



## Valorization of extracted lignin to enable the lignocellulosic biomass as a sustainable source for enhanced biofuel

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### ABSTRACT

The most abundant biopolymer feedstock is lignin. Because lignocellulosic resources are the world's most plentiful, low-cost, and sustainable material, recent advances in the manufacturing of chemicals and bio-materials products have focused on them. Lignin valorization consists of fuel and chemicals and lignin-based materials. They're mostly made up of cellulose, hemicellulose, and lignin, with a few ashes and extractives taken for good measure. The high-value usage of lignin needs to be investigated and improved. Industrial biomass made up of lignocellulose waste is a low-cost that can be used to collect bioenergy. Biofuel created from biomass can be used to replace conventional fuels while lowering greenhouse gas emissions. In this regard, green biotechnology appears to be a potential strategy. Here, lignin is more in walnut shell compared to neem tree bark and babool tree bark. However, lignin which is extracted from lignocellulose biofuels will take longer to reach the market. After the multi-step processing for converting agricultural biomass to fuel ethanol. Ultimately, we look at the obstacles, opportunities, and prospects for lignin value-added products. Which can be effective in the importance of renewable fuels and lignocellulosic biomass to biofuel is highlighted.

### Keywords:

Lignocellulose  
biomass  
Lignin  
Bio-energy  
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### 1. Introduction

Polysaccharides (cellulose and hemicellulose) and aromatic macromolecules make up lignocellulosic biomass (lignin). Concerns about the energy crisis and climate change have prompted increased initiatives to create value-added fuels and chemicals from renewable feedstocks such as lignocellulosic biomass[1]. Polysaccharides found in lignocellulosic biomass, for example, have been chemically or biologically converted into platform chemicals (such as lactic acid, 1,4-butanedione, and levulinic acid) and biofuels (e.g., ethanol and butanol)[2]. The

depletion of fossil resources, growing energy costs, and environmental concerns have encouraged the development of sustainable technologies for the production of renewable energy and chemicals. In this context, the use of lignocellulosic biomass as a renewable resource is gaining traction: lignocellulose is the major component of plants, making it the most plentiful renewable resource on the planet [3]. Lignin is the most prevalent macromolecule in nature, accounting for 10–35 percent of lignocellulosic biomass. The oxidative coupling reactions of monolignol building blocks (syringyl unit [S-unit], guaiacyl unit [G-unit], and p-hydroxyphenyl unit [H-unit]) coupled by different bonds, including -O-4 aryl ether, 5-5 biphenyl, -5-phenylcoumaran, and 4-O-5 diaryl ether linkages, produce lignin. Lignin also contains a variety of functional groups, including methoxyl, carbonyl, phenolic hydroxyl, and benzyl alcohol groups [4]. Lignocellulosic material known as advanced biofuel which consists of agricultural and forest waste contributes to about 50% of total obtainable biomass globally. This condition makes crops and forest residues a high-potential bio-conversion feedstock [5]. Because of its availability and renewability, the use of biomass has direct and indirect economic, environmental, and social benefits. Biomass industries improve chances for domestic industry and economic growth from a financial standpoint, [5]. Animal, plant, and microorganism waste is referred to as biomass. Such waste can be converted and used as a source of energy. In terms of industry, it may be the green route because its conversion into fuels extinguishes and reduces waste. In plants, it provides structural support for the tissues [7]. It's a phenyl propane amorphous heteropolymer network. Because it is water-insoluble, it aids in the binding of the various components of lignocellulose biomass. Despite its potential, lignin is an underutilized material. It can be utilized to develop and synthesize a catalyst that can be used instead of a typical catalyst in the Fischer Tropsch process to produce fuel. To develop catalytic active sites, its surface can be physically stimulated with ferrous nanoparticles. These sites will play a critical role in accelerating the Dimethyl Ether production process [8]. Lignin uses have been studied for decades, and the potential for high-value products has been demonstrated [9]. Because raw lignin has no reactivity in catalytic reactions, it is also utilized as a catalyst after modification. The presence of impurities and the smaller surface area of lignin, which limits the active sites for catalytic reactions, are two key reasons for its usage as a catalyst. The lignin has been modified using a variety of approaches [10]. Microwave-Assisted Pyrolysis (MWAP) is a promising attempt to address these issues by reducing pre-pyrolysis process delays and allowing for a quick start-up procedure, internal and volumetric heating of solid materials due

to sufficient microwave penetration capabilities [6]. Due to their limited microwave (MW) absorption capability, most solid biomass materials cannot be heated to the necessary pyrolysis temperature [11]. Pyrolysis takes place at temperatures ranging from 400 to 650 degrees Celsius. In terms of heating rate, the process can be classed as slow or fast pyrolysis depending on the product preferences. On the one hand, slow pyrolysis is a technique that favors the production of solid biochar and can take up to a few hours to complete. Fast pyrolysis, on the other hand, is a method for increasing bio-oil output[12]. Lignin is an aromatic polymer composed of cross-linked phenolic alcohol molecules[13]. The macromolecular structure changes significantly depending on the initial bioresource and pretreatment procedure. It's difficult to develop lignin depolymerization technologies that can degrade lignin's diverse and complicated structure into monomers. Several groups are actively investigating advancements in such technology. Bio-based heterogeneous catalysts (lignin-derived) are nontoxic, noncorrosive, and may be easily recycled and activated. In particular, lignin-derived catalysts can catalyse both transesterification and esterification events in a cost-effective and environmentally friendly manner [14].

## 2. Materials and Methods

### 2.1. Selection of materials

There were four biomass materials in the research-related work. The Neem tree bark, Babool tree bark, almond shell, and walnut shell were taken and purchased from the shop of dry fruits shells from Quetta Baluchistan and some from Jamshoro, Pakistan. The samples shells were crushed, ground & sieved. Drying oven and Muffle furnace was used at particulate technology lab of chemical engineering, Mehran University of Engineering and Technology, Jamshoro, Pakistan. The overall process steps are schematically depicted in Fig. 01.

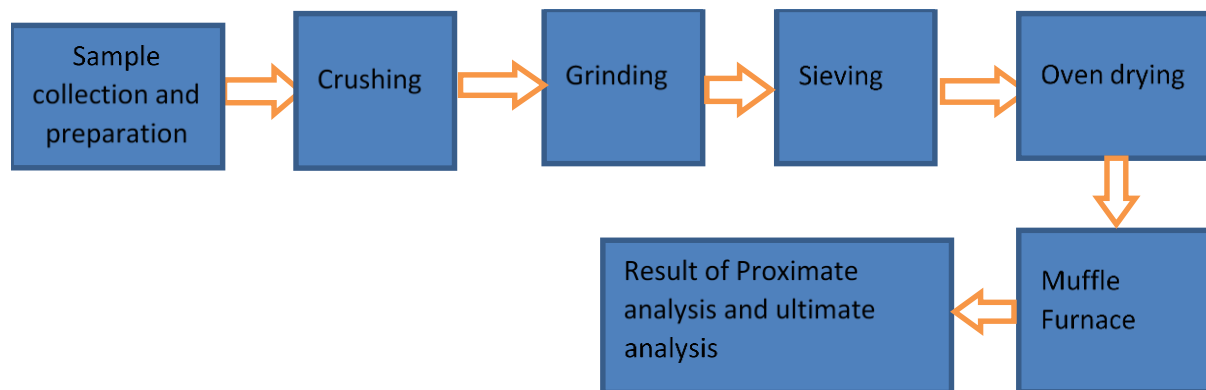


Fig. 01: Research Methodology

For the drying purpose, it was carried out using the drying oven (Fig. 02) at the temperature of 105 °C for 2 hours and did shopper weight 7gram. Biomass weight is taken 550 grams. For all four samples and kept the material in the oven and did the same method for four biomass after drying in oven weight was 509 grams remained. We check the weight on the electronic weight balance. The weight was decreased and moisture was removed.



Fig. 02: Drying Oven

In a particle technology laboratory, a sample of biomass such as Neem tree, Babool tree, Walnut shell, and Almond shell was collected and crushed. The particle size of the sample was determined using sieve analytical equipment. The biomass samples for this investigation were from a separate region of Sindh province. The American Standard Testing Methods apply to the analysis of biomass fuels (ASTM). The ASTM machine standard test procedures were used to undertake chemical and structural evaluations of lignocellulose fuels such as agricultural waste, tree bark, dry fruit shell, etc. The biomass was sieved using a sieve shaker machine (Fig. 03). Biomass was gathered for investigation with several sieves for assessing the particle size of 300 grams. The sample was tested in an electronic balance to see the varying particle sizes at different sieves. The biomass from different sample is shown in Fig. 04. The heating of sample was done in a muffle furnace (Fig. 05) at temperature of 650 °C for 4 hours. The sample was cooled to room temperature, and the moisture, ash, and volatile matter levels were determined.



Fig. 03: Magnetic Sieve shaker



Fig. 04: (a) walnut shell, (b) Almond shell, (c) Neem tree bark and (d) Babool tree bark



Fig. 05: Electrical muffle furnace for sample

## 2.2. Moisture analysis

Oven test standard method was employed to determine the moisture percentage (ASTM D2867-09). In a preheated oven, the sample was dried at a set temperature (145-155 °C). After the sample has been dried, it was removed from the oven and allowed to cool at room temperature before measuring its weight. The percent difference measured was taken as the sample's moisture content.

## 2.3 Analysis of Volatile matter

The percentage of volatile matter in activated carbon was assessed using the Standard test method (ASTM D5832-98). 1 gram of sample was placed in a covered weighted crucible, which was then placed in a muffle for 7 minutes at (950 °C), after which the sample was allowed to cool to ambient temperature in a desiccator, the percent difference obtained was considered as content of volatile matter.

## 2.4 Ash content

The electrical muffle furnace test method is used to determine the ash content (ASTM D 2866-94). First, the weigh the crucible cup by electronic balance and place the sample 1g of activated carbon respectively, then place it in a muffle furnace at a constant temperature (650 °C) until it reaches a consistent weight and cools it to room temperature in a desiccator, the fixed carbon is calculated using the formula below.



Fig. 06: Hammer Mill

Experiments were carried out on samples from selective biomass like an almond shell, walnut shell, neem tree, babool tree. Waste particles was fed to the hammer shredder (Fig. 06) and rotary shear during the single-particle was crushed in the machine. Hammermills were used to reduce the particle size. Depending on the design and size of the metal-like screen, the hammer mill has the required size of biomass particles to pass through and contain the coarse biomass sample.

## 2.5 Lignin extraction of different biomass

To generate high value and pure lignin, a selective approach for biomass fractionation is required. Temperature, duration, and pressure are all key characteristics to consider while optimizing the extraction process. The solvent, as well as the solid-to-liquid ratio (S/L). S/L was not considered in this study, and 1:20 was chosen as the ratio for all tests. The following approach was used to extract lignin from various biomass. A two-weight-percent (W/V) NaOH solution is typically employed. So, 20 grams of NaOH were mixed with 1000 mL of distilled water and chilled for 5 hours in a drying oven at 100 °C. The liquor solution is then blended with biomass such as babool tree bark, neem tree bark, walnut shell, and almond shell at 1:20. It means that 50 grams of biomass and 1000 milliliters of liquor were dried in a dry oven at 100 degrees Celsius. After that, a biomass sample was added to the beaker, and filter paper was used to remove water and extract lignin from the mixed liquid on the filter paper, and pretreatment biomass was recovered by filtration. After being cleaned with distilled water to remove excess alkali, all four tests were performed in order. So, using filter paper, I drained the water and collected, dried the residue. Using a pipette and a pH meter, the aqueous filtrate was acidified to pH reach 1 with concentrated sulfuric acid, first acidifying with sulphuric acid and then decreasing the pH with acid. The mixture was then allowed to boil for one hour before being cooled and the solid residue was added to distilled water The lignin residue was removed by filtering with filter paper and then washing with distilled water

until pH 7 was obtained and undesirable material and contaminants were eliminated. The lignin samples were dried at 105°C in a dry event for further processing. The chemicals used in this research were sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and sodium hydroxide (NaOH).

### 3. Results and Discussion

#### 3.1 Proximate and Ultimate analysis:

In table 01 shows the proximate analysis such as moisture content, volatile matter, fix carbon, and ash content at 650 °C for 4 hours. These results were obtained using an electric muffle furnace.

Table 01: Proximate analysis of the samples

Type of biomass	Moisture content %	Volatile matter %	Ash content %	Fixed carbon %
Walnut Shell	4.1	76.97	1.93	17.00
Almond Shell	5.69	74.75	1.68	17.88
Babool Tree bark	3.08	77.09	1.83	18.00
Neem Tree bark	4.28	75.79	2.87	17.06

These results are on a dry basis; the material was sieved at 150 microns and dried at 105°C for one hour. The ultimate analysis of the raw sample, such as C, H, N, and O, is given in table 02. The babool tree has the highest concentration of C and the lowest content of Sulphur in the final examination of raw materials.

The oxygen concentration of almond shells was higher than that of babool trees. Acid washing may modestly enhance the concentrations of C, H, and O in lignocellulose biomass while lowering the levels of N and S.

Table 02: Ultimate analysis of pre-treated raw biomass samples (Presented on dry basis)

Biomass	C	H	N	S	O
Walnut shell	47.7	7.1	0.84	0.36	44
Almond shell	46.20	6.54	0.88	0.27	45
Neem Tree	52.80	4.6	0.64	0.17	41
Babool Tree	54.70	4.3	0.19	0.14	38

Tables 03 and 04 explain the different liquor formulations used in the complete methodology of this work about lignin extraction. For each biomass, the time was kept as 5 hours, 4 hours, 3 hours respectively. The temperature was 100 °C, 130 °C. The liquid solvent concentration and biomass to liquor ratio were kept constant at 2% and 1:20 respectively.

Table 03: Lignin Yield at 100 °C for different time intervals

Type of biomass	Temperature (°C)	Time (hr)	Liquid solvent concentration percent	Biomass to liquor ratio	Stirrer speed	Yield (wt.%)
Babool Tree bark-1	100	5	2%	1:20	Constant	12
Babool Tree bark-2		4				9
Babool Tree bark-3		3				7
Neem Tree bark-1		5				11
Neem Tree bark-2		4				8
Neem Tree bark-3		3				7

Table 04: Lignin Yield at 130 °C for different time intervals

Type of biomass	Temperature (°C)	Time (hr)	Liquid Solvent concentration percent	Biomass to Liquor ratio	Stirrer speed	Yield (wt.%)
Walnut shell-1	130	5	2%	1:20	Constant	14
Walnut shell-2		4				9
Walnut shell-3		3				6
Almond shell-1		5				13
Almond shell-2		4				10
Almond shell-3		3				8

#### 4. Conclusion

In lignocellulose biomass, there is no direct relationship between cellulose and fixed carbon. The results are obtained by using a laboratory of equipment. In proximate analysis, the walnut shell and almond shell contain more moisture as well as the neem tree, while the babool tree contains the least. The abundance of lignocellulose wastes inspired the researchers to use this low-cost source for biofuel production. By utilizing an electrical muffle furnace, the time and resources required to conduct tests to discover the structural components of biomass can be reduced. The results of investigating the biomass conversion process. The extraction of lignin from lignocellulosic plant biomass was examined and explored in this study. The yield of lignin from various raw materials (industrial processing by-products) was also examined. We extracted the



most lignin from Babool tree bark and Walnut shell, and the least amount from Neem tree bark. More study is needed to optimize this process from an economic standpoint to create biofuel from biomass renewable energy sources found in nature.

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