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Advancing Lignin Extraction Recovery from Natural Lignocellulosic Biomass into Biochemicals

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Abstract

Worldwide population increase and economic development are the two reasons that signify a vital need to produce biofuels to fulfill contemporary energy demands. In this context, Lignocellulosic biomass as a renewable energy source has the potential to produce biofuel. It comprises of lignin, cellulose, and hemicellulose components. It can be considered a primary source of energy if utilized efficiently. Present research studies pinpoint to exploit locally accessible biomass sources to extract lignin from plants using an acid or alkali pretreatment. Lignin is extracted from biomass sources including the bark of babul (BTB) and neem tree bark (NTB). In this article, the proximate and final analyses are performed on the lignin separation using a pretreatment procedure. The characterization methods such as Energy dispersive spectroscopy (EDS), Scanning electron microscopy (SEM), and Thermogravimetric analysis (TGA) are performed. It is observed that BTB has an improved lignin recovery in comparison with NTB. On the other side, NTB produces a low lignin production around 12% after 5 h as compared to a 13% yield from BTB with the same time duration. Consequently, lignin greater yield is obtained utilizing BTB which can be further exploited in biomaterial production applications. This research outcome are promising and achieved with precise evaluation.

Keywords: Lignocellulosic Biomass, Lignin extraction, Ecofriendly, value-added products, Green energy, Alkali pretreatment.

Introduction

The three adverse effects that human civilization faces are a growing population which increases energy consumption, reduction of fossil fuel reserves, and change in weather patterns. Therefore, there arises a need to exploit renewable energy sources such as lignocellulosic biomass to shift energy generation from fossil fuels that generate harmful environmental contaminants [1]. Lignocellulose biomass has the potential to generate chemicals, minerals, and biofuels. Their main constituents are cellulose, lignin, and hemicellulose. Lignin consists of 15–35% of the lignocellulose biomass dry weight. Due to this reason, it is widely used as a sustainable aromatics compound. Global lignin resources are around 300 billion tonnes [2]. It has unique features which are resistance to both chemical and biological oxidation [3]. There are developed chemical methods to depolymerize lignin into low-molar mass particles. After that, lignin can be

processed into valuable chemicals [4]. For example, the most followed processing technique is alkaline pretreatment which makes lignin recovery. Their drawbacks are numerous continuous reaction phases, high residence time, and energy consumption [5]. Lignin also causes side effects such as water discoloration, and filtration problems upon their complete separation from Lignocellulose biomass. Till the recent past, Lignin is also the second most used biopolymer in the world [6]. Its depolymerization can result in the generation of a variety of aromatic chemicals such as phenol, catechols, syringol, ketones, vanillin, guaiacol, hydroxyl acetophenone, pyrocatechol, and their derivatives [7].

Lignin bioresource can be recovered from the paper industry and can be used to treat biorefineries. Lignin-based thermoplastic polymers have various benefits including environmentally affable nature, bio-degradability, resemblance to polystyrene, and the possibility to generate additional revenue by exploiting industrial effluents in comparison with petroleum-based thermoplastics [8]. Moreover, kraft lignin-polyvinyl acetate and lignin-polyurethanes can be made from coconut shells using alkali-based lignin and have better chemical and physical properties [9]. Lignin can also produce useful compounds such as coatings, resin, adherents, adsorbents, agricultural chemicals, and anti-microbial compounds. It can certainly raise commercialization and upgrade economic sustainability [10].

The enzymatic method used in the pretreatment stage of lignocellulosic biomass converts it into bioethanol. It consists of breaking cellulose to remove hemicellulose, lignin, and acetyl groups [11]. Different pretreatment techniques can also upgrade the cellulose content of lignocellulosic biomass which causes enzymatic saccharification. The most commonly used lignin extraction techniques include the usage of acids, alkalis, ionic solutions, and hydrothermal processes. The high content of lignin removal makes the residual polysaccharide more sensitive. The separation of uronic and acetyl acid modifications from lignocellulosic materials makes the cellulose surface more accessible to enzymes [12]. Alkaline pretreatment of lignocellulosic biomass breaks the lignin structure and the carbohydrate-lignin linkages which helps in carbohydrate separation [13]. Pretreatment, extraction, and depolymerization are typically required to extract lignin from biomass. Hemp, cotton, jute, and wood pulp materials comprise cellulose and lignin. As a result, their physical and chemical characteristics get altered depending on their extraction method. For instance, lignosulfonates are used in conventional sulfite pulping methods [14]. Strong binding and emulsifying characteristics are obtained due to sulfonic acid functional groups present in lignin. In that case, the extraction procedure consists of both alkaline and acidic solutions.

In this study, an increased lignin separation efficiency was obtained from the lignocellulosic biomass extraction method which was experimentally tested using crop leftovers. This work emphasizes exploiting sustainable renewable energy assets such as lignocellulosic biomass material. It is because of this reason that fossil fuel reduction and harmful environmental influences make a call to use clean fuels [15]. Lignin has been used in recent years for the synthesis of activated carbon and also for catalytic support. Previously, activated carbon was synthesized from coal, agricultural waste, and wood [16]. Researchers have developed an interest in lignin valorization which results in the functionalization of inactive lignin produced from the pulp industry for ten years. Catalysts made from lignin are found as chemically and physically activated. Lignin-derived carbon

material also has high porosity due to its physical activation [17].

In this paper, there is also highlighted the most recent progress in both traditional and cutting-edge lignin extraction techniques. Lignin has been used in different polymers during the past decades to create blends and composites [18]. The main goal of the present study is to remove lignin from lignocellulosic biomass. Lignocellulose-based fuels are considered carbon-neutral vectors for conventional petroleum sources in the transportation and energy sectors. Various biofuels can be manufactured in both gaseous and liquid forms such as syngas, biogas, biomethane, and biofuel using lignin [19]. Examples of liquid biofuels are jet fuel, bio-oil, bioethanol, biobutanol, and biodiesel. These fuel resources can be synthesized by employing thermochemical and biochemical conversion processes. Thermochemical conversion processes are pyrolysis, liquefaction, rapid pyrolysis, gasification, Fischer-Tropsch synthesis, and transesterification. On the other side, biological processes are hydrolysis, fermentation, and anaerobic digestion [20].

Materials and Methods

In this study, neem tree bark (NTB), and bark of babul (BTB) biomass were used for lignin extraction. Fig. 1 represents the schematic representation of lignin separation from lignocellulosic biomass. This biomass material was collected from different areas of Jamshoro, Sindh, Pakistan. However, the sodium hydroxide, sulfuric acid, beakers, and funnels were obtained from scientific store Haidar chowk, Hyderabad, Pakistan. Fresh biomass samples were cleaned and baked for ten days to reduce their water content by around 10%. For drying of samples, this material was first fed into a grinding machine where the material was cut into various sizes. The dried material was kept in tray for different particle sizes using magnetic sieve shaker. An ideal particle size for grinding feedstock is 250 nm. After that, biomass material was dried in the oven for 24 h at 70 °C. Distilled water was used for the test. All samples of biomass material were filtered using filter paper.

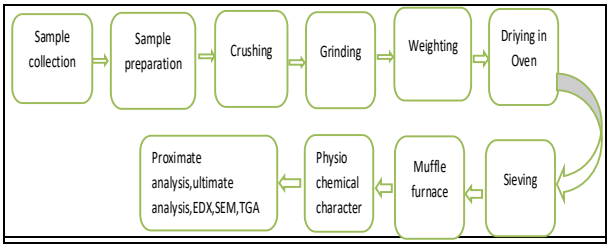

Figure 1. **Schematic representation of lignin separation from lignocellulosic biomass**

Lignocellulosic biomass quantity for pretreatment was taken up to 50 g. It was added in a beaker filled with distilled water around 1 L. NaOH was used in the pretreatment step. After this step, the sample was kept in an oven at temperature of around 110 °C. The pretreated solution was filtered using filter paper in a beaker. The dignified solid was washed through distilled water. A magnetic hot plate stirrer was used to quantify the solid/liquid ratio and magnetic stirrer in the beaker for agitation. The observed solid/liquid ratio was 1:20. This sample was kept in the oven for 3 hours. After 4 h, the observed temperature was 120 °C. In this pretreatment, lignin was recovered using filter paper, and a pipette was employed for dropwise addition of H_2SO_4 to attain a pH value of 1 of lignin precipitate. Lignin residue was separated and distilled water was used there until pH 7 was obtained. In the end, the lignin sample was kept in an oven for drying at a temperature of around 105 °C. After drying the sample lignin, it was kept in plastic bags for characterization.

Proximate Analysis

Table 1 represents the proximate analysis of biomass samples.

Table 1. **Proximate analysis of biomass.**

Biomass	Moisture content (%)	Volatile matter (%)	Ash (%)	Fixed carbon (%)
NTB	3.77	76.08	1.76	17.14
BTB	4.23	75.69	2.98	18.07

Moisture Content (%)

The moisture content was determined using the oven test standard method (ASTM D2867-09). The sample was dried out in a prepared oven at a determined temperature of around 130 to145 °C. After that, the weight of the dried sample was calculated. A sample moisture content is determined from the difference between the initial weight and final weight after drying.

Volatile Matter Content (%)

The volatile matter in activated carbon was estimated using the approved test technique (ASTM D5832-98). In this method, a covered, weighted crucible that contains one g of sample was heated in a muffle furnace around 950 °C for 7 min. After that, the sample weight in the crucible was measured.

Ash Content (%)

The muffle boiler method test (ASTM D 2866-94) was employed to calculate the ash content (%). The crucible china cup was weighed before filling 1 g of activated carbon. This sample is kept in an electric furnace at a pre-determined temperature of 600 °C and cooled to room temperature using a desiccator.

Ultimate Analysis for Lignocellulosic Biomass

A final analysis utilizing oxygen and the SC 832 LECO as the model was performed on the 350 mg biomass sample. The biomass sample was sieved at 150 microns and dried at 110 °C for 1 h. Table 2 presents the ultimate analysis of biomass raw samples that have been processed (pretreated on dry ground). It is proven that BTW has less sulfur and high content of carbon as compared to NTB.

Table 2. **Ultimate analysis of processed biomass raw samples (pre-treated on dry base).**

Biomass samples	C (%)	H (%)	N (%)	S (%)	O (%)
NTB	52.79	4.7	0.65	0.17	41
BTB	55.71	4.3	0.18	0.14	39

Characterization of Lignin using Energy Dispersive Spectroscopy (EDS)

EDS is a method that is frequently used for measuring sample composition. Lignin presence can be determined using the EDS. Two samples of each BTW and NTB were subjected to elemental analysis using EDS instrument. The X-ray emissions were examined by an energy-dispersive detector. Further, a solid-state instrument can distinguish the difference between X-ray energies.

SEM Analysis of Biomass-derived Lignin

SEM is an imaging technique which is used to examine the surface morphology of material such as lignin. Lignin is found as a complex organic polymer which is located in the biomass cell. SEM analysis proved to be valuable in lignin characterization by using model JEOL JSM-5410.

Thermogravimetric Analysis (TGA) of Lignin

Perkin-Elmer Pyris V-381 Thermogravimetric analyzer was used to measure the thermal breakdown of the lignin sample. Its pan is made up of aluminum and used to hold the lignin sample. It is heated to a temperature between 40 to 550 °C for TGA.

Results and Discussion

Feedstock Analysis for Lignin Extraction

The proximate and ultimate analysis of biomass feedstock was performed in the lab. Their results reveal that BTB and NTB can be used to extract lignin. The BTB and NTB samples were subjected to alkali pretreatment. Fig. 2 shows the relationship between time and lignin yield. Table 3 demonstrates lignin yield which is obtained around 13% from BTB after 5 h duration at 120 °C. NTB has a minimal lignin yield of around 12%. It is also revealed that lignin obtained from BTB has a sulfur content of around 6.43% and NTB contains a sulfur content of around 2.74%.

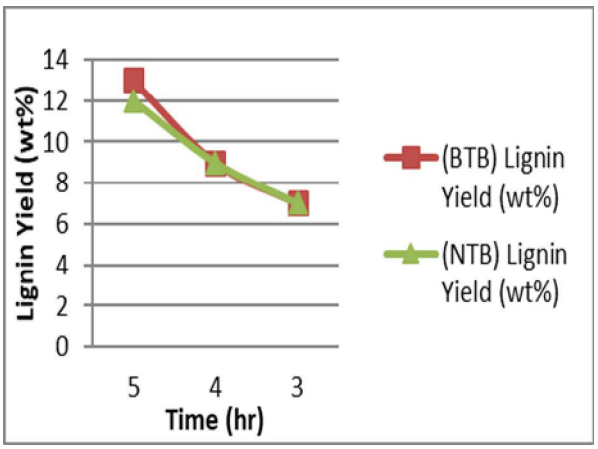

Figure 2. **Lignin yield from biomass at 120 °C.**

Fig. 3 demonstrates the EDS spectrum which are utilized for elemental analysis of materials. Each peak shows the content of specific element in the biomass sample. The peak intensity represents the element concentration in the sample. The EDS results showed the labelled peaks of calcium (Ca), sodium (Na), oxygen (O), magnesium (Mg), silicon (Si), carbon (C), and aluminium (Al). There is signification content of these elements, as observed from large peaks.

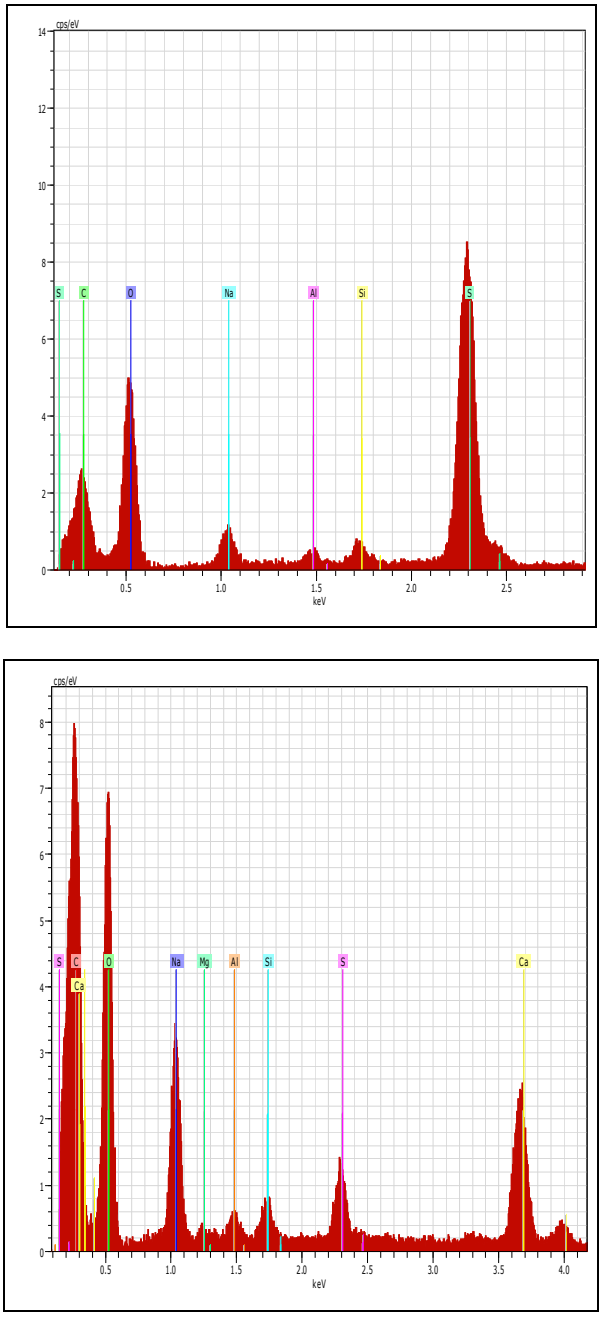

Figure 3. **EDS analysis (a) NTB and (b) BTB**

Table 3. **Yield of lignin from the bark of the babul tree and bark of neem tree over various periods.**

Biomass samples	Temperature (°C)	Time (h)	Liquid solvent concentration (%)	Raw material to liquid ratio	Speed of stirrer (rpm)	Lignin Yield (wt.%)
BTB	120	5	2%	1:20	30	13
		4				10
		3				8
NTB		5				12
		4				9
		3				7

Fig. 4 presents SEM biomass analysis for NTB and BTW. SEM produces a high-resolution image of a lignin sample surface using an electron beam. Lignin is found in different substrates according to their SEM results. Their surface morphology was examined using SEM. The side chain length and acylating agent erosion contributed to the formation of the surface layer.

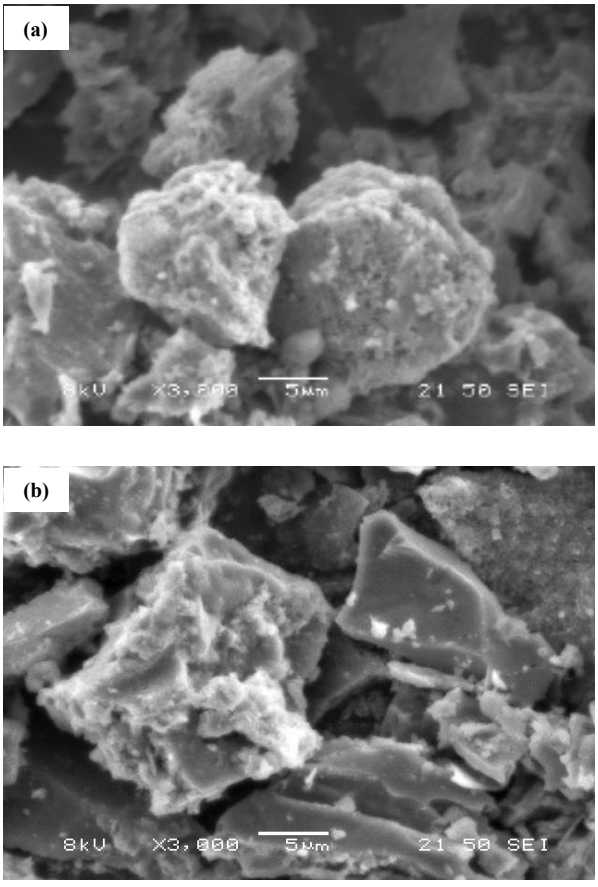

Figure 4. **SEM analysis of (a) NTB and (b) BTB.**

Fig. 5 and 6 present TGA analysis of BTB and NTB biomass, respectively. TGA can be used to measure the sample's volatile and moisture contents. In these TGA curve plots, there is an observation that as the temperature increases the sample mass percentage decreases. It can also be decreased in different processes as mentioned under.

1. Dehydration: When material temperature increases - dehydration occurs due to loss of water molecules. As a result, the sample mass reduces. The TGA curve shows a decreasing trend for biomass material mass change due to dehydration.
2. Desorption of volatile components: Substances which contain volatile elements and have low boiling points when subjected to temperature rise; they get evaporated from the sample resulting in mass loss. TGA demonstrates their change in composition with a diminishing trend.

3. Decomposition or degradation: Organic and inorganic substances can experience a thermal breakdown or degradation at high temperatures. Complex molecules disintegrate into small molecules during these processes and emit gases, vapors, or volatiles during degradation. The sample mass decreases gradually because of the loss of breakdown byproducts and is shown in the TGA curve with a declining trend.

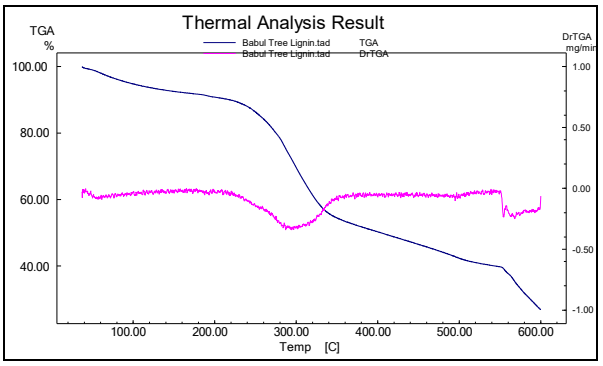

Figure 5. **TGA analysis of BTB**

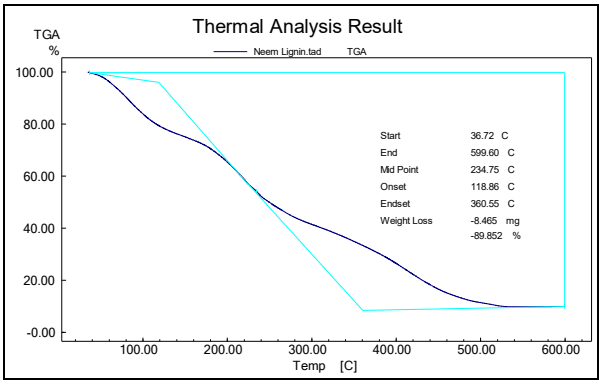

Figure 6. **TGA analysis of NTB**

Conclusion

The present study confirms that lignin can be recovered from NTB and BTB biomass resources, efficiently. It is observed that lignin extract from BTB has a high yield in comparison with lignin recovered from NTB using alkaline pretreatment. The time and temperature are found as important parameters that can increase lignin recovery from lignocellulosic biomass. There is obtained lignin yield of around 13% with pretreatment of BTB for 5 h duration. While lignin yield is obtained around 12% from NTB pretreatment. The extracted lignin is also characterized using EDS, SEM, and TGA characterization methods. These characterization analyses show that a small portion of sugar impurities are found in biomass-derived lignin and it can be removed employing acid treatment. Alkaline pretreatment is emerged as a feasible technique to be exploited in commercial and domestic sectors. From future perspectives, lignin can be utilized in composite materials, pharmaceutical, and wood-related sectors because of the reason that it is a biodegradable and biocompatible substance.

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Conflict of Interest

The authors declare no competing interests.

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