Advancing Lignin Extraction Technique from Lignocellulosic Biomass for Sustainability. A review

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Received 23/11/2023; accepted 15/03/2024
https://doi.org/10.4152/pea.2025430505

Abstract
Bm has the best role in the economy of a country. Ln is an essential structural component that is present in all vascular plants' cell walls. It is essential for the development of connective tissues, since it gives stiffness, strength and resistance to external threats like infections. Ln has numerous economic uses, and its extraction might lead to the development of several novel applications. Therefore, it is of the utmost significance to develop efficient and long-lasting solutions for Ln extraction from Bm. For this reason, one of the goals of the current study was to examine optimized Ln extraction from Bm, SB, rice and WS, by chemical methods. Further, Ln chemical extraction process characterization, optimization, and its applications in resins have herein been carried out.

Keywords: Bf; Bm; chemical; greenhouse gas; Ln; LnC; resin.

Introduction•

It has previously been established that Bm from LnC may be used in the manufacture of chemicals and biomaterials, and it is the most abundant renewable resource of this kind in the world. Bm from LnC material is widely accessible and affordable. Primary structural components of Bm material include HmCl, Cl and Ln. Bm is the most accessible, eco-friendliest and biocompatible material, which is boosting its demand. Numerous sectors, including building, paper, textiles and gear, now use Bm material [1]. Incorporating Bm into composites as reinforcement for polymeric materials is an emerging practice. There are still restrictions on the use of Bm material, such as its high water absorption qualities, incompatibility with hydrophobic polymers and propensity to become lumpy during processing. These features, which may be a direct consequence of the extraction method and plants employed in the process, may

•The abbreviations list is on page 331.

drastically diminish the overall properties of Bm material [2]. 10 to 25% of Bm is Ln, making it the second most prevalent natural polymer of this material. Ln, which is inherently stable and water-insoluble, serves as the “glue” that bonds Bm material. Ln is an heteropolymer composed of aromatics that contain cross-linked substituted phenolic alcohol units (i.e., monilignols): coniferyl, sinapyl and p-coumaryl. The enzymatic polymerization of these substituted phenols results in Ln formation, a three-dimensional and strongly cross-linked macromolecule [3]. As a renewable, chemically and physically superior inexpensive raw material, Ln has the potential to replace any product now made from petrochemicals. Ln has several applications, including emulsifiers, dyes, synthetic flooring, binding, thermosets, dispersion agents, paints, fuels and road treatments [4].
Excellent sources of Bm and Ln materials include wood pulp, jute, hemp and cotton. Depending on the originating source and extraction method, their physical and chemical qualities will change. Therefore, their applications may vary based on the employed formulae. Traditional Ln forms, such as lignosulfonates, have been used in sulfite pulping, due to the strong binding and emulsifying capabilities of their sulfonic acid functional groups [5].
Bm from LnC is the earth’s most prevalent biorenewable Fs, which is produced employing sunlight energy for photosynthesis from atmospheric water and CO_2. Bm from LnC has different structures, which contain Cl, HmCl and Ln [6]. Three categories of waste, including Bm, energy crops and virgin Bm, are used to group LnC. Bushes, sand grass, stover and bagasse are classified as Bm waste, virgin Bm and AW, respectively. Energy crops are essential components in the creation of Bf, since they provide a high level yield of Bm [7]. Bm has been used for a long time as an energy source around the world. Pollution is the root of the issue, and using FF has increased atmospheric emissions. The first Bf to be developed were initially achieved from sugars, starch, oils and fats. However, Bf based on the conversion of Bm from LnC components were developed, employing waste and dedicated grown nonfood crops on marginal land, and allowing an increased yield [8]. These procedures, which rely on chemical reactions, are used to harvest enzymes, microorganisms and mushrooms. When there is a higher percentage of Bm available, thermochemical processes are applied. However, one issue is the hydrolytic stability and hardness of Bm from plants’ cell walls, which must be fragmented and liberated. The most effective raw material for making Bf is Bm from LnC, which is also inexpensive and environmentally friendly. [9] have described the concept of Bm refinery to produce chemicals and fuels.

Plants

Since plants are naturally abundant and renewable, they are primary potential Cl, HmCl and Ln resources, which include cotton fibers, coatings, wood pulp and paper.. Ln can be taken from water plants, grasses, jute, sisal, flax and hemp [10]. Bm from AW, like RS, WS and SB, are also Cl and Ln sources. Pretreatment is essential for separating Ln from Bm of LnC. Bm pretreatment enables extractng high amounts of Ln, HmCl and other highly valuable materials. Therefore, alkali and acid treatment were herein used to separate impurities from Ln [11].

Composition

Bulky plants, hardwood and softwood are also known as Bm from LnCl, since they are fundamentally composed of Cl, Ln and HmCl. Cl makes up a large portion of plants, givig them physical and mechanical stability. HmCl, made of several C5 and C6 sugar monomers, is the another copolymer in the structure of a plant [12]. Finally, Ln is created by the biosynthetic cycle within the structure of plants, and it is their cell walls' most important protective layer, giving them different fragrances. In addition to these main components, plants' cell walls also contains small amounts of other elements, such as water, proteins and minerals. A pretreatment cycle is required to hydrolyze HmCl, debase Ln and open the chains of glucose in plant matter and rural waste Bm [13].

Various sources of LnC material

Bm from LnC is obtainable for many purposes, taken from three sectors, and it can be divided into many groups, e.g.: AW (leaves, straws, husk, manure, pods, seeds, roots, bagasse, seedpods, solid cattle and spruced willow); forest Bm (cedar, willow, spruce and hardwoods); forest residues (slashes, dead trees, burning residues, SD and wood chips); industrial matter (pulp, paper and primary wastewater solids); and MSW (newspaper, food and sorted wastes) [14]. AW forests residues are considered the best Bm for Fs, since they are abundant, more available and comparatively less costly. Different prospects related to the energy of various Bm organic wastes and by-products have potential, such as the land area availability and the kind of yield and production. MSW is not only a source, but also a reasonable, economic Bm resource that covers all domestic and industrial trash which is gathered in special areas. AW mainly includes cotton stalks, RS, WS, maize cobs, jute sticks, RH and WH, which are produced at a low density [15]. Forest residues include Bm from dying trees and waste removal. Forest waste is comprised of wood chips, bark and SD, which provide 65% of the potential for Bm energy. Different sources of Bm are described in Fig. 1, which include industrial residues and wood waste, AW and MSW.

Figure 1: Bm sources [15].

Bm types

RH

Different Bm are researched for power generation and environmental problems [16, 17]. Rice is an important source of carbohydrates. RH is also considered to be AW. Cultivation of crops materials like RH (Fig. 2) is intensive, since it is a major agricultural commodity that is growing day by day, and it has many applications for power generation, such as co-combustion of coal and Bm.

Figure 2: RH [17].

SD

When woody material is cut to the required shape, SD is generated (Fig. 3) from various places. Regarding combustion, SD can be used in many ways. Also, as technology improves, SD can be a valuable source of power generation.

Figure 3: SD [17].

AW

AW (Fig. 4) is generated during the harvesting of crops, and it includes anything produced by leftovers that are not used or sold. AW can be used by food processing, residues and livestock, being made into fertilizer. However, much of it is left unused in fields. AW can lead to water pollution and greenhouse gas emissions, if it is disposed in hazardous ways and burned, wasting energy. Some efforts have been made to convert Bm from AW into some better useable materials [18, 19].

Figure 4: AW [18].

SB

Bm from LnC, such as SB, is the remains from the extraction of juice from sugar. It is a readily available, low-cost and renewable resource that has a high potential for use in various applications, including bioplastics, Bf and other value-added products. SB (Fig. 5) is made out of Cl, HmCl and Ln [20].

Figure 5: SB sample [20].

Cl and HmCl can be hydrolyzed into straightforward sugars, which may be used as Fs to produce materials, synthetic chemicals and Bf. Ln can be separated from SB and used as Fs for the creation of high-worth synthetic compounds and materials. Furthermore, SB has been employed as a substrate for the creation of catalysts and other added items, e.g., xylitol, a characteristic sugar. The creation of these items from SB enhances Bm and increments the general financial reasonability of its usage [21].

Biofuel
Bf have an organic biological origin, from both animals and plants, and they can burn. Because they are non-polluting, Bf are very significant. They are more extensively used and environmentally sustainable than FF. Bf is now manufactured from any substance with an organic origin. As a result, according to IEA predictions, Bf will have a bright future by the middle of this century [22].

Applications of Ln
Ln is an abundant, eco-friendly, low cost, less toxic and renewable polymeric material. For several years, Ln from Bm has been used for heating, soil, water reduction, oil extraction, power generation, medicine, adhesives, flocculent, cement, glue, resin, asphalt emulsifier and Fs (Fig. 6).

Figure 6: Different applications of Ln [24.]

Ln phenolic resin has been used as a binder and insulation foam, with environmental benefits [23]. Ln from Bm can also serve as raw material for C fibers production. Researchers recommend that Ln extraction be used in chemicals and Bf, since it is more efficient, clean and environmental friendly [24].

Existing distinct pretreatment processes
Bm pre-treatment
Ln material produced from Bm from LnC by the pretreatment method is abundantly available on earth. It also can be produced by LnC waste. This means changing waste to valuable material. Bm from LnC consists of Ln, Cl, HmCl and other compounds, like extractives and inorganic materials [25].

Bm pre-treatment is a better step to get new materials, chemicals, medicines and another kind of residues that will be used as resorces. This method involves alkali treatment and acid treatment. Bm from LnC is mixed with distilled water, at different ratios, for delignification process, which is applied in pulp industries. In the beaker, a heated stirrer is used to maintain the required results. Distilled water is used several times, so that results are obtained and pH becomes neutral. The obtained material, like Ln products, is precipitated. The Ln sample is finally kept in a dried oven at 100 ºC. Other impurities are separated. The alkaline treatment is used to eliminate polymers and Ln [26].

Biological pretreatment process

Biological pretreatment process conserves energy, being environmentally friendly. During the process, hazardous gases are released, and liquid pollutant discharge is avoided. It does not produce fermentation-inhibiting compounds. Since it has high process time and space requirements, impacting negatively on CAPEX, investigations aimed at combining this technique with another kind of pretreatment methods should be done [27]. Such a proposed combination might still negatively affect the overall cost. Research on process kinetics must be done, so that the time for process completion could be reduced. Latest molecular-level research is required, to identify the microbes that can optimally digest/break down the more complex and rigid part of Ln [28].

Mechanical pretreatment

Bm size reduction not only enhances the surface area, but also improves handling and gives better hydrolysis. However, it consumes much energy, increases OPEX, and its operation is uneconomic. Bm pulverization needs to be designed and optimized following the advanced understanding of the materials' strength. Process efficiency must be improved to outweigh CAPEX and OPEX. Size-reducing facilities must be located, to avoid high costs with Bm supply and transport [29].

LHW method

Since LHW reduces inhibiting byproducts generation, washing and neutralizing operations at the end of the process area are needless. Since no chemicals are added, material degradation problems and requirements for material recovery operations are reduced. LHW enhances the breakdown of heterogeneously composed HmCl, and it gives less fermentation, hindering hydrolysates [30]. It produces higher solubilized products achieved at lower concentrations. Energy demands for the successive processing steps increase drastically, due to the high volumes of water involved. Eco-friendly renewable energy technologies could be developed and integrated into the process, to reduce energy costs and C footprint [31].

Chemical pretreatment method

Diluted acid pretreatment

Abundantly and easily available diluted acids, such as H_2SO_4, are the strongest. They chemically disrupt Bm from LcN and give better Cl and HmCl hydrolysates, achieved through varying acid concentrations. During the fermentation process, Furfural and HMF are generated by sugar decomposition. Since acid-induced material degradation/corrosion of expensive process equipment occurs, it has low efficacy [32]. HmCl dissolution during DA pretreatment also gives fermentable sugars, avoiding the need for HmCl enzyme digestion. Keeping the temperatures of the process low would help restrict the sugar decomposition and, therefore, inhibit fermentation. Steam pretreatment in combination with DA pretreatment can increase sugar generation in comparison to one-step pretreatment [33].

Alkaline extraction method

$Ca(OH)_2$ and NaOH are low-cost and safe alkalis. Ln and majorly Xylan containing HmCl get so solubilized that the efficiency of enzymatic hydrolysis is greatly increased. Bm fractionating is promoted, imparting flexibility in its utilization. The process requires moderate conditions, but needs more time to complete the pretreatment/LnC componential dissolution. It poses hydrolysate neutralization problems. Two-step acid-alkaline pretreatment could be the way forward [34].

IL pretreatment method

IL are green solvents that can be recovered and reused. Although IL can be custom designed, to suit the process as per Bm characteristics, they are too costly. Mineral acid neutralization of organic amine generates a type of IL that does not require any purification. Therefore, protic IL has the potential to emerge as a commercially viable alternative to the traditional dialkyl imidazolium-based salts [35]. IL hydrolysis pretreatment is carried out at lower temperatures, resulting in reduced possibilities of hydrolysate degradation and promotion of IL recovery [36]. A design that includes H_2SO_4 pretreatment before IL pretreatment, targeting a >96% recovery, is less than 1 USD Kg, and > 90% heat recovery can make the process viable and commercially applicable [37].

Conclusion

There is huge potential for research work on Bm from LnC, which is an abundant available and renewable resource on earth that can be used for various applications, including Bf production, bioplastics and other value-added chemicals and products. Optimization of the extraction process is a more efficient and sustainable method, to valorize the yield of Ln derived from different Bm from LnC. It also decreases the environmental impact of the extraction process, which used to depend on petroleum-based products. Bf are used for different purposes, such as the production of bio-based chemicals, energy and materials. This approach can increase the overall economic viability of Bm utilization, improve the sustainability of the economy and also make pulp and paper industry profitable.

Acknowledgments

The research was performed in the Coal and Study Laboratory at Mehran University of Engineering and Technology, Jamshoro, Pakistan.

Authors' contributions

Namatullah Jafar: data setting. **Mohammad Siddique**: wrote the manuscript. **Kamran Khan**: contributed to the figures. **Saadatullah K. Suri**: helped with the abstract and conclusion. **Muhammad Asif**: worked on editing. **Nazia Karamat**: removed mistakes in the manuscript.

Abbreviations

AW: agricultural waste
Bf: biofuel
Bm: biomass
$Ca(OH)_2$: calcium hydroxide
CAPEX: capital expenditure
Cl: cellulose
CO_2: carbon dioxide
DA: dilute acid
FF: fossil fuels
Fs: feedstock
H_2SO_4: sulfuric acid
HmCl: hemicellulose
HMF: hydroxymethylfurfural
IEA: International Energy Agency
IL: ionic liquids
LHW: liquid hot water
Ln: lignin
LnC: lignocellulose/lignocellulosic
MSW: municipal solid waste
NaOH: sodium hydroxide
OPEX: operational expenditure
RH: rice husk
RS: rice straw
SB: sugarcane bagasse
SD: sawdust
WH: wheat husk
WH: wheat straw

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