

Lignin extraction and green-like lignocellulose biomass pyrolysis as an alternative sustainable biofuel

Abstract

Cellulose, hemicellulose, and lignin make up the majority of biomass energy, which is a sustainable and renewable feedstock. Since lignin is the most common naturally occurring aromatic polymer on Earth, it holds great promise for useful products. Separating lignin from cellulose in biomass before converting it to biofuels or bioproducts is a crucial pre-treatment step. Alkali acid can be used to extract lignin from non-food components that remain following agricultural processing. As a result, we achieve the required lignin by the above procedure was used. The results demonstrate an extraction process of 5 hours, 4 hours, and 3 hours at 100 degrees Celsius, 130 degrees Celsius. Utilizing NaOH and H₂SO₄ for liquor and biomass to liquor ratio of 1:20. The total lignin content of the walnut shell was 13% lignin yield at 5 hr as well as neem tree bark biomass was found to be 5 % at 3 hours and walnut shell 14 % at 5 hr as well as 8% at 3 hours for almond shell lignin yield. It can be seen that the walnut shell produced the most lignin when compared to other types of biomass.

Keywords: lignin, biofuel, lignocellulose, pyrolysis, sustainable, extraction

Volume 8 Issue 2 - 2023

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Received: June 06, 2023 | **Published:** June 26, 2023

Introduction

Lignocellulose biomass, going from softwood to farming and ranger service squanders, addresses the most plentiful asset for the current bio treatment facility. Somewhat recently, we have seen the ascent of 'reductive reactant fractionation' cycles of lignocellulose in which need consideration is given to lignin that is 'first' changed over into sweet-smelling feedstock.¹ Because of the ongoing scarcity of fossil fuels, the use/application of renewable materials, such as biomass-based goods, has gotten a lot of attention recently. Second, environmental challenges such as pollution (water and air) caused by many sorts of chemical businesses, the greenhouse effect, and global warming are diverting researchers' attention away from green and sustainable products.² In businesses, the assembling of synthetics like various surfactants, emulsifying specialists, and polymers is for the most part founded on fossil repositories, which are quickly exhausting and ending up costly. Any natural substance delivered by living life forms, as well as their metabolites, is alluded to as feedstock. This term is regularly utilized with regards to energy to allude to lignocellulose materials, (for example, horticultural buildups and ranger service squanders) and energy crops, (for example, tree covering, pecan shell, sugarcane, sweet sorghum, and microalgae).³ Biomass yield is assessed to be at 170 billion tons each year around the world, representing around 10% of worldwide essential energy, making biomass the fourth most significant energy source after oil, coal, and regular gas.⁴ Besides, among other sustainable assets (like sun based energy, wind energy, flowing energy, etc), biofuel is the main inexhaustible carbon asset in nature, giving it particular advantages in the creation of significant worth added thing.⁵ Lignocellulose biomass (LBM) has emerged as the most crucial renewable resource for creating a variety of goods in what is now known as the "bio refinery idea." Forest residues and leftover agricultural waste are two of the

most typical kinds of LBM. The most prevalent agricultural wastes/residues include crop stalks, leaves, roots, fruit peels, and nutshells; these materials are normally burned or disposed of but might be a rich source of feed.⁶ Biomass is a renewable resource that is abundant and widely available in nearly all ecosystems. It is now possible to grow biomass for use in fuels and bio products. However, because most biomass has a low density, transporting it to bio refineries is expensive in terms of fossil fuel and carbon dioxide emissions.⁷ Therefore, using leftover biomass from food production that is already kept at a central processing plant to transform it into goods is a realistic option. The energy crisis and environmental issues are a result of the continued use of fossil fuels.⁸

Food wastes and agricultural/forestry leftovers, such as fruit and vegetable waste, have all been researched as lignocellulose biomass. Examples of these include sugarcane bagasse, maple wood, corncob, and crop residues. The largest quantities of lignin, between 15 and 30 percent by weight, are found in wood.⁹ Relative to other sources, which often contain 3 to 25 weight percent of materials like rice straws and maize cobs. Lignin content in hardwoods and softwoods varies, with the latter having the highest concentrations. The bark of the neem tree, for example, shows how it differs between species of the same genus. It is possible to use lignin, a naturally occurring polyphenol, to permanently replace the hydrocarbon phenol.¹⁰ A few examples of uses include polymer composites, aerogels, adhesives, paints, thermosets, emulsifiers, dyes. The final product of biomass fractionation is typically greatly influenced by the lignin extraction technique used. Sulfite processes and organosolv pre-treatments are typical techniques for lignin isolation. In contrast to other solvent systems. The Kraft and sulfite procedures, as well as organosolv pre-treatments, are common methods for isolating lignin. Because of their apparent greater selectivity for this polyphenol, DESs have been successfully

utilized for extraction of lignin from biomass sources among the various solvent systems.¹¹ The most plentiful feedstock for modern bio refinery is lignocellulosic biomass, which ranges from softwood to agriculture and forestry wastes. In recent years, we've seen the growth of lignocellulosic reductive catalytic fractionation techniques, in which the lignin that is 'first' transformed into aromatic feedstock receives special attention. The lignin extraction, depolymerization, and stability of the resulting phenolic units are discussed together with recent advancements in the reductive valorization of lignocellulosic biomass employing a lignin-first biorefinery technique.¹² The process by which monomeric units produced from lignin, such as phenolics, are converted into high-value chemicals, fuels, polymeric materials, and active pharmaceutical ingredients is briefly reviewed at the end.

Because of their low price and abundant availability, residual and non-edible lignocellulosic biomass are important feedstocks for modern biorefineries. The year has seen the development of a number of biorefinery technologies, many of which call for physicochemical pretreatments to enable the conversion of biomass's holocellulosic (cellulose and hemicellulose) components into fuels and chemicals while relegating lignin to the role of "terrible duckling."¹³ Additionally, the natural structure of lignin was irreversibly altered during biorefinery processes, significantly restricting its ability to be chemically upgraded into value-added chemicals. For a lignocellulosic biorefinery, on the other hand, intending to create green aromatic compounds in a sustainable manner, the native phenolic contents of lignin are of particular interest.¹⁴ Examples of biofuels that are great fuel substitutes include biodiesel, biogas, and bioethanol. These fuels can be produced from a number of biomass sources, such as agricultural waste, food crops, forest timbers, organic wastes, and even algae.¹⁵ Renewables made from biomass have some advantages, including their potential to be renewable and their low impact on pollution and global warming.¹⁶ However, the combustion of fossil fuels produces carbon dioxide, with variable amounts of carbon dioxide produced by different types of fossil fuels. CO₂ is a major source of greenhouse gas emissions at the same time. Lignocellulose offers special qualities that are useful for both commercialization and research. The production of thermal energy, which has a variety of uses, is the main objective of fuel burning.^{17,18}

Materials and methods

Material

In this research, 4 raw materials are used. These raw materials; walnut shell, babul tree bark, almond shell, neem tree bark are collected from, Jamshoro Patak near and Quetta Baluchistan then all the materials are shifted to coal resource and research laboratory, MUET Jamshoro (Figure 1–3).



Figure 1 Raw material used like WNS,AS, NTB, BTB.



Figure 2 Sieve size NTB, Sieve size BTB, Sieve size WNS, Sieve size AS sample.



Figure 3 Electrical Muffle furnace.

Moisture analysis

The moisture percentage can be calculated using the oven test standard method (ASTM D2867-09). A sample should be put into a dry, properly weighted crucible. The sample is dried in an oven that has been preheated between 145 and 1550C. The sample is dried, then taken out of the dry oven at room temperature to cool and being weighed once more. Sample's moisture content is determined by the percent difference.

Volatile substances

The amount of volatile matter in activated carbon is measured using the Standard Test Procedure (ASTM D5832-98). In order to determine the amount of volatile matter in a sample, 1 gram of the sample is put into a covered, weighted crucible and heated to 950°C for 7 minutes. The percentage difference between the two is what is referred to as volatile matter. The sample is then allowed to cool at room temperature in a desiccator.

Content of Ash

Using the muffle furnace test method (ASTM D 2866-94), ash content is assessed. An electronic scale is used to weigh the crucible cup before the addition of the sample of 1g of activated carbon. It is then placed in a muffle furnace and heated at a steady temperature of 650°C after reaching the necessary weight. It is then chilled in a desiccator to room temperature. To obtain the fixed carbon, the percentages of moisture content, volatile matter, and ash had to be added, and the resulting number had to be deducted from one hundred.

Extraction of lignin from different feedstock

To obtain extremely valuable and pure lignin, a selective method to biomass fractionation is essential. It's crucial to take into account variables like temperature, time, solid-to-liquid ratio (S/L), and solvent when optimizing the extraction process. This study did not account for S/L and used the ratio 1:20. The next technique was used to remove lignin from various biomasses. It is common practise to use a two weight percent (W/V) NaOH solution. So, 20 grammes of NaOH and 1000 mL of distilled water were combined, and the mixture was refrigerated for five hours at 100 degrees Celsius in a drying oven. At 1:20, biomass, including babul tree bark, neem tree bark, walnut shell, and almond shell, is added to the liquor solution. This demonstrates that 50 grammes of biomass and 1000 millilitres of alcohol were dried at 100 degrees Celsius in a dry oven. The pretreated biomass was then recovered by filtration after a sample of biomass was added, water was removed from the mixture, and lignin was extracted using filter

paper. The four tests were conducted one after the other after being cleansed with distilled water to remove excess alkali. Filter paper was used to collect and dry the remnants after first emptying the water. The aqueous filtrate was first acidified with sulphuric acid and then the pH was reduced with acid using a pipette and a pH metre. After boiling for an hour, the mixture was cooled, the solid residue was added, and then distilled water was added. This precipitate was separated by filtering it using filter paper, then washing the lignin residue away with distilled water until pH 7 was attained and every undesired substance and impurity was eliminated. The lignin samples were dried at 105°C in a dry event for further processing. In this experiment, sodium hydroxide (NaOH) and sulfuric acid (H₂SO₄) were used as the materials (Figure 4 & 5).

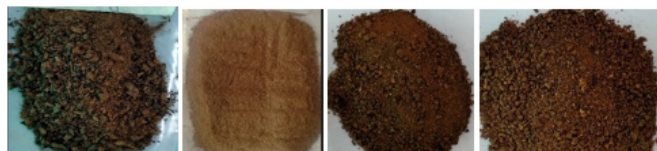


Figure 4 Residue extracted from biomass a) NTB(b)BTB (c) WNS (d)AS.



Figure 5 Extraction of Lignin from different biomass a) NTB(b)BTB (c) WNS (d)AS.

Methods of characterization

The FT-IR spectrophotometer was employed to analyse the functional groups. Fourier Transform Infrared Spectra of KBr Pellets (SHIMADZU with DRS-8000). The KBr pellets have 0.1 mg of lignin powder and 300 mg of KBr. The scans ranged from 400 to 4000 cm⁻¹ and had a resolution of 16 cm⁻¹. Numerous methods, including Fourier transform infrared spectroscopy (FT-IR), were used to study lignin. It was feasible to obtain the lignin spectrum obtained from biomass. While the peak at 1603 cm⁻¹ displays the carbon stretching frequency as a result of O-H stretching vibration, the peak significant at 3327 cm⁻¹ depicts the hydroxyl stretching frequency. Lignin was identified using an FT-IR spectrometer and the air sampling method. Direct transmittance was employed to generate the sample on a diamond, which was then used for diamond ATR. The bands between 3000 and 2800 cm⁻¹, which are primarily C-H stretching vibrations, are produced by lipids. In the 1043 cm⁻¹ band, lignin synthesis reaches its maximum. Comparing the C-O stretching connection in the lignin of almond and walnut shells to the shoulder at 1603 cm⁻¹, which is a strong bond, the latter is hardly noticeable. As a result of this, the lignin that was produced contained guaiacyl units. The adhering fractions' bands and the lignin products' bands in the FTIR spectra were contrasted (Figure 6).

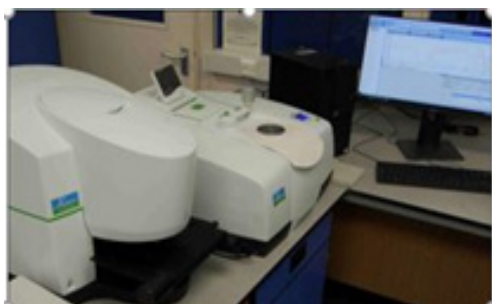


Figure 6 Fourier transform infrared spectra (FTIR).

Pyrolysis (Horizontal flow, Forced type oven)

The pyrolysis experiment was carried out for a maximum duration of a one-hour pyrolysis system consisting of a reactor. Before starting the pyrolysis the weight of the reactor was taken at 155.8 grams then did the weight of paper on electronic weight balance and tared. The weight of biomass walnut shell (WNS) was 20 grams as well as other materials and started the pyrolysis forced type oven and the best temperature is 600°C and presses the start button for a while to start equipment. The initial temperature was at start 23°C when the time was 8:45 am. When increasing the temperature to 200°C the time was 9:00 am. When the temperature reached 600°C. The time was noted at 9:22 am. The temperature started decreasing after 600°C the required temperature. After cooling the furnace and that the sample was taken outside and did the final weight which was 11.21 grams and the weight loss in the bio-oil of volatile matter production. The porous graphite structure can be used as a catalyst as well as other uses. Biomass can be converted to fuel and catalyst by fast pyrolysis methods. This method is the most appealing one for using heating rate and temperature without oxygen to convert lignin yield to catalyst development. Such as, pyrolysis temperature increased, the mass percentage of char decreased.

Results

We estimate the crystallite size of biomass tests based on their approximate time in the research facility. Size decrease tests were applied in this review. The biomass particles went through to the sifters' gaps, yet the large particles remained behind. Sieve 1 has a diameter of 1000 micrometers, sieve 2 has a diameter of 850 micrometers, sieve 3 has a diameter of 800 micrometers, sieve 4 has a diameter of 750 micrometers, sieve 5 has a diameter of 600 micrometers, sieve 6 has a diameter of 400 micrometers, sieve 7 has a diameter of 300 micrometers, and sieve 8 has a diameter of 200 micrometers. It was discovered that some sieves retain more almond shell particles while others do not retain the same amount of Walnut particles. The highest sieves have a greater aperture than the sieves in the bottom half of the sieve shaker. These investigations also revealed that the majority of the sample had a thickness of 4.75mm to 4mm, with a minimum proportion of 0.3mm to 0.15mm (Figure 7).



Figure 7 Sieve size of almond shell large particles on right and small on left.

Discussion

The report's figures show the features of a prominent peak with a 3327 cm⁻¹ diameter and a 1043 C-O bond. The lignin walnut shells, babul tree barks were examined using FTIR-ATR to establish the functional group of the materials. It was feasible to obtain the silica-containing lignin's spectrum, which was produced from bioenergy. It was applied to understand the surface behaviour of ready-to-use lignin (Figure 8–11) (Table 1–3).

Strong peak 3327cm⁻¹ and 1043 C-O bond properties are shown in (Figures 10 & 11) of the study. The lignin in almond and walnut shells, babul tree bark were examined using FTIR-ATR to establish the functional group of the samples. It was feasible to obtain the silica-containing lignin's spectrum, which was produced from biomass.

It was applied to understand the surface behaviour of ready-to-use lignin. The spectra were collected in the 500–4500 cm⁻¹ wavelength range. The majority of the lignin features band was discovered by FTIR study.

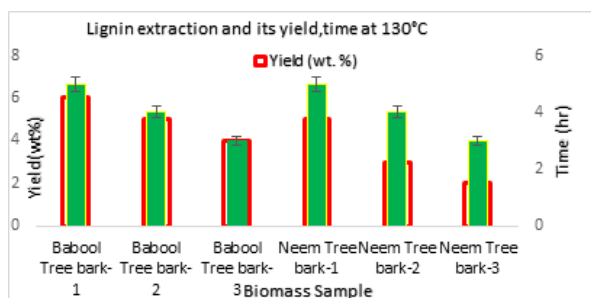


Figure 8 Lignin extraction and its yield.

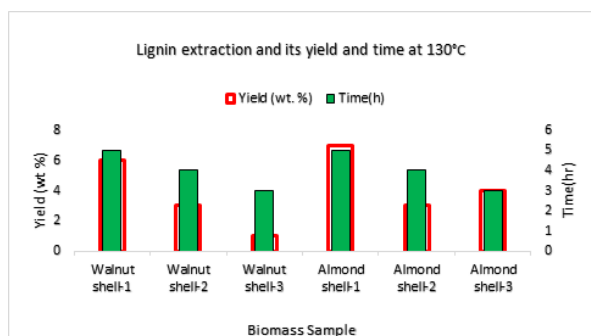


Figure 9 Lignin extraction and its yield

Table 1 Lignin pyrolysis to prepare a catalyst

Pyrolysis type	Sample name	Initial weight	Time of heating	Heating Temperature		Final weight	Change in weight (Loss in weight %)	Catalyst yield
				Temp initial	Temp final			
Fast pyrolysis	WNS					11.21	43.95	56.05
	AS	20 g	40	23°C	600°C	11.73	41.35	58.65
	BTB)					11.88	40.6	59.4
	NTB					11.96	40.2	59.8

Table 2 Yield of Lignin from Babul tree bark (BTB) and Neem tree bark (NTB) at 130 °C of various time

Type of biomass	Temperature (°C)	Time (hr)	Liquid solvent concentration percent	Biomass to liquor ratio	Stirrer speed	Yield (wt.%)
BTB		5				13
BTB		4				8
BTB		3				7
NTB	100	5	2%	1:20	Constant	11
NTB		4				8
NTB		3				5

Table 3 Yield of Lignin from walnut shell (WNS) and almond shell (AS) at 130 °C in various interval of time

Types of biomass	Temp (°C)	Time(hr)	Liquid Solvent concentration percent	Biomass to Liquor ratio	Stirrer speed	Yield (wt.%)
WNS		5				14
WNS		4				9
WNS		3				6
AS	130	5	2%	1:20	Constant	14
AS		4				10
AS		3				8

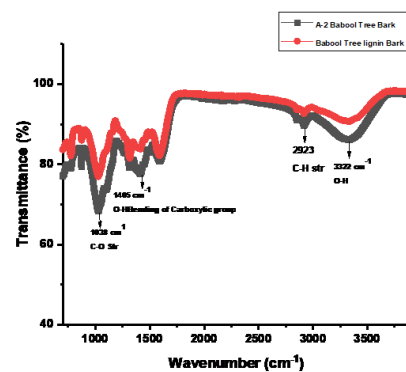


Figure 10 FTIR Spectra of lignin extracted from BTB.

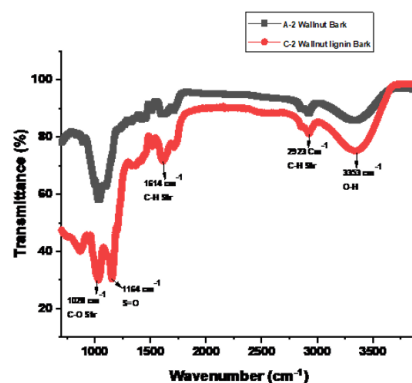


Figure 11 Spectra of FTIR for lignin extracted from WNS.

Conclusion

The solvent is capable of increasing the yield of extracted lignin from biomass such as AS, WNS, BTB,NTB. The best conditions for extraction of lignin from lignocellulose biomass are like 1:20 solvent to solid ratio. Lignin amount which is extracted varies depending on the conditions. The biomass obtained possesses properties that are similar to extracted lignin from different biomass bases. Lignin, on the other hand, shows particular characteristics in the 2360.78 and 2075.41 cm⁻¹ bands, according to FT-IR spectra. A typical Si-H bond is found between 2100 and 2360 cm⁻¹. The lignin was precipitated by adding H₂SO₄ until the pH reached 1. After that, the remaining material is heated on a stirrer for 1 hour. The accelerated lignin was dried for two hours at 100°C and reused several times without impairing the execution and explicitness of the extraction. When considering the ideal “green” elements of this novel dissolvable framework as well as the astounding extraction limit and lignin selectivity. This study paves the way for the potential use of biodegradable and biocompatible lignin in coatings, medication delivery, and other applications such as nanocomposite materials.

Acknowledgments

The authors are thankful to the employees at MUET’s Department of coal resource and research laboratory Jamshoro, Pakistan, for their invaluable guidance and assistance in the conduct of this study.

Conflicts of interest

The authors declare that there is no conflict of interest.

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