

Lignocellulosic Biomass for Biofuel, Pretreatment Methods and its Application in Different Materials. A Review

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Received 26/04/2024; accepted 10/10/2024

<https://doi.org/10.4152/pea.2026440501>

Abstract

LcBm is gaining popularity as an alternative energy source, due to the depletion of petroleum derivatives and environmental concerns. Characterizing Lcbm intermediates and products is critical for turning it into Bf. LBm chemical composition is crucial in creating successful pretreatment methods that break down its stiff structure and convert sucrose to glucose via enzymes and microorganisms. The steps herein reviewed allow for C₂H₅OH synthesis and additional value-added green chemicals. This review examines various feedstock and pretreatment techniques for C₂H₅OH production, including Ln degradation, breakdown, hydrolysis and fermentation. While combined pretreatment improves chemical production and enzymatic hydrolysis of LBm, it has greater operating costs. Acids pretreatment procedures, steam explosion and hydrothermal treatments effectively remove Hc fractions. Alkali, oxidative or organosolve pretreatment is more successful in removing and degrading phenols. The aim of this study was to improve the understanding of current and future bio refinery processes, identify constraints and develop technologies to improve pretreatment procedures.

Keywords: Bf; LcBm; pretreatment.

Introduction*

Growing energy scarcity is now viewed as a worldwide issue. C₂H₅OH is often regarded as the most important renewable energy source capable of replacing

*The abbreviations list is in page 331.

petroleum-based fuels such as diesel and gasoline. Global C_2H_6O from Bm output has increased from roughly 50 million m^3 in 2007 to more than 95 million m^3 in 2013 [1]. Yearly output of LcBm is around 181.5 billion tonnes, making it an abundant commodity [2].

C_2H_6O is often used as an engine gasoline and additive in a variety of fuel combinations. It works well with internal combustion engines that use spark ignition. Engine octane level and research octane level are 80 and 112, respectively. C_2H_5OH low octane rating hinders compression ignition, being difficult to combine it with gasoline and diesel. Several attempts have been made to improve the use of C_2H_6O in CI engines, including emulsifiers to increase its miscibility with diesel. Adding ethyl hexyl nitrates or diterbutyl peroxide can boost octane value. Dual fuel operation involves introducing C_2H_6O and petrol into separate cylinders, or modifying diesel engines to improve auto-ignition [3].

The Chinese government began producing C_2H_5OH ten years ago, to address the widening disparity between petroleum consumption and economic development, which is reducing local reserves and output. The first C_2H_6O factory in Jilin Province, northeast China, was created in August 2002, using maize as a valued feedstock. Five well-known C_2H_6O -for-fuel facilities use starch-based resources such as wheat, maize and cassava, to create 1.52 million tonnes of alcohol per year across the country [4]. Despite all, there are not any reasonable established methods for convenient Bm conversion. Therefore, farmers burn most Bm, causing environmental pollution and polluting the air. United States and Australia account for over 81% of C_2H_5OH global supply, with maize or sugarcane being the most popular crops [5].

Types of pretreatment

Physical pretreatment

Steamed, crushing, milling, radiation, heating and pressure are common procedures applied to feedstock for breaking down Lcl waste (Table 1).

Table 1: Physical treatment of Lcl and its impact on various feedstock.

Raw material	Treatment	Conditions	Efficacy	Ref
Corn	Ultrasound	Sonication with maize starch slurry for 40 s.	Increased sugar yield by 5–6 times	10
Wheat straw	Ball milling	Residence time: 110 min	Increased sugar yield by 4–5 times	10
Agricultural waste	Pyrolysis	Prepared Bm was subjected to mild acid hydrolysis using 1 N H_2SO_4 at 97 °C, for 2.5 h.	70% Cl conversion to reduce sugars and >5% glucose	11
Corn stover	Ball milling	30 °C for 5120 min	Increased ethyl levulinate output by 31.23% at 160 C; improved direct conversion to methyl levulinate.	11
Cotton stalk	Ball milling	Residence time:110 min	Improved sugar yield by five to six times	10
Mustard stalk	Pyrolysis	Pretreated Bm subjected to mild acid hydrolysis using 1 N H_2SO_4 at 97 °C, for 2.5 h.	80% conversion of Cl to reducing sugars and >5% glucose	11
Sugarcane bagasse	Pyrolysis	Mild acid hydrolysis with 1 NH_2SO_4 , at 97 °C, for 2.5 h, on pyrolysis pretreated Bm.	Cl converted into reduced sugars at 75%, with >5% glucose	12

Grinding and milling are the main pretreatments for all Bm, lowering particle size and crystallinity. Grinding rice straw in wet disc milling produces superior outcomes for glucose recovery along with energy savings than those from ball milling [6]. Depending on the Bm, improved pretreatment technologies, such as grinding with balls, roll milling and wet disc milling, allow for enzymatic saccharification. Bm of Lcl plants is composed of a variety of carbohydrates and polymers that are densely packed by layers of fibers, Hcl and Ln [7]. Their Ln coatings shield them against deterioration including hydrolysis by enzymes. Treatment is essential for breaking down the Ln layer and extracting both Hcl and Cl via an enzymatic process. Preliminary treatment reduces cellulosic crystallinity and increases Bm surface area, leading to Hcl decomposition [8]. It is also a crucial step for converting Cl material, making it more accessible to enzymes, and allowing for quick and high-yield conversion of carbohydrates into fermentable sugars. Pretreatment procedures may be classified into four categories: chemical, physical, physicochemical and biological [9-12].

Combination of pretreatment techniques

To address the disadvantages of single pretreatment approaches, several researchers have attempted to combine them for improving treatment efficiency. Nowadays, several studies have been undertaken using a mix of pretreatment methods. For fungal pretreatment, the biggest drawback is the extended operating time of cleaning procedures that increase its efficiency [13]. Another study has found that, whenever H₂O₂ was coupled with steam pretreatment techniques, xylose and glucose yields rose by 34 and 12%, respectively, whereas arabinose and mannose total yields did not increase appreciably. In the pretreatment process, adding H₂O₂ did not enhance the synthesis of Lc-derived products [14]. In recent research, alkaline H₂O₂ has been commonly used due to it is effective against a wide spectrum of LcBm, and its significant enzymatic hydrolysis capabilities when used individually or in combination. Pretreatment of grain straw using alkaline NaOH along with H₂O₂ leads to 90.4% sugar conversion [15]. However, steam pretreatment yields 75% glucose and 65% xylose. It was hypothesized that treating maize stover with a sodium chloride-methanol mixture enhances enzyme accessibility. Maize stover processed using C₂H₆O-water and diluted sulfur dioxide had a combined effect on delignification, increasing Cl enzymatic breakdown [16].

Chemicals derived from pretreatment procedures

Chemical intermediates, such as petroleum alternative items, are produced during pretreatment procedures across multiple industries, including meals, paper, lumber and other fibers. They may have new or multiple better properties than original petroleum commodities, such as phenolic compounds made from Ln (Fig. 1), which

have several applications, including chemical fertilizers, thermal and electrical energy, diesel fuel, carbon fibers, adhesives and additives [17].

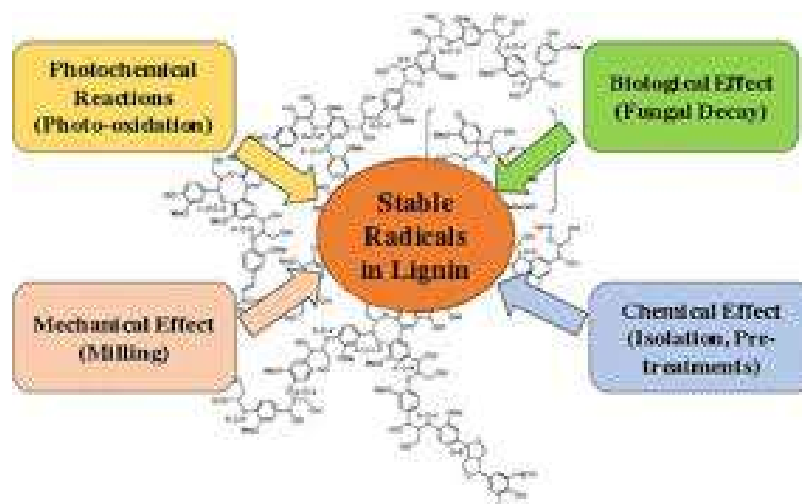


Figure 1: Phenol structure containing prominent monolignols [18].

New and evolving pretreatment techniques

Hydrothermal treatment

Hydrothermal treatment employs elevated T of subcritical water (< 374 °C), to denature the walls of plant cells, break down Hcl and turn Ln into sugars/syngas. Depending on the intended product, this approach may be classified into three different types of carbonization. The method involves being carried out at T from 200 to 270 °C, yielding solid char rich in carbon [19], and at T from 250 to 400 °C. The process produces soluble water components, biological oil and charcoal, in addition to a gas phase including oxygen and CO₂. Gasification is a type of hydrothermal process that requires an environment above 400 °C, to produce gas used as fuel. Hydrothermal gasification produces faster reactions than liquefaction and carbonization, due to higher T [20].

Enzymatic hydrolysis

Enzymes are used to break Cl and Hcl polymers. Hcl is made up of xylan, glucan and galactan, while glucose solely includes glucan. Hcl and Cl hydrolysis produces pentoses and glucose [21, 22]. High Ln levels can hinder enzyme accessibility and inhibit end products, while decreasing hydrolysis' efficiency and output. Ln, which is made of cellobiose and glucose, is a potent cellulase inhibitor [23]. Several variables influence the production of monomeric carbohydrates, including liquid-solid ratio, acid type, T, reaction time, Bm size of particles and macromolecular length. Plant cells walls contain many polymeric components, such as Ln, pectin, Cl derivatives, proteins and other mineral elements [24].

Advantages of C_2H_5OH

C_2H_5OH , also known simply as C_2H_6O , is a renewable and bio-based alcohol that is primarily produced through the fermentation of sugars derived from plant materials. C_2H_5OH has several advantages, which contribute to its increasing use in various applications. It is produced through renewable resources such as sugarcane, maize, wheat and other biological sources. Unlike fossil fuels, these resources can be renewed through farming methods, making C_2H_5OH a more sustainable option. C_2H_5OH has reduced greenhouse gas emissions compared to traditional fossil fuels [25], since plants used to produce it absorb CO_2 during their growth, offsetting emissions released when it is burned as fuel. This helps to minimize global warming and lowers total carbon impact.

Since C_2H_5OH is made from locally grown crops, it enhances energy security, by lowering reliance on imported fossil fuels. This can be especially useful for nations looking to diversify electricity sources and increasing energy independence [26]. C_2H_5OH is biodegradable and less harmful to the environment than certain fossil fuels, and, in the event of a spill or release, it poses fewer ecological risks and is less persistent in the environment.

C_2H_5OH can be mixed with petrol, in various ratios, to create C_2H_6O -gasoline blends such as E10 (10% C_2H_6O : 90% petrol) and E85 (85% C_2H_6O :15% petrol). These mixes may be used in normal petrol engines, which reduces total fossil fuel usage. C_2H_6O can help to revitalise rural economies by producing jobs in agriculture and Bf [27], and it enables farmers to diversify their crops and sources of revenue. C_2H_5OH is commonly used as an oxygenate additive in gasoline, as it improves combustion efficiency, reduces emissions of certain pollutants and enhances the octane rating of gasoline.

While C_2H_5OH offers these advantages, it is vital to consider the entire lifecycle, including feedstocks farming and energy-intensive processes involved in its production, to ensure overall sustainability and environmental benefits of this Bf [28].

Ln-based substances

Fig. 2 shows processes for extracting and isolating Ln.

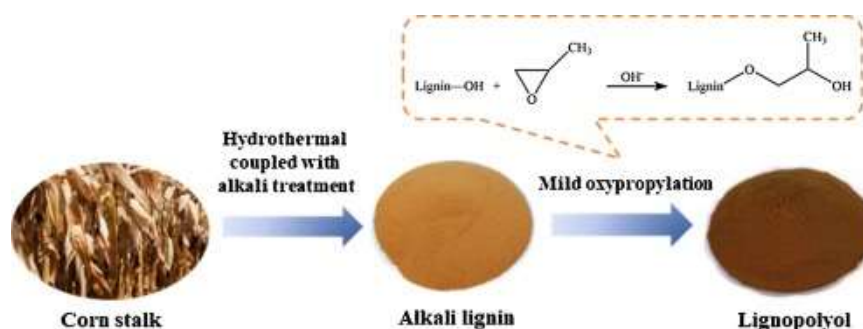


Figure 2: Processes for extracting and isolating Ln, including key requirements [29].

These systems have been employed for a wide range of applications, including sorbents for hazardous metal ions, environmentally acceptable polymer fillers, rough tool additives, medicines, drug delivery systems and electrochemically active materials. They are also employed in compounds manufacture such as adipic acid, vanillin, cycloalkanes and phenols. Vanillin may be used to create amine hardeners and epoxy cross-linkers, among other compounds [30]. Selecting Ln with a high β -O-4 bond content improves the strength and electrical characteristics of carbon fibers. Esterification and fractionation of technical phenol can provide sustainable biological plastics with customized characteristics for specific applications.

Ln-based degradable composite sheet materials offer a wide range of applications, including sensors, sensitive materials, systems for storing energy, multifunctional packaging and biological materials [31]. Recovered Ln using LcBm may be used to make bioplastics with high mechanical strength, T and water stability and UV resistance.

Adding phenol phthalates to an existing poly(butylene adipate-co-terephthalate) polymer results in biodegradable materials with UV protection and adjustable mechanical properties. These materials might be used for packaging. Additionally, Ln can provide low-carbon floating agents for water treatment [32]. Ln-based nanotechnology, formed by self-assembly in a naturally occurring solvent-water combination, is a highly attractive Bm product. Ln may be used to make a variety of electrode materials, including hierarchical porous carbon monolith, nanoporous carbon, associated hierarchical porous nitrogen-doped carbon [2] and other energy storage materials, as shown in Fig. 3 and Table 2 [33].

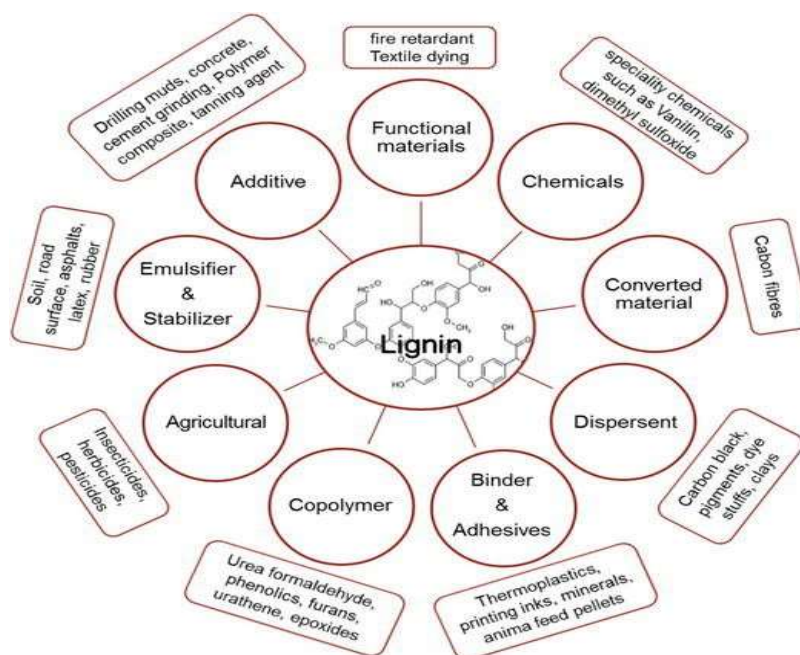


Figure 3: Use of Ln and polymer system derivatives [33].

Table 2: Ln functionalization strategies and potential applications of its derivatives.

Ln type	Reagents	Reaction parameters	Potential applications
Kraft functionalized Ln	Pyridine, 20% ammonia	2h, 180 °C, 21 bar, nano Al-based catalyst	Curing agent for epoxy resin
Alkali Ln	36% dimethylamine formaldehyde (aq.), and	Acetic acid- 60°C, 3 h	Reactive, biobased, additive, fertilizer
Alkaline Ln	Anhydrous ethylene and formaldehyde	65 °C, 3 h, 4 wt% NOH	Catalytic activity composite to reduce Ag
Epoxidized alkali Ln	Propanediamine	75 °C, 3-4 h	Epoxy resins, reactive, additive

Ln and its near relatives are frequently used in environmentally friendly construction, such as cement-based additives, components for stiff polymers, foams, anti-corrosive and anti-microbial resins and bitumen substitutes in asphalt manufacture (Table 3) [34].

Table 3: Ln use for the production of stiff foams made of polyurethane.

Types of Ln	Production method	Applications	Ref
Kraft Ln	By-product of pulping process in paper industry	Polyol replacement in polyurethane foam synthesis	[35]
Organosolv Ln	Extracted using organic solvents	Polyol substitution in rigid polyurethane foams	[36]
Lignosulfonates	By-product of sulfite pulping in paper industry	Used with other Ln or polyols in foam synthesis	[36]
Enzymatic hydrolysis Ln	Produced through enzymatic breakdown	Polyol replacement in foams	[36]
Pine kraft Ln	Liquefied using microwaves, pure glycerol and 1,4-butanediol to yield polyols	Binder for particleboard, composite wood products	[37]

LCA in the building sector

The building industry consumes 30-40% of the world's electricity, emitting 40-50% greenhouse gases. LCA for building structures covers the initial material extraction process, material manufacture, structure design and operation, as well as utilization. LCA has four steps: identifying the goal and scope of the study; developing a LCA inventory; assessing the effect; interpreting and analyzing results [38].

Fig. 4 depicts LCA approach used in construction industry. There are two distinct forms of LCA. The problem-oriented mid-point technique focuses on real-world ecological consequences such as climate change, pH imbalances, degradation of the ozone layer and eutrophication, along with human toxicity. The damage-oriented end-point method includes estimating the midpoint's effect on people, the natural world, the environment and financial resources. This research was among the initial studies to employ LCA in buildings. Nonetheless, before the turn of the century, the use of LCA to analyze long-term sustainability of structures increased considerably [39]. However, others argue that LCA outlined in the aforementioned standards might be less appropriate for complicated endeavors like buildings.

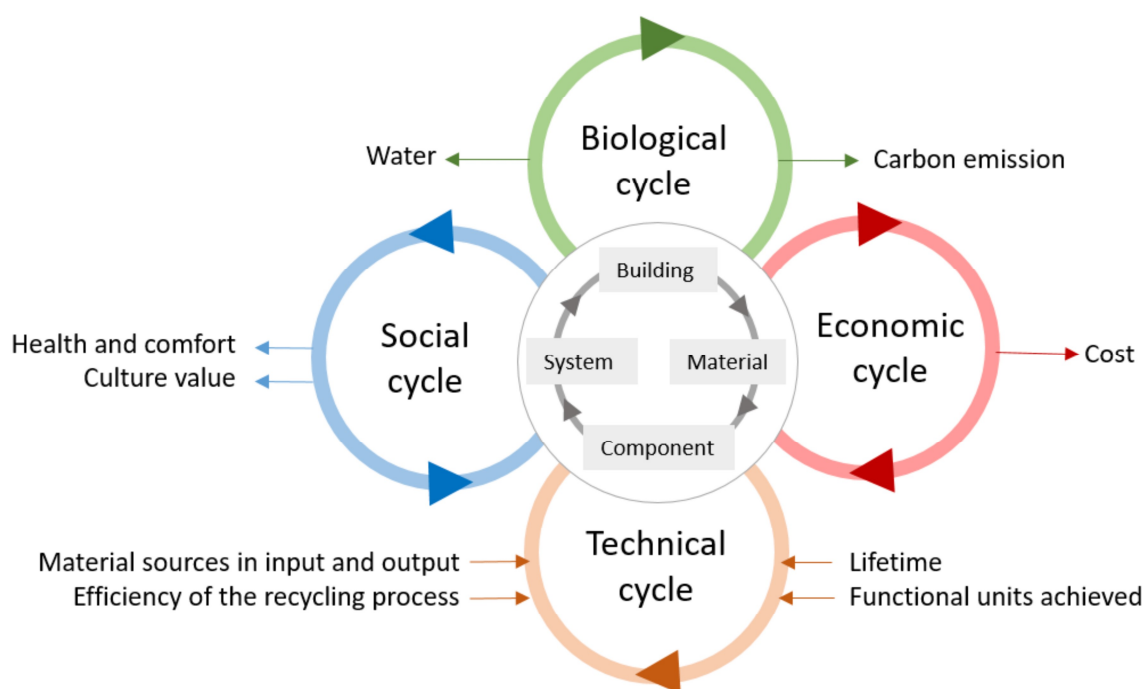


Figure 4: Framework for LCA in building industry [37].

Many articles have been written in recent years about the use of LCA in buildings. As in [40], it was found that most power is spent during the usage phase. The heating of spaces is most energy-consuming in cold places, but less so in tropical climates with higher T. Concrete has minimal initial embodied energy consumption, but contributes significantly to total embodied electricity, due to its widespread usage in buildings.

Conclusion

Ln in feedstock slows Cl and Hcl degradation. As a result, extensive research has been conducted to develop a variety of pretreatment techniques for advancing bioenergy. The combined use of two separate types of previous treatments often has beneficial results, including increased chemical output and enzyme-mediated hydrolysis of LBm, but it also increases operational expenses.

Acid medication, steam explosion and other hydrothermal procedures effectively remove Hcl from Bm. Alkali, oxidative and organosolv pretreatments efficiently remove and degrade Ln. However, organosolv and oxidative delignification methods have greater expenses for both operation and upkeep than those from alkali treatments. Biochemical pretreatment successfully removes Ln from LBm. Alkali pretreatments remain the most popular and cost-effective approach for Ln removal. Preparing LBm using a mixture of diluted acid, hydrothermal and steam explosion

alkali is the most effective method, depending on the analysis. In contrast, advanced hydrothermal pretreatment using biorefinery platforms seeks to manufacture added-value commodities from phenol and additional components, with a current focus on energy generation.

Research suggests that treatment strategies should be tailored to each Bm's unique features. Bm with high water (>30%), Hcl and Cl content, with a carbon-to-nitrogen ratio lower than 30, is ideal for biochemical conversion. To improve the sustainability of concrete composites, it is important to explore novel additives and admixtures that are not derived from crude oil, while still improving their qualities. Materials having a moisture content lower than 30%, high Ln content and carbon:nitrogen ratio exceeding 30% are ideal for thermochemical conversion and Bf production. This review of chemical, physicochemical and biological pretreatment methods, together with their focal points and obstructions, can assist professionals in organizing their researches.

Acknowledgment

The authors are thankful for the Chemical Engineering Laboratory Services at BUITEMS, Quetta.

Authors' contributions

M. Asif: worked on paper. **A. A. Bhutto:** treated the table; addressed plagiarism. **M. Siddique:** helped with abstract and conclusion. **S. K. Suri:** references sequence. **S. Tayyab:** abbreviations; proofreading. **N. Karamat:** doi setting. **A. A. J. Alfi:** setting of table and figures.

Abbreviations

Bf: biofuel

Bm: biomass

C₂H₅OH: bioethanol

C₂H₆O: ethanol

Cs: cellulose

H₂O₂: hydrogen peroxide

Hcl: hemicellulose

LBm: lignin biomass

Lc: lignocellulosic/lignocellulose

LCA: life cycle assessment

LcBm: lignocellulosic/lignocellulose biomass

Ln: lignin

T: temperature

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