hydrogen peroxide. In this study, the biomass used for the extraction of lignin were pistachio shells and pine sawdust. Herein, organic solvents are used for the extraction of lignin from the pistachio shells and pine sawdust.

There are several methods reported for the depolymerization of lignin such as pyrolysis, acid-catalyzed depolymerization, base-catalyzed, enzymatic depolymerization, using ionic liquids, supercritical CO_2 depolymerization, and metal-catalyzed depolymerization.[227] In the pyrolysis method, lignin is subjected to temperature in the range of 300-1000 °C in the absence of air.[228] In this study, subcritical water and catalyst were used for the depolymerization of extracted lignin. Subcritical water is defined as, water that exists in a liquid state above its boiling point and below its critical temperature. This technique is the environmentally friendly and green approach for the depolymerization of lignin.

Graphical Abstract:



4.2. Materials

Pine sawdust and Pistachio shells biomass were obtained from the Department of Agricultural and Biosystem Engineering, South Dakota State University. These biomasses were blended and reduced the particle size to 850 µm. The extraction solvents methyl isobutyl ketone, ethanol, and H_2SO_4 were purchased from the Fisher Scientific store. The catalyst (Ni-Graphene) was obtained from the Department of Agricultural and Biosystem Engineering for depolymerization reaction. DMSO-d_6 was purchased from the Fisher Scientific store (Fair Lawn, New Jersey).

4.3. Experimental procedure

4.3.1. Extraction of Lignin from Pine sawdust and Pistachio shells

The biomass used for the extraction of lignin were pistachio shells and pine sawdust. The Accelerated Solvent Extractor (ASE Dionex model 350, Thermo-Fisher, Sunnyvale, CA) was used for the extraction of lignin from the biomass. The 34 ml of stainless-steel cells were used for the loading biomass. Biomass samples (0.5 -1 g) were loaded into the cell and cell packed with Diatomaceous earth. The ASE bottles were used for the collecting sample. The solvent mixture used for the extraction was Methyl Isobutyl ketone and ethanol in the ratio of 7:3 (v/v %) as a solvent A and water and 0.1 M H_2SO_4 used as a solvent B. The following conditions were used for the extraction of lignin from the pistachio shells and pine sawdust.

- Temperature: 200°C
- Pressure: 1400-1530 psi
- Heat time: 9 min
- Static time: 60 min
- Purge time: 300 sec
- Rinse volume %: 100
- Cycles: 2

The liquid fraction was collected after the digestion process and added water to separate two phases and collected the organic phase from the aqueous phase. The organic phase was separated and concentrated overnight in a fume hood and dried the sample in the oven at 50°C for 30 minutes and weighed the sample. The extracted lignin was confirmed with the ^1H NMR, FTIR, and TGA analysis.

4.3.2. Sample Preparation

Figure 4.1 shows the sample preparation for the extraction of lignin from the pine sawdust and pistachio shells biomass.

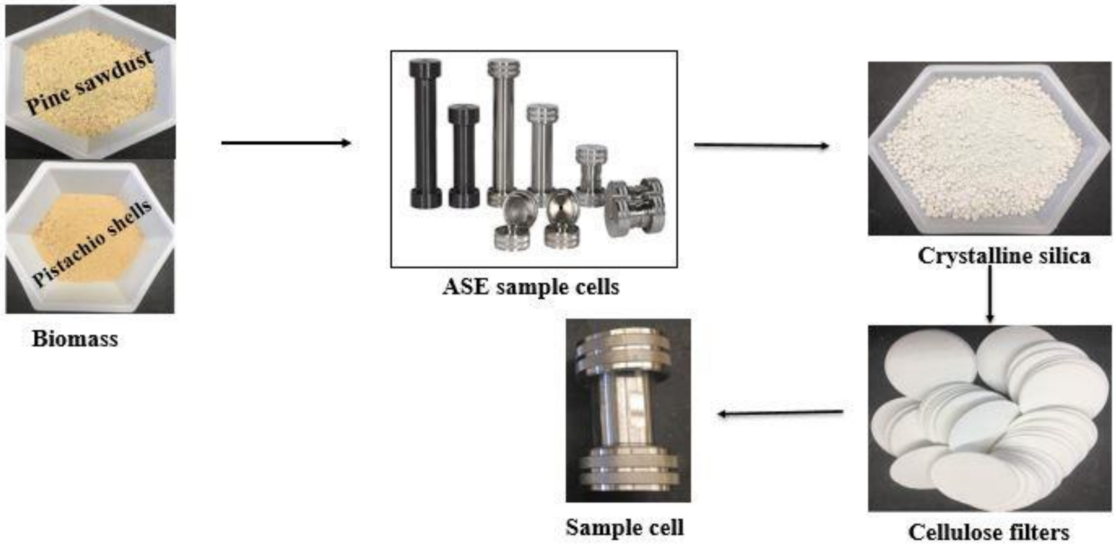


Figure 4.1. Sample preparation for the extraction of lignin from the biomass

4.3.3. Experimental setup

Figure 4.2 shows the stepwise process for the extraction of lignin from the pine sawdust and pistachio shells biomass.

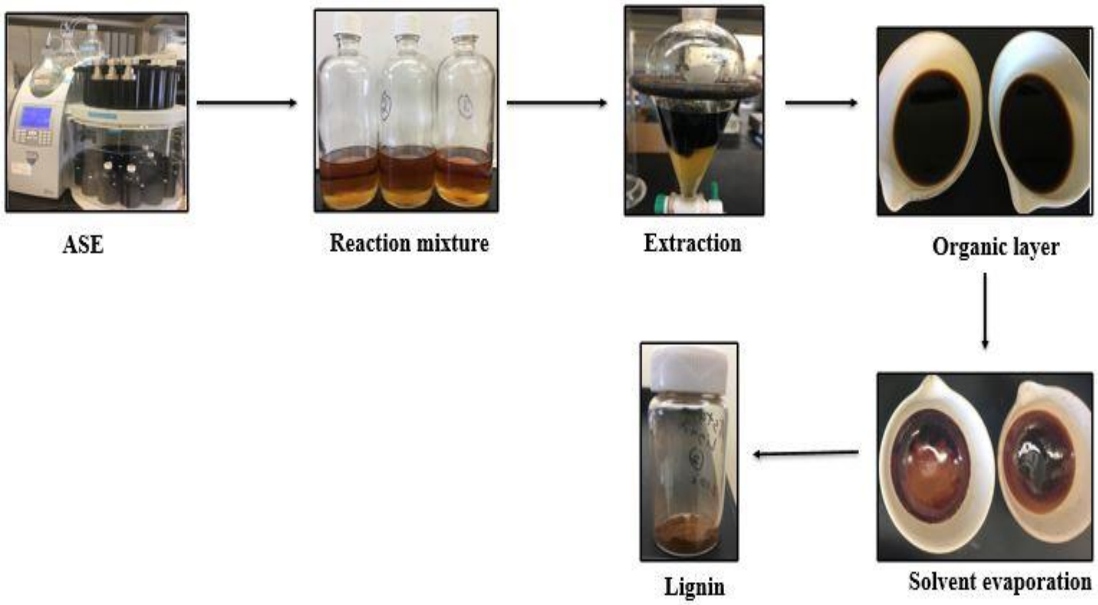


Figure 4.2. Stepwise process for the extraction of lignin from the biomass

Figure 4.3 shows the extraction of lignin from the different temperature conditions. The three different temperature conditions were used for the extraction process. The temperatures were used for this process was 140°C, 170°C, and 200°C. The extraction yield was showed at 140°C is 6.63%. 170°C is 17.3%, and at 200°C is 23.5%. The highest extraction yield was achieved at 200°C for 60 min.

Figure 4.3. Extraction of lignin from biomass at different temperatures.

4.3.4. Depolymerization of Extracted lignin from Pistachio shells

The depolymerization of extracted lignin was performed in the Helix Subcritical H_2O instrument (Applied separation, Allentown, PA) using subcritical water and catalyst. The Ni-Graphene catalyst was used for the depolymerization process. 0.2500 g of extracted lignin and 0.025 g of Ni-Graphene was loaded into the 24 ml stainless-steel vessel. The optimized conditions from previous studies were applied for the process. 21 ml/min distilled water passed into the stainless-steel vessel. The temperature was used for the reaction was 240°C for 10 minutes. The reaction mixture was collected after the reaction and filtered under a vacuum. The acetic acid was added to the filtrate for the protonation of phenoxide ion. The phenolic monomers extracted using ethyl acetate. The sample was concentrated under N_2 gas. The concentrated sample was analyzed by using GC-MS.

4.4. Results and Discussion

4.4.1. Characterization of extracted lignin

The extracted lignin was confirmed by using Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), and ^{1}H NMR. These techniques provide detailed qualitative information on structural futures including functional groups and types of chemical bonds.

4.4.1.1. FTIR Spectroscopy

FTIR spectroscopy is a popular technique for the identification of functional groups present in the lignin. The extracted sample dissolved in DMSO for the analysis. FT-IR measurements of extracted lignin were taken using the Nicolet iS5 Thermo Scientific instrument. The typical functional groups present in the lignin such as hydroxyl, carbonyl, methoxy, carboxyl, and aromatic and aliphatic C-H, can be identified in the FTIR spectrum. Figure 4.4 shows the FTIR spectrum of extracted lignin from the pine sawdust, and Figure 4.5 shows the FT-IR spectrum of extracted lignin from pistachio shells. Figure 4.6 shows the FT-IR spectrum of commercial lignin. Table 4.1 shows the identified functional groups and their frequency range.

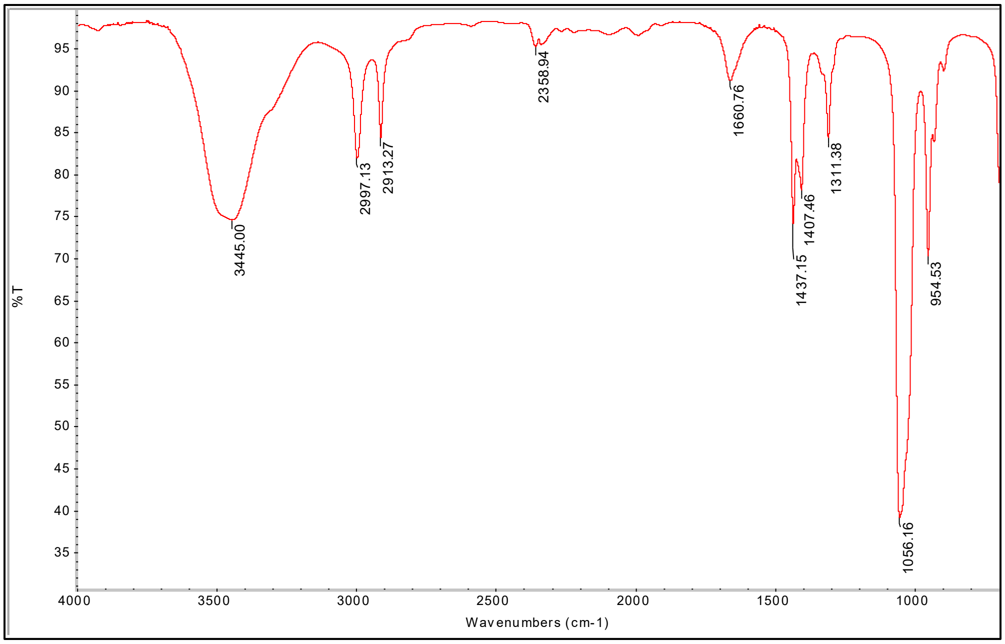


Figure 4.4. FT-IR spectrum of extracted lignin from pine sawdust biomass.

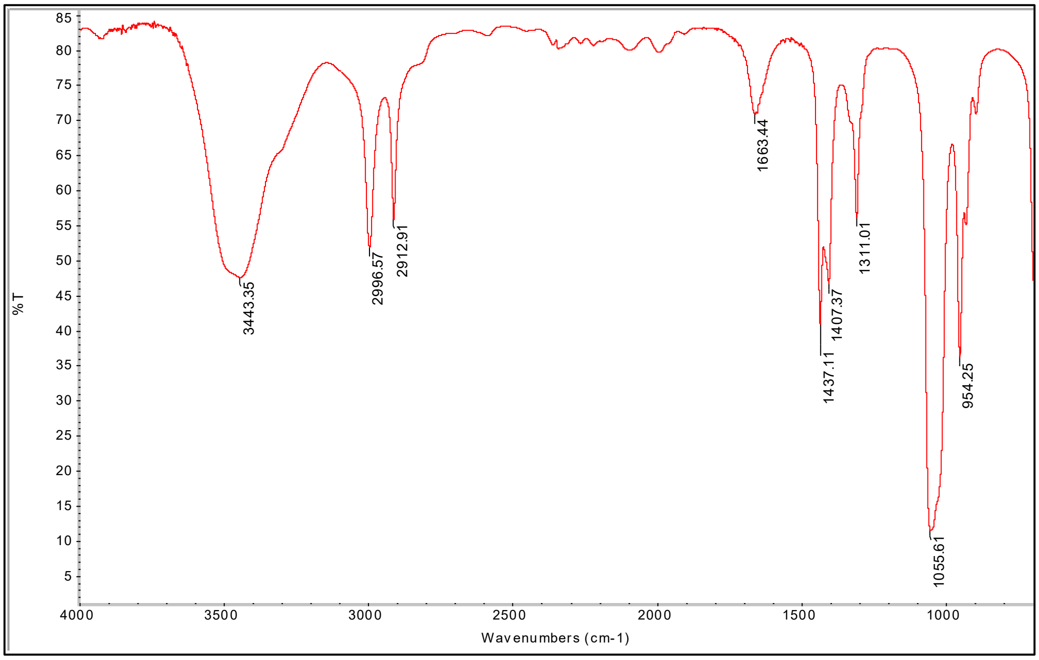


Figure 4.5. FT-IR spectrum of extracted lignin from pistachio shell biomass.

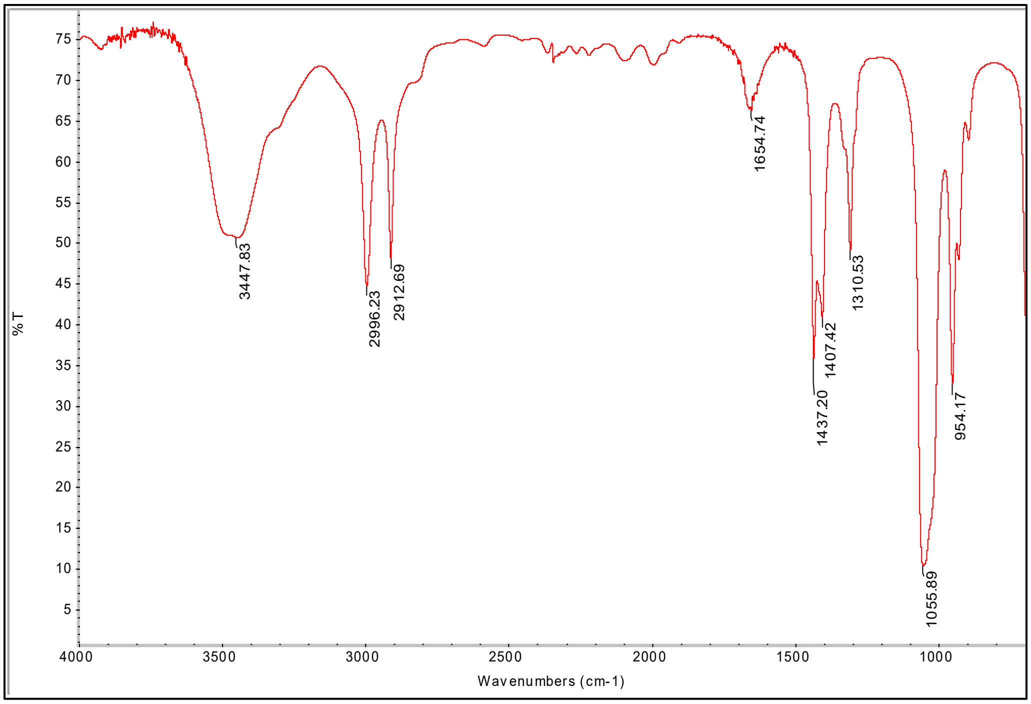


Figure 4.6. FT-IR spectrum of commercial lignin

Table 4.1. Functional group assignment of FTIR analysis of extracted lignin from pine sawdust and pistachio shells biomass.

Absorption band (cm^{-1})	Functional group
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 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

4.4.1.2. ^{1}H NMR Spectroscopy

^{1}H NMR spectroscopy used for the qualitative analysis of the extracted lignin from the biomass. The extracted lignin sample was dissolved in DMSO-d_6 solvent for the analysis.

600 MHz Bruker Spectro spin NMR (Billerica, MA) 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. ^{1}H NMR is used for the detection of the chemical environment of the proton. In the spectra, the signal observed around 7.5 ppm can be assigned to aromatic protons of H units, and the other two chemical shifts 7.5 ppm and 6.5 ppm are attributed to aromatic protons in G and S units. The signals in the range of 4.0-3.5 ppm are attributed to the proton in methoxy groups. The signal in the range of 0.5-1.0 ppm is attributed to $-CH_3$ proton and 1.0-1.5 from $-CH_2$ proton. Figure 4.7 shows the ^{1}H NMR spectrum of extracted lignin from pistachio shells (green), pine sawdust (red), and commercial lignin (blue). Table 4.2 shows the assigned functional groups and their chemical shifts.

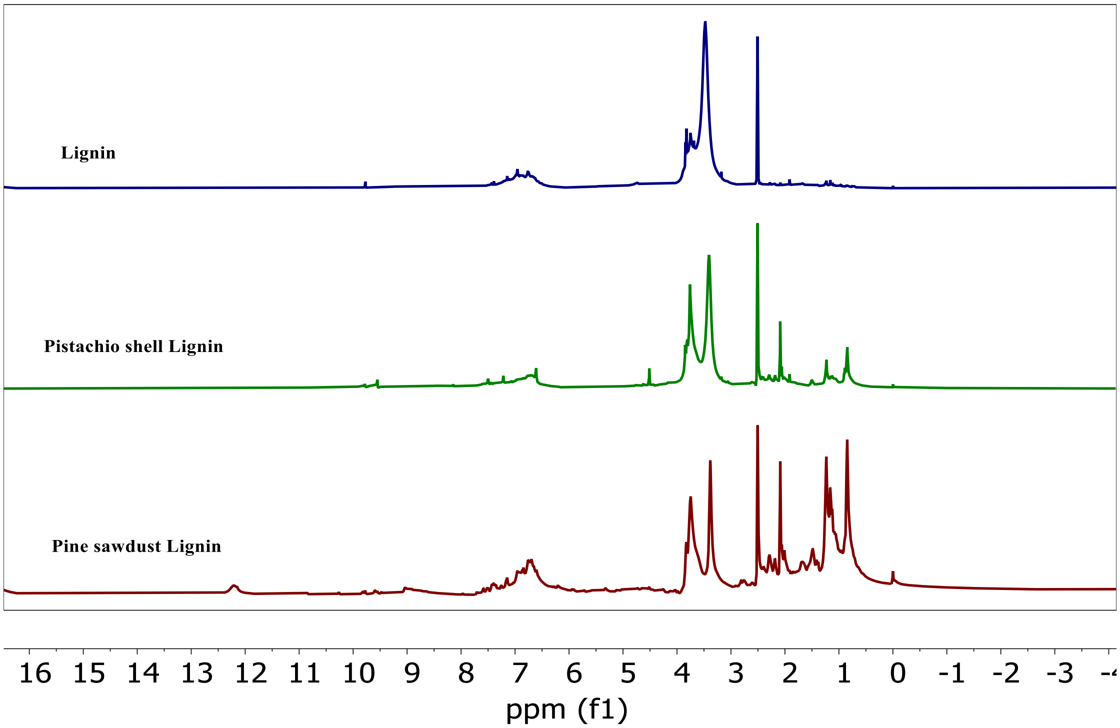


Figure 4.7. ^{1}H NMR spectrum of extracted lignin from pistachio shells (green), pine sawdust (red) and commercial lignin (blue)

Table 4.2. Functional group and chemical shift

Chemical shift (ppm)	Group
0.5-1.0	$-CH_3$
1.0-1.5	$-CH_2$
3.5-4.0	$-OCH_3$
6.5-7.5	Aromatic -H

4.4.1.3. Thermogravimetric analysis (TGA)

The thermo-gravimetric analysis was to determine the thermal stability and decomposition temperature of the extracted lignin from pine sawdust and pistachio shell biomasses. TGA measurements were taken using TG/DTA220 Seiko (Tokyo, Japan) Instruments operating in a nitrogen environment. 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 sources. TGA curves reveal the weight loss percentage of materials with respect to the temperature of thermal degradation. Thermal degradation data indicates weight loss. Lignin structure is composed of mostly aromatic rings having various branching, these chemical bonds lead to a wide range of degradation temperature from 100 to 560 °C. Figure 4.8 shows the TGA plots of extracted lignin from pine sawdust and pistachio shells and commercial lignin obtained under nitrogen atmosphere at 10℃/min. Degradation of the lignin sample is divided into three stages. In stage one, the initial weight loss step occurred at 30-120°C due to the evaporation of water absorbed. Stage two is seen to take place around 180-350°C and is attributed to the degradation of components of carbohydrates in the lignin samples, which are converted into gases. The final stage of the degradation occurred over a wide range of temperatures above 350°C. Within this stage, degraded volatile products derived from lignin including phenolics and alcohols.

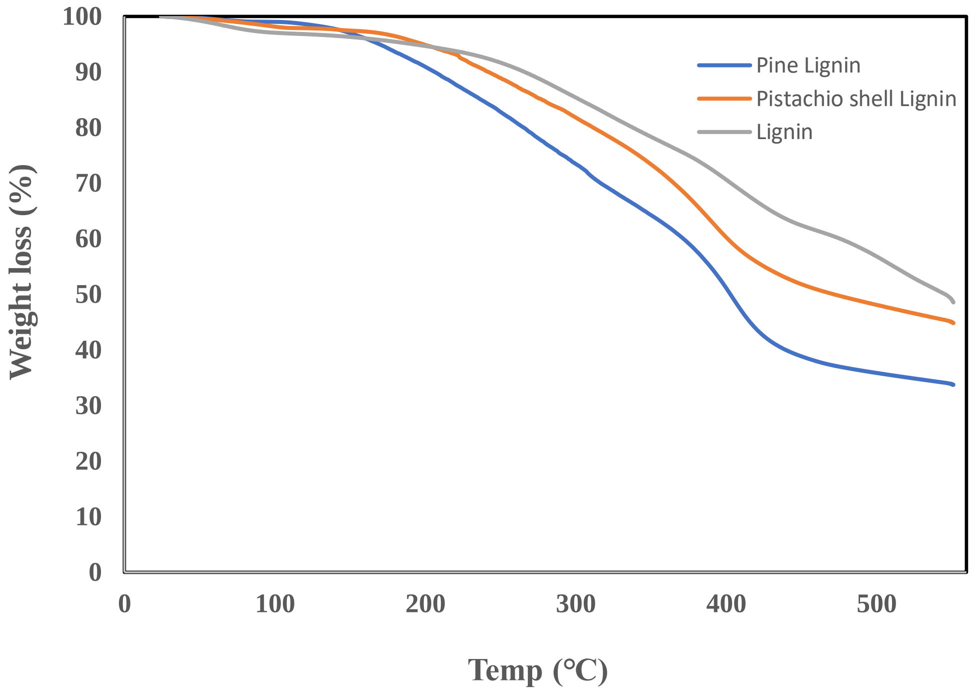


Figure 4.8. TGA plots of extracted lignin from pine sawdust and pistachio shells and commercial lignin obtained under nitrogen atmosphere at 10°C/min

4.4.1.4. Identification of Phenolic monomers using GC-MS

Phenolic monomers from the lignin were identified by GC-MS. 5977B MSD and 7890B GC system from Agilent Technologies (Wilmington, DE) used for the GC-MS analysis. This GC-MS was equipped with a 30m*250µm*0.25µm film thickness DB-5 MS capillary column. Hydrogen was employed as a carrier gas at a constant flow rate of 1.2 ml/min. The initial temperature of the oven was 50°C held for 0 min and then programmed from 50°C to 200°C at 12°C/min with an isothermal held for 1 min and from 200°C to 300°C at 20°C/min held for 1 min. The injection volume was 2µl. The ion source was electron impact (EI) and used total ion chromatogram (TIC) used in GC-MS. The compounds were identified by comparing the data with the NIST library. Figure 4.9 shows the GC-MS chromatogram of depolymerization products of extracted lignin from pistachio shells and Figure 4.10 shows the relative abundance of phenolic monomers from the pistachio shell lignin.

Table 4.3 shows the identified phenolic monomers from the extracted lignin from the pistachio shell biomass. 12 different phenolic monomers were identified from the extracted lignin at 240°C for 10 min reaction time with subcritical water and Ni-Graphene catalyst. The reaction time and temperature are very low comparative other depolymerization reactions. Subcritical water is used for the depolymerization of lignin. This solvent is green and environmentally friendly comparative other solvents.

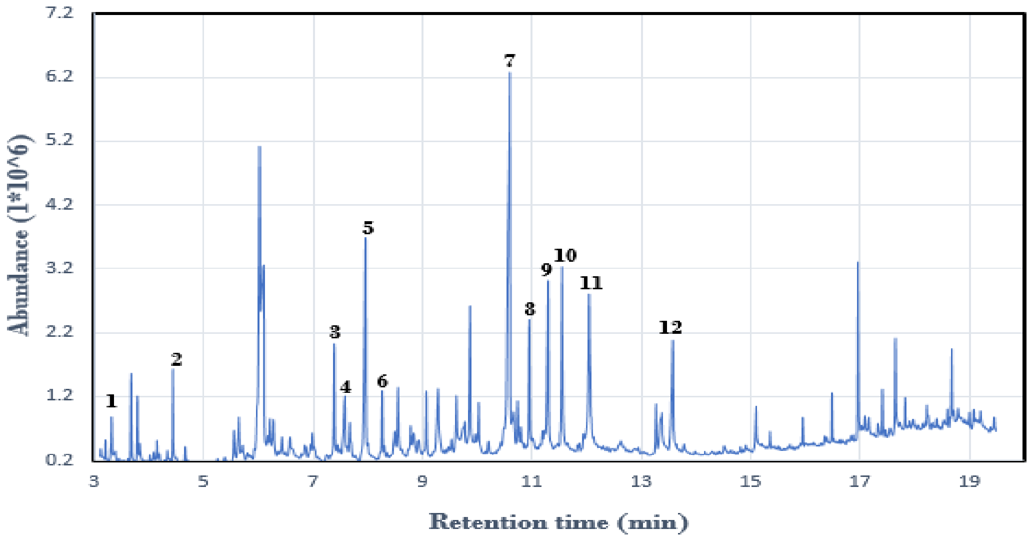


Figure 4.9. GC-MS chromatogram of phenolic monomers from the pistachio shell lignin

Table 4.3. Identified phenolic monomers and retention time of Pistachio shell lignin.

No	Retention time (min)	Phenolic monomer	Relative abundance (%)
1	3.319	Phenol	0.63
2	4.429	Guaiacol	1.15
3	7.384	Syringol	2.02
4	7.574	m-Hydroxy benzaldehyde	2.23
5	7.948	Vanillin	5.52
6	8.548	Propyl guaiacol	1.95
7	10.584	Syringaldehyde	12.82
8	10.958	Methoxy eugenol	2.41
9	11.290	Coniferyl aldehyde	4.13
10	11.545	Synapyl alcohol	3.85
11	12.050	Trimethoxybenzylalcohol	4.93
12	13.569	Synapaldehyde	3.51

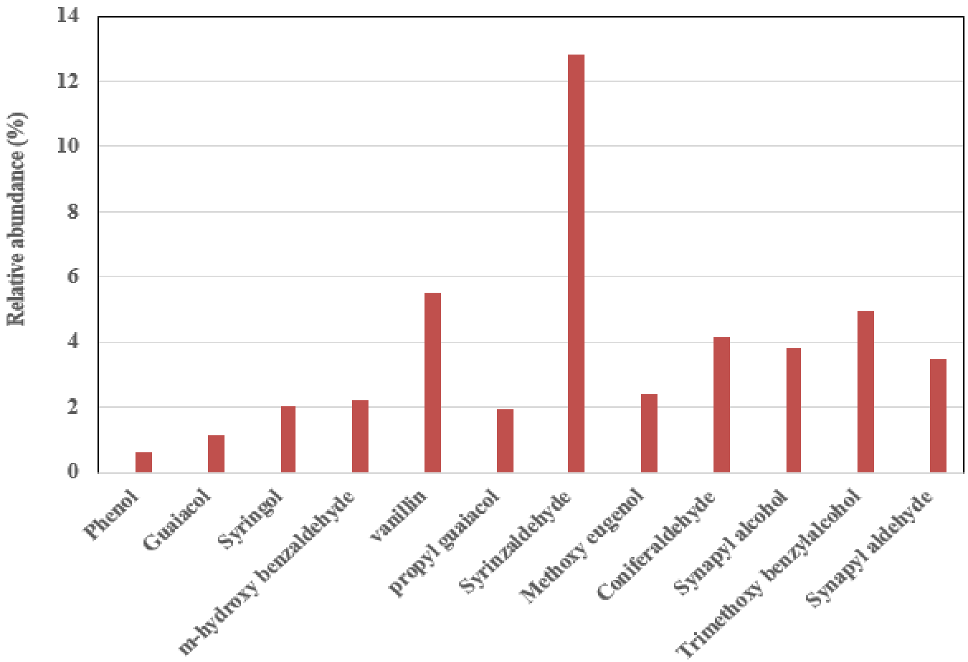


Figure 4.10. The relative abundance of phenolic monomers from the pistachio shell lignin

4.5. Conclusion

The extraction of lignin from the pine sawdust and pistachio shells were studied using organic solvents. The yield was found from the pistachio shell was 23.57 ± 3.38 % and from the pine sawdust was 22.86 ± 1.52%. The depolymerization of extracted lignin from pistachio shell was studied using subcritical water and Ni-Graphene catalyst at 240°C for 10 minutes. The phenolic monomers from the lignin were identified using GC-MS. The total yield of phenolic monomers was found to be 45.2% from the extracted lignin from the pistachio shell.

CHAPTER FIVE

CONCLUSION AND FUTUREWORK

The renewable energy sources brought the special attention to replace the nonrenewable resources such as coal, natural gas, and fossils. Utilization of nonrenewable sources for the production of chemicals impact on the environment as well as human health. It is necessary to use the renewable energy sources such as biomass, solar energy, and wind to save the nature and reducing global warming. Biomass is a promising resource to produce the chemicals and biofuels for future generation and replacing the fossils. Biomass is an organic material that comes from plants and animals. Lignocellulosic biomass is a plant derived material and excellent source for the generating biofuel, chemicals, and energy. Lignocellulosic biomasses consist of cellulose, hemicellulose, and lignin.

This dissertation is completely focused on utilization of lignin to produce value added aromatic chemicals for the various industrial application. Lignin is a highly complex biopolymer and copolymer of coniferyl alcohol, synapyl alcohol, and *p*-coumaryl alcohol. These monomers are excellent chemicals to synthesis of resins and polymers. The challenging question is to break the chemical bonds in lignin to produce the aromatic monomers. There are several techniques such as acid catalyzed depolymerization, base depolymerization, pyrolysis, ionic liquid depolymerization, and sub-and supercritical fluid depolymerization reported for the depolymerization of lignin. But these methods have few drawbacks such as high operating conditions (temp and pressure), uses of chemicals, and special designed equipment for the process.

The first part of this dissertation is that to develop the ecofriendly method for the depolymerization of lignin. In this study, the green solvent (subcritical water) and catalyst used for the depolymerization process. Subcritical water and catalysts were promoting the depolymerization of lignin. The operating conditions were used for this study was 240°C and 10 minutes reaction time. The different types of heterogeneous catalysts were used for this study. The Ni-Graphene catalyst showed the highest yield of phenolic monomers from the lignin. 12 different phenolic monomers were identified by using GC-MS. The major phenolic monomers were identified as vanillin and homovanillic acid. The reaction temperature, pressure, and time lower than traditional methods. The conclusion of the first objective is that developed the viable, green, and environmentally friendly technique to produce bio-oil and value-added chemicals.

The second part of this study was to optimize the conditions for the depolymerization of lignin. The depolymerization of lignin studied at 200 and 240°C for 5, 10, and 15 minutes rection time using subcritical water and selected catalysts. The highest conversion yield was found at 240°C for 10 minutes reaction time. The possible reason for showing the lower yield at 200° C and 15 minutes reaction time is repolymerization of lignin. Increased in temperature resulted in an increased the phenolic monomers.

The final part of this study was to extract the lignin from the waste biomaterial and perform the depolymerization of extracted lignin using subcritical water and Ni-Graphene catalyst. The biomass was used for the extraction of lignin was pine sawdust and pistachio shells. These biomasses consist high percentage of lignin. The ASE instrument used for the extraction of lignin from the biomass. The solvents were used for the extraction of lignin were MIK, H_2SO_4, ethanol, and water. The extraction of lignin was performed at 140°C, 170°C, and 200°C for 60 minutes reaction time. The highest extraction of lignin was observed at 200°C for 60 minutes reaction time. The extraction yield was found from the pine sawdust was 22.86 ± 1.52% and pistachio shell was 23.57 ± 3.38%. The depolymerization of extracted lignin was performed using subcritical water and Ni-Graphene catalyst at 240°C for 10 minutes reaction time. The 12 different phenolic monomers with 45.2% yield were found from the extracted lignin. This study concludes that the utilization of biowaste materials to produce the valuable chemicals will bring the more profit to the industries and decrease the global warming as well as environmental pollution.

The future work includes, this depolymerization method using green solvent (subcritical water) and catalyst need to be evaluated to determine the applicability of the process on industrial scale. The future generation needs to be more focusing on green chemistry to save the environment and utilization of waste biomaterials to produce the greener chemicals. The proposed methods and conditions help to study the depolymerization of lignin and extraction of lignin from the biomass in the future. The detailed mechanism of the cleavage of bonds in lignin need to be investigate in the future. The characterization and behavior of the catalysts used for this study need to be study in the future. The applications of subcritical water as a green solvent need to be explore in the future.

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