Clean Energy Science and Technology Volume 1 Issue 2 (2023) doi: 10.18686/cest.v1i2.70

Review Article

Chemical pretreatment of lignocellulosic biomass in anaerobic digestion and biomethanation

Erick Auma Omondi[1,*], Arnold Aluda Kegode[2]

[1] *Department of Civil and Construction Engineering, University of Nairobi, 10344-00100 Nairobi, Kenya*

[2] *Department of Civil and Structural Engineering, Moi University, 3900-30100 Eldoret, Kenya*

*** Corresponding author:** Erick Auma Omondi, omorric@gmail.com

Abstract: The current impacts of climate change necessitate the promotion and use of renewable energy sources to avert the growing environmental and health concerns emanating from the use of fossil fuels. Lignocellulosic biomass (LCB) is a promising, renewable, and sustainable energy source based on its abundance and feedstock properties. Anaerobic digestion (AD) involves a biochemical process that can convert LCB to biogas through hydrolysis and biomethanation processes through the action of microorganisms, such as methanogens and sulfate-reducing bacteria. The hydrolysis of LCB releases various reducing sugars, which are essential in the production of biofuels, such as bioethanol and biogas, organic acids, phenols, and aldehydes. The resultant biogas can complement energy needs, while achieving economic, environmental, and health benefits. Enhancement of the AD process for converting LCB into bioenergy can be realized through appropriate pretreatment capable of disrupting the complex lignocellulosic structure and freeing cellulose and hemicellulose from the binding lignin for enzymatic saccharification and fermentation. Determining the optimal pretreatment technique for AD is critical for the success of the LCB energy production process. This study evaluated the application of chemical pretreatment techniques for the improvement of LCB digestion for bioenergy production. The study reviewed LCB characteristics, AD processes, and the role of various chemical pretreatment techniques, such as acid, alkali, organosolv, ozonolysis, and ionic fluids. The findings of this study can create an understanding of the action methods and benefits of different LCB chemical pretreatment techniques, while highlighting the outstanding drawbacks that require divergent strategies.

Keywords: pretreatment; lignocellulosic biomass; chemical pretreatment; anaerobic digestion

1. Introduction

The growing global energy demand associated with the rising world population and affluence impacts a major energy crisis involving the overutilization of fossil fuels, such as coal, oil, and natural gas, which form about 80% of the total energy requirement[1]. The overreliance on fossil fuels imposes a depletion challenge and immensely persistent environmental degradation, with short- and long-term effects. The glaring threat compels the search for alternative energy sources considered clean, renewable, and with the potential to avert the dangers associated with fossil fuels.

Bioenergy, such as biogas produced through the anaerobic digestion (AD) of lignocellulosic biomass (LCB), is considered a possible alternative to fossil fuel energy due to its feedstock abundance, widespread distribution, and limited adverse environmental effects[2]. The AD of lignocellulosic biomass comprises a biochemical process that can convert the biomass into biogas, which is applicable as an energy source, such as electricity, heat, or fuels[3]. The techniques and practices are associated with several economic, environmental, and climatic benefits. The benefits have seen the adoption and integration of AD in the power industry, with several full-scale plants currently in operation worldwide[4,5]. While traditional plants have used bio-renewable feedstocks, such as sugar and starch-based crops, current plants have largely adopted LCBs from crop residues

Received: 9 October 2023 Accepted: 30 October 2023 Available online: 20 November 2023

and energy crops in the production of bioenergy and other bio-based products. The AD of lignocellulosic biomass can potentially produce alternative and supplementary fuels and chemicals through a biological conversion process. Traditionally, the AD process has provided attractive and efficient waste treatment and conversion methods into biogas, thereby mitigating pollution, while promoting energy recovery[3,6]. Lignocellulosic biomass remains undervalued despite its huge potential for biogas production.

The primary constituents of LCB are 38%–50% wt cellulose, 23%–32% hemicellulose, 10%–25% lignin, and 2%–15% extractives, with varying levels of inorganic salts[7]. The interactions between these constituents form a highly resistant and recalcitrant biomass structure that can adversely affect its energy valorization. Such complexity is aggravated by the formation of heterogeneous embedment of the cellulose fibers in a lignin-polysaccharide matrix, making it less accessible to enzymatic hydrolysis[8,9]. The complex structure reduces surface area accessibility through the crystallization of cellulose, hemicellulose, and lignin. The lignin component is considered the rate-limiting proportion in lignocellulose material degradation in either natural or industrial processes[10]. Despite the challenges attributable to lignocellulosic bioenergy conversion, it is still considered the most promising raw material for renewable biofuel production, considering its availability, economic viability, and promising characteristics, such as a good C/N ratio. Most LCBs have favorable C/N ratios, with examples such as 20:1 for water hyacinth[11], 11:1 for sugar beet[12], and 28:1 for sugarcane bagasse[13]. However, some other biomasses have a high C/N ratio, such as 120:1 for corn cob[14], 60:1 for sorghum bagasse[15], and 55:1 for wheat straw. A higher biomass C/N ratio can be a major limiting factor affecting the biomethanation process and overall biogas yield. Thus, synergistic integration of low C/N ratio biomass with high C/N ratio lignocellulosic biomass in an AD system, such as through co-digestion, presents an ideal option to enhance biogas yield for such biomass[8].

Pretreatment presents a critical intervention step in the utilization of LCB to optimize its conversion and valorize the biomass AD process. Traditionally, chemical, biological, physical, and physicochemical pretreatment methods have been commonly applied, with varying levels of success and challenges[16]. The role of biomass pretreatment is to remove the physical and chemical barriers that make lignocellulosic materials inaccessible by enzymes for the hydrolysis process[10]. The hydrolysis process presents a vital stage in the biochemical process for the conversion of lignocellulose materials to sugar-based energy.

Chemical pretreatment receives the most research interest based on its effectiveness and enhanced biodegradation of complex materials[17]. The technique involves the use of chemicals, such as acids, bases, and ionic liquids, to alter the physical and chemical characteristics of the biomass and solubilize its cellulose, hemicellulose, and lignin[18]. The most popular methods of chemical pretreatment include alkaline, acid, ozonolysis, and oxidation pretreatment methods[19]. Although many chemical pretreatment methods have been studied for cellulosic ethanol production, only some of them have been applied to biogas production in AD processes[18].

The choice of a pretreatment technique should be based on its efficiency, economy, and eco-friendliness. The adopted pretreatment must focus on easing the accessibility of enzymes to the chemical components of the biomass, leading to its depolymerization and biodegradation. Thus, pretreatment is an important tool for cellulose conversion processes and is essential to the modification of the cellulosic structure of the biomass, making it more available to the enzymes responsible for the conversion of carbohydrate polymers into fermentable sugars. **Figure 1** presents the types of LCBs and the pretreatment process.

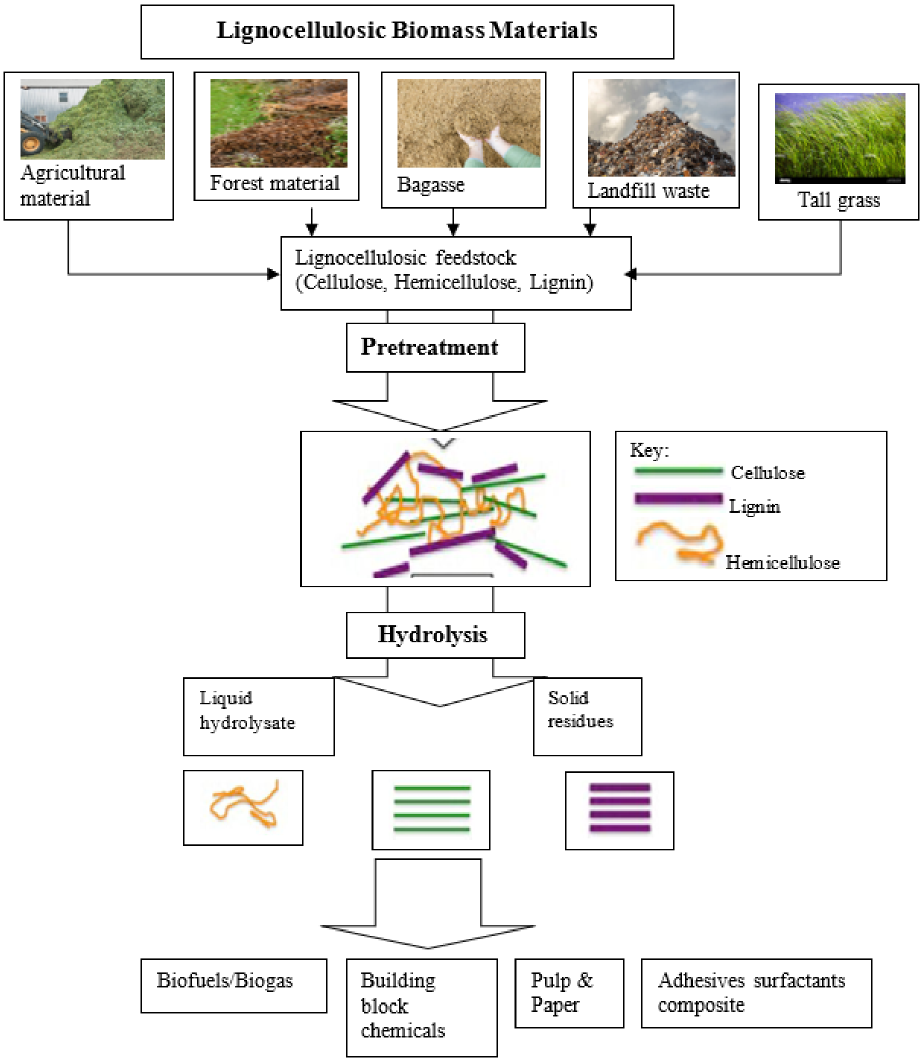

Figure 1. LCB pretreatment process[20].

2. Anaerobic digestion of lignocellulosic biomass

Lignocellulosic materials, largely available in their constituent forms of cellulose, hemicellulose, and lignin, hold great potential for biogas (biomethane) production through the AD process and liquid fuel (bioethanol) production through fermentation[21]. Exploitation of LCB with a well-informed approach can unlock the biomass potential and significantly supplement the energy demand as a sustainable energy source. Biomass can be obtained from numerous sources, including rural agricultural waste, forest materials, urban LCBs collected from municipal and sewage waste, and industrial LCBs contributed by cellulose and agri-food industries[22]. The properties of LCB may vary by critical constituents depending on the considered parent source (**Table 1**). Some of the LCBs considered abundant with great bioenergy potential include rice straws, wheat straws, agro-industrial wastes, and aquatic macrophytes[23,24]. The bioenergy value of such biomass can be exploited through the AD process. The efficiency of AD in biogas generation using lignocellulosic biomass can be greatly improved using an appropriate pretreatment process[21]. With many possible pretreatment techniques, determining a suitable and specific method particular to a lignocellulosic material with optimal pretreatment conditions for an improved rate of hydrolysis remains an area of interest. While a lot of research on the pretreatment of lignocellulosic materials in bioenergy production has focused on bioethanol production and value-added chemicals, limited work has been done in the area of pretreatment for biomethanation.

Table 1. LCBs and their biomethane potential for select feedstocks.

Feedstock	Cellulose (%)	Hemicellulose (%)	Lignin (%)	C/N ratio	Biogas yield (mL CH_4/g.VS)	Ref.
Rice straw	32–47	19–27	5–26	80	152–263	[25–27]
Wheat straw	35–45	20–30	10–15	50–60	250.5	[28–30]
Corn stover	~35	~20	~12	50–64	260.5	[31,32]
Soya bean straw	40	22	13	20–40	290.8	[33,34]
Switch grass	39	20	21	80	256.6 ± 8	[35,36]
Barley straw	37	35	16	54–80	-	[37,38]
Water hyacinth	25	33	10	20	251.3	[8,11,39]
Sugarcane bagasse	25–47	19–33	14–23	60	247.60	[40–42]
Poplar	45	21	24	103	81.1	[43,44]
Green beans	17	16	8	25–30	-	[45,46]
Pine	54	12	24	80	348	[47,48]
Soft wood stems	40	30	25–35	80–100	125	[49,50]
Sunflower	34–42	19–33	12–30	73	210–286.1	[51–53]
Tomato plant	39	29	12	39	128–307	[54,55]

Enhancing the AD process involves a set-up for efficient substrate degradation targeting balanced critical parameters, including pH, temperature, nutrient (C-N-P) composition, substrate total and volatile solids, hydraulic retention time, feedstock loading rate, organic loading rate, and management of inhibitors, such as NH_3 and furfural[56]. Primarily, the nutrient composition plays a critical role that points to its final biomethanation potential[57]. For example, the optimal C/N ratio for a suitable LCB substrate should be in the range of 20 to 30. High C/N ratios can affect the total ammoniacal nitrogen (NH_3-N) and fatty acid production, which may also adversely affect hydrolysis and methanogenesis processes, lowering the biogas yield and rate[58]. Conversely, a low C/N ratio is associated with the development of excessive ammonia and pH rise, leading to unbalanced nutrient composition in the reactor and limited methanogenesis[59]. The biodegradation process is also pH-dependent, whereas pH fluctuations can affect the microbial action on the substrate. For example, an optimal pH for methanogens lies between 6.5 and 7.5; however, acidogens can adapt to a wide pH range between 3 and 12[60]. Acidic pH is known for the formation of volatile fatty acids responsible for deeper pH drops and inhibition of biomethanation.

Similarly, the operating temperature in a digester plays a central role in the efficiency of biomethanation by providing a conducive environment for propagation and action by microorganisms[6]. Different microbes can adapt to different temperature ranges and thus the temperature range can be psychrophilic (15–25 °C), mesophilic (35–40 °C), or thermophilic (55–60 °C). Most optimal-performing plants operate between the mesophilic and thermophilic temperatures, with mesophilic being the most popular due to the low energy requirement to achieve the necessary temperature with easily achievable thermal stability[61,62]. However, in the interest of high energy turnover, thermophilic temperature may be preferred, despite its high energy demand, as a traded-off for quick and increased biogas production and low pathogen slurry[57].

3. Role of lignocellulosic biomass pretreatment

Lignocellulosic biomasses are known for recalcitrance, a process of resistance to chemical and biological degradation through their crystalline cellulose structure, degree of lignification, structural heterogeneity, and complex cell wall composition[9]. Such complication limits the achievement of biomass potential conversion and energy release. Thus, pretreatment plays a significant role in overcoming the challenges limiting LCB exhaustive biodegradation for enhanced bioenergy generation[63]. The pretreatment process disrupts the recalcitrant structure, leading to the breakage of lignin bonds, allowing hemicellulose degradation, and reducing the degree of crystallinity and polymerization of the cellulose[64]. Numerous pretreatment strategies have been developed to enhance the reactivity of cellulose and increase the yield of fermentable sugars[65]. In summary, the pretreatment strategies seek the following: to produce highly digestible solids that enhance sugar yields during enzyme hydrolysis; to limit the degradation of sugars, such as pentoses and other derived forms of hemicellulose; to minimize the formation of inhibitors; and to maximize lignin recovery for conversion into other valuable co-products[66,67]. Pretreatment also seeks to lower the operating cost of reactors by lowering reactor size requirements for the sake of efficiency and minimizing heat and power requirements[66].

4. Chemical pretreatment of lignocellulosic biomass

Chemical pretreatment of LCB can be done with acids, alkalis, and organic solvents to degrade the more complex structures of substrates. The technique is regarded as one of the most promising ways of improving the bioavailability of carbohydrates because it also removes lignin by reducing polymerization and cellulose crystallinity[68]. The efficiency and affordability of chemical pretreatment techniques have made them appealing and attractive for adoption in enhancing the biodegradation of complex organic biomass[69]. Although sometimes the cost of chemical pretreatment has been perceived to be prohibitive, Jönsson et al.[70] established that the cost of catalysts is dependent on the amount used in the pretreatment, as well as on the purchase price, where, for example, lime is cheaper than sodium hydroxide, together with the cost of recovery and reuse.

In the following sections, the major chemical pretreatment techniques and their effects on the valorization of complex components of various LCBs are discussed.

4.1. Acid pretreatment

This involves the application of dilute or concentrated acids to improve the degradation of carbohydrate fractions of cellulose through the hydrolysis of hemicellulose. LCB pretreatment with selected acids can improve enzymatic hydrolysis, enhancing the release of fermentable sugar following the aided disintegration of its rigid matrix[63,65]. Dilute acids, such as H_2SO_4 and HCL, have been used successfully to treat lignocellulosic biomasses, such as switch grass[71], poplar[72], and corn stover[73]. The action of dilute acids, such as H_2SO_4, on biomass leads to the hydrolysis of hemicellulose into xylose and other sugars, which further break down xylose to furfural. The action of dilute acids on biomass involves efficient removal and recovery of hemicellulose in the form of dissolved sugars and glucose for eventual hemicellulose hydrolysis[74]. This improves the digestibility of cellulose in residual solids. Although H_2SO_4 is the most widely used acid in acid biomass pretreatment, other studies have also used nitric acid, phosphorous acid, and hydrochloric acid[75]. While the method involves the use of low-concentration acids, it also employs the intervention of thermal action, such as an autoclave operated between 130 °C and 200 °C[76]. High temperatures in dilute acid pretreatment are useful in enhancing cellulose hydrolysis. The optimal acid concentration is considered to be in the range of 0.2%–2.5% v/v, as high concentrations can be toxic, corrosive, and hazardous, inflicting high maintenance costs and the possible generation of inhibitory conditions in the reactor[65]. Furthermore, the use of concentrated acid calls for a post-treatment recovery strategy, which can further tilt the economic viability of the process.

4.2. Alkali pretreatment

Alkali pretreatment involves the addition of bases to biomass, leading to an increase in internal surface swelling and a decrease in the degree of polymerization and crystallinity of cellulose[64,77]. Alkali action further leads to the destruction of links between lignin and other polymers, while ensuring lignin breakdown and freeing biodegradable biomass content[78]. The technique has high efficiency, especially in the delignification process. Thus, alkali pretreatment works better for low-lignin-content biomass, as a high lignin content of the biomass makes the method less effective[79]. Therefore, the effectiveness of this pretreatment depends on the lignin content of the biomass[80].

To achieve optimal alkali action on biomass, accurate alkali loading, dosage, and reaction temperature are critical parameters to consider[65]. According to Hernández-Beltrán et al.[81], an optimal performance of alkali pretreatment demands the use of low concentrations of alkali at a low temperature and atmospheric pressure to prevent the generation of toxic compounds, such as furfurals and hydroxymethylfurfurals (HMF). High concentrations of alkali have been associated with the degradation and decomposition of polysaccharides[65]. The choice of alkali to use in pretreatment has arguably been based on the reagent cost, its performance, and its manipulation capability[82]. Out of the various alkali solutions, NaOH, KOH, CaO, and CaOH have been greatly used in pretreatment tests based on their merits and demerits[83].

Alkali treatment with NaOH and KOH is more effective in improving biomass biodegradability, with NaOH extensively used in the pulp and paper industry[77]. The function of alkaline pretreatment is believed to be the saponification and cleavage of lignin-carbohydrate linkages[64]. NaOH pretreatment has proven to be effective in improving digestibility and methane yield under anaerobic digestion. NaOH treatment of AD-digested rice straw increased the chemical oxygen demand (COD) of rice straw from 2,311 to 10,488 mg/L, as well as the crystallinity index of cellulose[18]. However, the use of NaOH faces the challenge of sodium discharge as an effluent in the process, making its substrate difficult to recycle and limiting its commercial application[77].

The application of NaOH as a pretreatment agent derives its preference from its ability to catalyze under mild conditions and efficiently degrade the bond between lignin and hemicellulose in lignin-carbohydrate[65]. Such action involves cleaving the ether and ester bonds in the lignocellulose structure and the further cleavage of ester and carbon-to-carbon bonds in lignin molecules. In a study to determine the optimal loading rate of NaOH in the pretreatment of giant reed, Jiang et al.[84] varied NaOH concentration between 0.5%–2% w/v while monitoring the methane yield. The increase in NaOH resulted in a significant methane yield from 217 mL/g.VS to 355 mL/g.VS following pretreatment with 2% w/v NaOH. Similarly, Kang et al.[85] achieved optimal biomethanation for 2% w/v NaOH upon testing with 2%, 4%, 6%, and 8% w/v, while in another study by Pavlostathis and Gossett[86], alkali pretreatment of wheat straw resulted in 100% methane production from biogas production experiments. In other studies, Fox et al.[87] and He et al.[88] established that rice straw pretreated with 4%–10% NaOH increased biogas production by 58%, whereas a combined action of 4% NaOH with thermal pretreatment raised the production to 112%.

In a study to test the effect of LCB with lime (CaO) or $Ca(OH)_2$, Zheng et al.[18] discovered a significant improvement in biogas production from rice straw, with the lignin, cellulose, and hemicellulose of rice straw showing the highest methane yield of 225 mL/g.VS, which was 74% higher than the control. The results were obtained with 9.8% $Ca(OH)_2$ (g/g TS) treatment at 25 ℃ for six days. CaO pretreatment on various lignocellulosic materials, such as sugar beet, sugar beet leaves, maize, ensiled hay, and straw, had realized increased methane yield from straw, maize, and a mixture of sugar beet and sugar beet leaves but decreased methane yield from other feedstocks, such as ensiled hay[89].

Comparative studies of the effectiveness of KOH in pretreatment have found that it compares very closely with that of NaOH and $Ca(OH)_2$. For example, a comparative study involving the pretreatment of OFMSW with NaOH, KOH, and $Ca(OH)_2$ demonstrated that KOH pretreatment generated 13% more biogas than NaOH and $Ca(OH)_2$[90]. The study recommended further research on biomass pretreatment using KOH, as the area is still inadequately studied, with the assumption that KOH would perform just like other alkalines[91].

4.3. Organosolv methods

Organosolv pretreatment presents a method used to extract lignin from lignocellulosic feedstock with organic solvents or their aqueous solutions[92]. Some of the organic solvents used in the process include those with low boiling points, such as ethanol and methanol, and those with higher boiling points, such as formic acid, acetic acid, phenol, glycerol, and acetone[93]. The technique has been popularly applied following the challenges of air and water associated with conventional pulping, kraft, and sulfite processes[94]. The organosolv process involves the addition of lignocellulose biomass to a combination of organic solvent and water with a solid-to-liquid ratio between 1:4 and 1:10 w/w and a solvent concentration of 35–70% w/w[93]. Optionally, the rate of reaction can be accelerated by the introduction of a catalyst[95]. However, organosolv pretreatment can occur with different organic or aqueous solvents even without catalysts in the temperature range of between 100–250 °C[92]. Organosolv pretreatment provides a highly efficient generation of ethanol, lignin, and other biochemicals from LCB compared with other pretreatment techniques[63,95]. The application of organosolv presents additional benefits, including ease of recovery of organic solvents through distillation and recycled pretreatment[96], isolation of lignin as a solid material, and carbohydrates as a syrup[97], which are both possible chemical feedstocks.

The organosolv method has been considered more viable in the biorefinery of lignocellulosic biomass, which focuses on the utilization of all biomass components[96]. However, the technique faces some drawbacks, including the high costs associated with energy consumption through the recovery process[95], the extreme conditions required following the volatility of organic solvents[98], and the need to wash the pretreated solids in organic solvents prior to water washing to avoid re-precipitation of dissolved lignin[99], which leads to cumbersome washing arrangements. Upon washing the solids in organic solvents, the pretreated solids undergo subsequent enzymatic saccharification and fermentation to produce value-added biochemicals, such as bioethanol[66], while a distillation process is employed in solvent recovery from spent liquor[92]. To manage the process costs, the organic solvents used should be recycled[96]. The eventual products of the process include dry lignin, aqueous hemicellulose, and a relatively pure cellulose fraction[92]. A summary of the oganosolv process is illustrated in **Figure 2**.

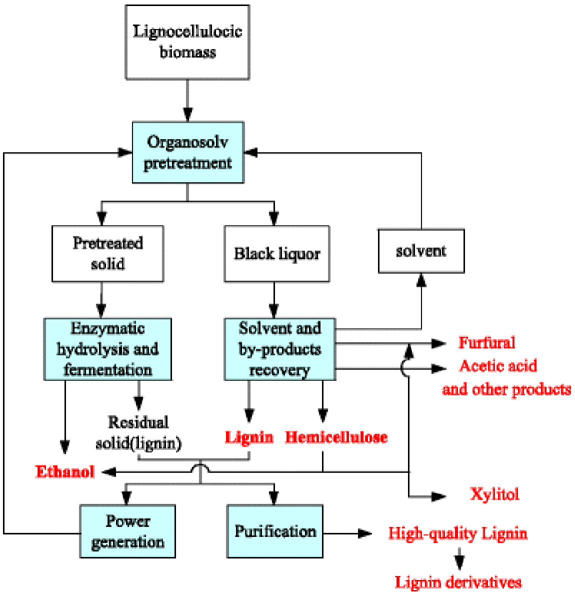

Figure 2. Schematic organosolv pretreatment steps for lignocellulosic biomass[92].

Mardawati et al.[100] investigated the effect of organosolv pretreatment on the delignification of bioethanol feedstock from empty oil palm fruit bunches. The study used ethanol as an organic solvent, and the results revealed significant disruption of the lignocellulosic matrix of the biomass and significantly increased hydrolyzability of the pretreated material. The study further obtained a maximum lignin degradation of 27.68%, which corresponded to 65% v/v of ethanol with a reaction time of 65 min. Another study by Viola et al.[101] investigated the optimization of organosolv pretreatment of wheat straw and eucalyptus residues using 2-methyltetrahydrofuran (2M-THF) and n-butanol. From the study, biomass fractionation with butanol demonstrated significant advantages over 2M-THF under the same process conditions, with a recovery yield of free glucose reaching 98% of the theoretical value for butanol compared with 67% for 2M-THF. The organosolv pretreatment process for various feedstocks is summarized in **Table 2**.

Table 2. Performance of organosolv pretreatment on different feedstock materials.

Raw material	Solvent	Catalyst	Pretreatment condition		Pretreatment impact/results	Ref.
			Temp (°C)	Duration (min)		
Oat husk	Aqueous ethanol	Oxalic acid	210	90	10.27% protein increase	[102]
Rice straw	75% aqueous ethanol	1% M H_2SO_4	180	30	46.2% glucose yield	[103]
Rice straw	Aqueous ethanol	Formic and acetic acids	60–100	10–50	73.17% delignification, 46.62% hemicellulose solubilized, and 74.09% cellulose release	[104]
Sugarcane bagasse	50% acetone	0.17M H_2SO_4	125	120	98.1% delignification and 74.5% cellulose digestibility	[105]
Wheat straw	50% acetone	None	205	60	79% delignification, 82% hemicellulose hydrolysis, 93% cellulose recovery, and 71% glucose yield	[106]
Corn stover	30% ethanol	1% Hydrogen peroxide	150	2880	69.7% glucose conversion	[107]
Barley straw	Acetone	0.1–0.35M H_2SO_4	140–180	40	75.4% glucose conversion and 66.7% xylose recovery	[108]

4.4. Ozonolysis

Ozonolysis as a pretreatment method involves an ozone reaction with lignin present in lignocellulosic biomass, i.e., delignification, thus allowing for enzymatic hydrolysis of the released sugars for energy production[109,110]. According to Kassim et al.[111], the process has minimal effects on the hemicellulose and cellulose components of lignocellulosic biomass. Ozone attacks the double bonds and electric donor centers present in lignin, hence releasing soluble compounds of lower molecular weight, e.g., formic and acetic organic acids, thus changing the material's pH to be more acidic[112]. According to de Cassia Pereira et al.[113], this allows for increased enzymatic hydrolysis yields by allowing increased enzyme access to polysaccharides and sugar release.

According to Onu and Mbohwa[114], the solubility of ozone in water and its instability around compounds with conjugated double bonds allow for efficient oxidation of lignin present in lignocellulosic biomass due to the presence of C=C bonds. Additionally, Traviani et al.[109] suggested that the process is promising due to the low formation of inhibitory compounds, the generation of weak carboxylic acids, minimal effects on sugar polymers, selective lignin degradation, and operation at ambient pressure and temperature, with subsequent generation of ozone. Inhibitors, such as acetic, formic, and oxalic acids, are produced during this process[115], which are effectively removed by water washing. Mulakhudair et al.[116] further emphasized that the resulting solution from the process is void of degradation by-products that interfere with downstream processing, such as enzymatic hydrolysis, particularly for *Pseudomonas putida* and the fermentation of *Zymomonas mobilis*. This method, however, is considered disadvantageous, as the process is expensive due to the requirement of a significant volume of ozone[117].

Patil et al.[118] conducted a study on the impact of ozonolysis in conjunction with thermal pretreatment on rice straw hydrolysis for energy production. The authors estimated the potential scale-up feasibility by calculating a net energy balance and obtained a net positive gain of 0.5763 kWh/kg of rice straw using this method of lignocellulosic biomass pretreatment. **Figure 3** below illustrates the process in which rice straw in deionized water is fed into an O_2 decomposer before thermal treatment to generate methane in a biomethanation chamber.

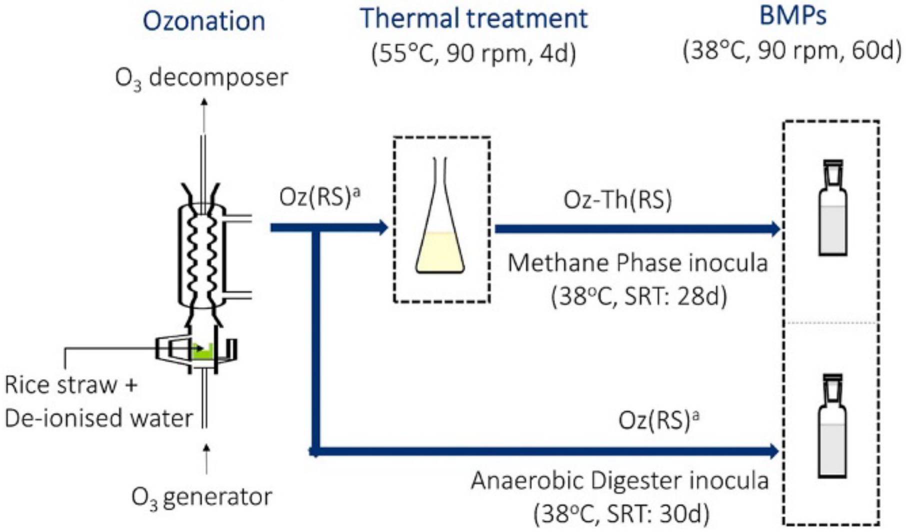

Figure 3. Ozonolysis and thermal pretreatment for energy production[118].

In other studies, ozonolysis resulted in an increase in fermentable carbohydrate release for sugarcane bagasse when used as a pretreatment method[112]. In the study, glucose and xylose yields improved from 6.64% and 2.05% to 41.79% and 52.44%, respectively, for raw bagasse under the best experimental conditions. Onu and Mbohwa[114] further suggested that ozonolysis has been effectively implemented in the pulp and paper industry.

4.5. Ionic fluids

Ionic fluids used in lignocellulosic biomass pretreatment are solvents containing paired ions that exhibit environmental compatibility due to their high thermal stability and negligible vapor pressures, which subsequently inhibit the release of toxic or explosive gases during utilization[119]. Ionic fluids have been applied in the pretreatment of lignocellulosic biomass through the dissolution of biomass, fractionation of biomass, and enzymatic saccharification of the pretreated biomass[120] for biofuel production. According to Moyer et al.[121], ionic fluids tend to activate lignocellulosic biomass, reducing biomass recalcitrance and minimally affecting the structural components of biomass for subsequent enzymatic energy conversion. **Figure 4** illustrates the utilization of ionic fluids for the pretreatment of lignocellulosic biomass for energy production. The harvested LCB undergoes a crushing and filtration process to produce crushed biomass that is then treated with ionic fluid to delignify the biomass and dissolve the cellulose component to produce biofuels, biochemicals, and biopolymers.

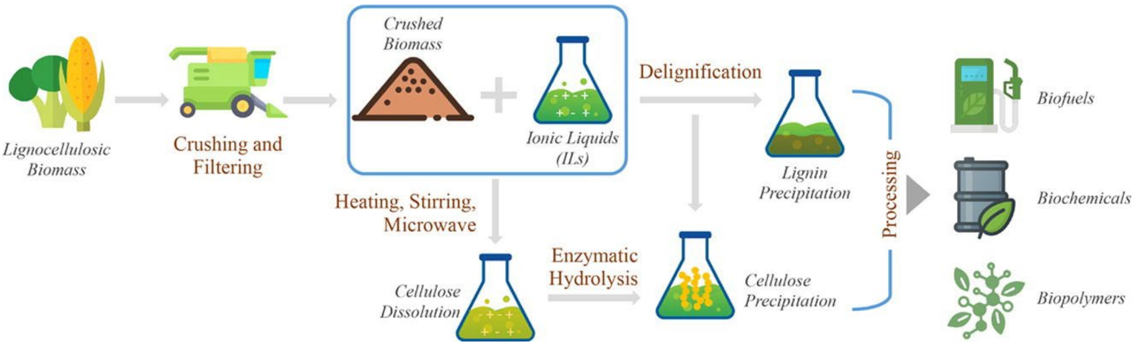

Figure 4. Pretreatment of lignocellulosic biomass using ionic fluid for energy production[122].

Ionic fluids are advantageous essentially due to their ability to significantly reduce cellulose crystallinity and the cleavage of acetyl groups in hemicellulose, subsequently resulting in changes in the overall biomass properties[121]. This allows for increased access to hydrolytic enzymes for energy conversion. Their ease of use, recovery, and reuse after pretreatment are also advantages of this method of pretreatment of lignocellulosic biomass[123].

The high cost of ionic fluids for the pretreatment of lignocellulosic biomass has proven to be a hindrance in the exploration of this method[124]. Socha et al.[125], however, illustrated a closed-loop process for bio-refineries that could reduce the significant costs associated with the utilization of ionic fluids for the pretreatment of lignocellulosic biomass. The authors suggested that the lignin and hemicellulose-derived compounds from the initial pretreatment of lignocellulosic biomass could be synthesized back into ionic fluids, as illustrated in **Figure 5**. From the figure, the LCB feedstock undergoes ionic liquid pretreatment that initiates enzymatic saccharification, stimulating the fermentation of fuels and chemicals. The process entails the depolymerization and conversion of lignin and hemicellulose to ionic fluids recycled through the process.

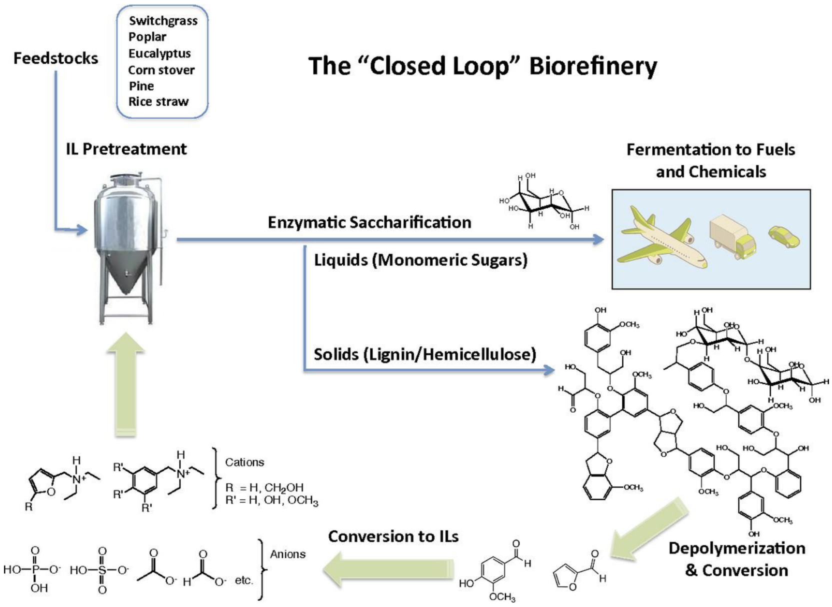

Figure 5. Closed-loop bio-refinery using ionic fluids derived from lignocellulosic biomass[125].

Brandt et al.[126] conducted the pretreatment of pine (*Pinus sylvestris*), willow (*Salix viminalis*), and ground lignocellulosic biomass (*Miscanthus giganteus*). The authors found that up to 90% and 25% of glucose and hemicellulose, respectively, were released from the original biomass by the combined ionic fluid pretreatment and enzymatic hydrolysis, with the ionic fluid liquor containing the majority of lignin and hemicellulose. Sriariyanun et al.[127] pre-treated rice straw with chloline acetate prior to enzymatic saccharification with ionic-fluid-tolerant cellulase. From the study, it was proven that ionic fluid pretreatment in conjunction with the use of ionic-fluid-tolerant cellulose was beneficial for enhancing sugar production that could be used for energy conversion.

4.6. Deep eutectic solvents

Deep eutectic solvents (DESs) used in lignocellulosic biomass pretreatment are low-cost eutectic mixtures prepared by combining hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs)[128]. They are liquid in nature when they have a eutectic or near-eutectic composition, appropriately formed by a mixed molar ratio of Brønsted or Lewis acids and bases[129]. They portray similar physical and chemical properties with ionic fluids[130] with regard to the potential pretreatment properties of lignocellulosic biomass for energy conversion.

According to Scelsi et al.[131], the intrinsic ionic nature of DESs allows them to break the complex molecular H-bond, thus stabilizing the hemicellulose-lignin complex and subsequently allowing for easier breakage of the covalent bond present in lignocellulosic biomass. The authors further suggested that this allowed for the reorganization of the components under very mild conditions without the generation of inhibitors of depolymerization of cellulose for energy conversion. **Figure 6** illustrates the LCB pretreatment process with DESs for energy conversion. The application of the DES breaks the covalent bond binding the hemicellulose to lignin, thereby releasing the cellulose-enriched substrate for enzymatic saccharification, leading to the release of biofuel products, such as ethanol, butanol, S-HMF, and levulinic acid.

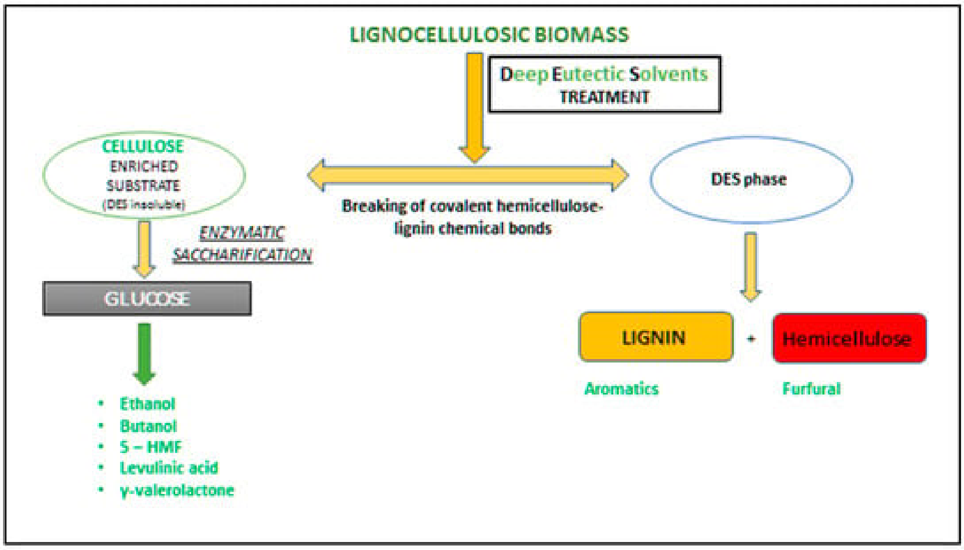

Figure 6. Pretreatment of lignocellulosic biomass with DESs for energy conversion[131].

According to Mbous et al.[132] and Bajpai[133], DESs are considered green alternatives to ionic fluids, easy to synthesize, and less expensive as a method of pretreatment of lignocellulosic biomass for energy valorization. DESs can also be recycled and reused effectively[134] and still exhibit efficient delignification capabilities. Among other methods that can be applied for recycling, according to the authors, are electrodialysis, freeze-drying, membrane separation, and rotary evaporation. This renders the DES method effective for large-scale industrial energy production at relatively low costs. Additionally, the intramolecular hydrogen bonds present in DESs also enhance the hydrogen bond breakage within the lignocellulosic biomass, thus promoting high solubility of the biomass and favorable energy conversion rates[135]. However, Wang and Lee[136] suggested that the high-viscous nature of DESs prevents heat and mass transfer during reactions, thus deteriorating the pretreatment performance for subsequent energy conversion. It has also been hypothesized that the presence of DESs can inhibit specific enzymes, thereby causing an alteration of the global biocatalytic reaction[137].

Kumar et al.[138] conducted a pretreatment process for rice hulls using DESs prior to enzymatic hydrolysis. The authors synthesized a DES and conducted conductive-heating pretreatment and microwave-heating pretreatment of the rice hulls. The biomass and DES were then separated via filtration prior to comparative enzymatic hydrolysis of raw and pre-treated rice hulls. From the study, it was found that up to 100 times more glucose could be obtained with the pretreatment as compared with the raw rice hulls. Fang et al.[139] explored how to reduce the recalcitrance of lignocellulosic date palm residues prior to pretreatment using DESs for energy conversion. The study adopted hydrothermal pretreatment in conjunction with DES pretreatment. From the study, the authors highlighted that there was a 1.7× increase in the enzymatic digestibility of the date palm residues, accompanied by 25% and 22% increased removal of xylan and lignin, respectively, rather than the cellulose crystallinity modification.

5. Discussion

The crystalline structure of LCB is the primary cause of its resistance to chemical and biological degradation processes. Optimizing LCB biodegradation and unlocking its energy potential demands lignin removal that reduces polymerization and cellulosic crystallization. Such can be achieved by chemical pretreatment, which in turn enhances biodegradation and biomethanation efficiency. Chemical pretreatment methods, such as the use of dilute acids, promise good results in LCB pretreatment; however, its action can be enhanced by thermal action for improved efficiency. Additionally, acid pretreatment requires application at optimal concentrations for the best performance. High acid concentrations are often characterized by system toxicity, corrosion, and the generation of counterproductive inhibitory conditions. Similarly, appropriate determination of alkali pretreatment dosage and concentration holds a bearing on the success of biomethanation process efficiency, as high concentrations can lead to the degradation and decomposition of polysaccharides. Alkali pretreatment is also temperature and atmospheric pressure dependent, as low temperature and atmospheric pressure can deter toxic substance formation and enhance biomethanation efficiency. The determination of an appropriate chemical pretreatment method requires knowledge of biomass lignin content. For example, alkali pretreatment is appropriate for low-lignin biomass but less effective for high-lignin biomass. Thus, an effective LCB pretreatment method should be determined based on biomass characterization and property determination.

In mounting efforts to overcome the challenges associated with traditional acid and alkali pretreatment techniques, the organosolv method provides a highly efficient generation of ethanol, lignin, and other biochemicals from LCB. Additionally, the method presents the advantage of ease of recovery of the used organic solvent through distillation and recycling pretreatment. The method is more attractive in its ability to fully utilize biomass components. Managing its drawback of high energy demand and solvent volatility can be a gateway to ensuring its sustainability and success.

Ionic fluids are effective in LCB activation, reducing LCB recalcitrance with minimal effect on the structural components of biomass. The use of ionic fluids presents the ability to reduce cellulose crystability and hemicellulose conversion by acetyl group cleavage, raising the performance of hydrolytic enzymes for efficient biodegradation. Ionic liquids, such as [Emim]Cl, [Bmim]Cl, and [Emim]Ac, have been widely reported for the pretreatment of lignocelluloses; however, the technique faces the drawbacks of high pretreatment temperature and long processing time. Using ionic fluids is relatively easy, with the additional benefits of recovery and re-use of pretreatment chemicals. Thus, its performance is promising despite the challenge of the cost of ionic fluids, which is prohibitive.

Deep eutectic solvents offer an alternative pretreatment that is equally environmentally friendly as ionic fluids but with a reasonable cost requirement. The method fits well in industrial applications, considering energy input and bioconversion efficiency. However, the method faces the challenge of inefficiency occasioned by its viscous nature, which prevents heat and mass transfer during reactions. Its poor performance is also attributable to the inhibition of specific conversion enzymes, altering biocatalytic reactions. This complicates process efficiency and demands a complementary technique, such as hydrothermal pretreatment, to improve enzymatic digestibility.

Other evolving methods, such as ozonolysis, which do not involve enzymatic hydrolysis, have delivered good results and performance efficiency improvements, such as improving glucose and xylose yields. However, ozonolysis is considered cost-prohibitive due to the volume of ozone required.

6. Conclusion

The concept of sustainable AD and biomethanation of LCB can be realized by developing efficient and eco-friendly biomass pretreatment technologies. An assessment of different pretreatment processes suggests that an ideal process must overcome the recalcitrant nature of LCB, increase cellulose crystallinity, and ensure maximum recovery of sugars along with other industrially relevant bio-products. Here, recent advances in selective pretreatment methods based on chemical approaches were reviewed. The effectiveness of chemical pretreatment methods for LCB depends on the characteristics of the biomass, optimal operating conditions, chemical dosage and concentration, prevention and management inhibitors, and the investment cost of set-up and maintenance. Following the noted drawbacks associated with each method, the desired performance can still be achieved through complementary techniques, such as physical, thermal, and physicochemical methods. Optimizing LCB performance in bioenergy conversion is a key to unlocking the green energy potential for sustainable benefits.

Funding

No funding was received for this work from any organization.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Surendra KC, Khanal SK, Shrestha P, Lamsal B. Current status of renewable energy in Nepal: Opportunities and challenges. *Renew Sustain Energy Reviews* 2011; 15(8): 4107–4117. doi: 10.1016/j.rser.2011.07.022
2. Blasi A, Verardi A, Lopresto CG, et al. Lignocellulosic agricultural waste valorization to obtain valuable products: An overview. *Recycling* 2023; 8(4): 61. doi: 10.3390/ recycling8040061
3. Kamperidou V, Terzopoulou P. Anaerobic digestion of lignocellulosic waste materials. *Sustainability* 2021; 13(22): 12810. doi: 10.3390/su132212810
4. Karki R, Chuenchart W, Surendra KC, et al. Anaerobic co-digestion: Current status and perspectives. *Bioresource Technology* 2021; 330: 125001. doi: 10.1016/j.biortech.2021.125001
5. Kusch-Brandt S, Heaven S, Banks CJ. Unlocking the full potential: New frontiers in anaerobic digestion (AD) processes. *Processes* 2023; 11(6): 1669. doi: 10.3390/pr11061669
6. Harirchi S, Wainaina S, Sar T, et al. Microbiological insights into anaerobic digestion for biogas, hydrogen or volatile fatty acids (VFAs): A review. *Bioengineered* 2022; 13(3): 6521–6557. doi: 10.1080/21655979.2022.2035986
7. Paul S, Dutta A. Challenges and opportunities of lignocellulosic biomass for anaerobic digestion. *Resources, Conservation and Recycling* 2018; 130: 164–174. doi: 10.1016/j.resconrec.2017.12.005

8. Omondi EA, Ndiba PK, Njuru PG. Characterization of water hyacinth (*E. crassipes*) from Lake Victoria and ruminal slaughterhouse waste as co-substrates in biogas production. *SN Applied Sciences* 2019; 1: 848. doi: 10.1007/s42452-019-0871-z
9. Zoghlami A, Paës G. Lignocellulosic biomass: Understanding recalcitrance and predicting hydrolysis. *Frontiers in Chemistry* 2019; 7. doi: 10.3389/fchem.2019.00874
10. Zhang W, Diao C, Wang L. Degradation of lignin in different lignocellulosic biomass by steam explosion combined with microbial consortium treatment. *Biotechnol Biofuels* 2023; 16: 55. doi: 10.1186/s13068-023-02306-2
11. Su W, Sun Q, Xia M, et al. The resource utilization of water hyacinth (*Eichhornia crassipes* [Mart.] solms) and its challenges. *Resources* 2018; 7(3): 46. doi: 10.3390/resources7030046
12. Whitmore AP, Groot JJR. The decomposition of sugar beet residues: Mineralization versus immobilization in contrasting soil types. *Plant and Soil* 1997; 192: 237–247. doi: 10.1023/A:1004288828793
13. Hagos A, Jembere K, Feyisa T. Effects of soil and water conservation measures and soil depths on selected soil physico-chemical properties at asera watershed, Northern Ethiopia. *Journal of Agricultural Science and Food Research* 2023; 14(2): 144. doi: 10.35248/2593-9173.23.14.144
14. Osunde MO, Olayinka A, Fashina CD, Torimiro N. Effect of carbon-nitrogen ratios of lignocellulosic substrates on the yield of mushroom (*pleurotus pulmonarius*). *Open Access Library Journal* 2019; 6(10): 1–8. doi: 10.4236/oalib.1105777
15. Matsakas L, Bonturi N, Miranda EA, et al. High concentrations of dried sorghum stalks as a biomass feedstock for single cell oil production by *Rhodosporidium toruloides*. *Biotechnology for Biofuels and Bioproducts* 2015; 8: 6. doi: 10.1186/s13068-014-0190-y
16. Carlini M, Castellucci S, Mennuni A. Water hyacinth biomass: Chemical and thermal pre-treatment for energetic utilization in anaerobic digestion process. *Energy Procedia* 2018; 148: 431–438. doi: 10.1016/j.egypro.2018.08.106
17. Zhou S, Zhang Y, Dong Y. Pretreatment for biogas production by anaerobic fermentation of mixed corn stover and cow dung. *Energy* 2012; 46(1): 644–648. doi:10.1016/j.energy.2012.07.017
18. Zheng Y, Zhao Jia, Xu F, Li Y. Pretreatment of lignocellulosic biomass for enhanced biogas production. *Progress in Energy and Combustion Science* 2014; 42: 35–53. doi: 10.1016/j.pecs.2014.01.001
19. Deepanraj B, Sivasubramanian V, Jayaraj S. Enhancement of biogas production by pretreatment: A review. In: Proceedings of the IVth International Conference on Advances in Energy Research. December 2013; Mumbai, India.
20. Den W, Sharma VK, Lee M, et al. Lignocellulosic biomass transformations via greener oxidative pretreatment processes: Access to energy and value-added chemicals. *Frontiers in Chemistry* 2018; 6: 141. doi: 10.3389/fchem.2018.001
21. Koupaie EH, Dahadha S, Bazyar Lakeh AA, et al. Enzymatic pretreatment of lignocellulosic biomass for enhanced biomethane production—A review. *Journal of Environmental Management* 2019; 233: 774–784. doi: 10.1016/j.jenvman.2018.09.106
22. Eswari AP, Ravi YK, Kavitha S, Banu JR. Recent insight into anaerobic digestion of lignocellulosic biomass for cost effective bioenergy generation. *e-Prime—Advances in Electrical Engineering, Electronics and Energy* 2023; 3: 100199. doi: 10.1016/j.prime.2023.100119
23. Pandit S, Savla N, Sonawane JM, et al. Agricultural waste and wastewater as feedstock for bioelectricity generation using microbial fuel cells: Recent advances. *Fermentation* 2021; 7(3): 169. doi: 10.3390/fermentation7030169
24. Devi A, Bajar S, Kour H, et al. Lignocellulosic biomass valorization for bioethanol production: A circular bioeconomy approach. *BioEnergy Research* 2022; 15: 1820–1841. doi: 10.1007/s12155-022-10401-9
25. Sari FP, Budiyono B. Enhanced biogas production from rice straw with various pretreatment: A review. *Waste Technology* 2014; 2(1): 17–25. doi: 10.14710/2.1.17-25
26. Lo CC, Chang YW, Chen YL, et al. Lignin recovery from rice straw biorefinery solid waste by soda process with ethylene glycol as co-solvent. *Journal of the Taiwan Institute of Chemical Engineers* 2021; 126: 50–57. doi: 10.1016/j.jtice.2021.07.030
27. Gou G, Wei W, Jiang M, et al. *Environmentally Friendly Method for the Separation of Cellulose from Steam-Exploded Rice Straw and Its High-Value Applications*. InTech; 2018. doi: 10.5772/intechopen.79014
28. Tufail T, Saeed F, Afzaal M, et al. Wheat straw: A natural remedy against different maladies. *Food Science & Nutr* 2021; 9(4): 2335–2344. doi: 10.1002/fsn3.2030
29. Chen HZ, Liu ZH. Multilevel composition fractionation process for high-value utilization of wheat straw cellulose. *Biotechnology for Biofuels* 2014; 7: 137. doi: 10.1186/s13068-014-0137-3
30. Silanikove N, Brosh A. Lignocellulose degradation and subsequent metabolism of lignin fermentation products by the desert black Bedouin goat fed on wheat straw as a single-component diet. *British Journal of Nutrition* 1989; 62(2): 509–520. doi: 10.1079/bjn19890049

31. García-Negrón V, Toht MJ. Corn stover pretreatment with Na_2CO_3 solution from absorption of recovered CO_2. *Fermentation* 2022; 8(11): 600. doi: 10.3390/fermentation8110600
32. Woźniak M, Ratajczak I, Wojcieszak D, et al. Chemical and structural characterization of maize stover fractions in aspect of its possible applications. *Materials (Basel, Switzerland)* 2021; 14(6): 1527. doi: 10.3390/ma14061527
33. Kim S. Evaluation of alkali-pretreated soybean straw for lignocellulosic bioethanol production. *International Journal of Polymer Science* 2018; 2018: 5241748. doi: 10.1155/2018/5241748
34. Nishida VS, Woiciechowski AL, Valladares-Diestra KK, et al. Second generation bioethanol production from soybean hulls pretreated with imidazole as a new solvent. *Fermentation* 2023; 9(2): 93. doi: 10.3390/fermentation9020093
35. Doczekalska B, Bartkowiak M, Waliszewska B, et al. Characterization of chemically activated carbons prepared from miscanthus and switchgrass biomass. *Materials* 2020; 13(7): 1654. doi: 10.3390/ma13071654
36. Liu W, Wang K, Hao H, et al. Predicting potential climate change impacts of bioenergy from perennial grasses in 2050. *Resources, Conservation and Recycling* 2023; 190: 106818. doi: 10.1016/j.resconrec.2022.106818
37. Loomis G, Dari B, Rogers CW, Sihi D. Evaluation of residue management practices on barley residue decomposition. *PLoS One* 2020; 15(5): e0232896. doi: 10.1371/journal.pone.0232896
38. Yang C, Li J, Zhang G, et al. Barley straw combined with urea and controlled-release nitrogen fertilizer improves lint yield and nitrogen utilization of field-seeded cotton. *Agronomy* 2022; 12(5): 1208. doi: 10.3390/agronomy12051208
39. Chaiwarit T, Chanabodeechalermrung B, Kantrong N, et al. Fabrication and evaluation of water hyacinth cellulose-composited hydrogel containing quercetin for topical antibacterial applications. *Gels* 2022; 8(12): 767. doi: 10.3390/gels8120767
40. Mahmud MA, Anannya FR. Sugarcane bagasse—A source of cellulosic fiber for diverse applications. *Heliyon* 2021; 7(8): e07771. doi: 10.1016/j.heliyon.2021.e07771
41. Rezende CA, de Lima MA, Maziero P, et al. Chemical and morphological characterization of sugarcane bagasse submitted to a delignification process for enhanced enzymatic digestibility. *Biotechnology for Biofuels and Bioproducts* 2011; 4: 54. doi: 10.1186/1754-6834-4-54
42. Zhou Z, Cheng Y, Zhang W, et al. Characterization of lignins from sugarcane bagasse pretreated with green liquor combined with ethanol and hydrogen peroxide. *BioResources* 2016; 11(2): 3191–3203.
43. Rego Filipe, Soares Dias AP, Casquilho M, et al. Fast determination of lignocellulosic composition of poplar biomass by thermogravimetry. *Biomass and Bioenergy* 2019; 122: 375–380. doi: 10.1016/j.biombioe.2019.01.037
44. Biswal AK, Hengge NN, Black IM, et al. Composition and yield of non-cellulosic and cellulosic sugars in soluble and particulate fractions during consolidated bioprocessing of poplar biomass by *Clostridium thermocellum*. *Biotechnology for Biofuels and Bioproducts* 2022; 15: 23. doi: 10.1186/s13068-022-02119-9
45. Stolle-Smits T, Beekhuizen JG, Kok MTC, et al. Changes in cell wall polysaccharides of green bean pods during development. *Plant Physiology* 1999; 121(2): 363–372. doi: 10.1104/pp.121.2.363
46. Elfalleh W, Guo L, He S, et al. Characteristics of cell wall structure of green beans during controlled freezing point storage. *International Journal of Food Properties* 2015; 18(8): 1756–1772. doi: 10.1080/10942912.2014.933437
47. Valentín L, Kluczek-Turpeinen B, Willför S, et al. Scots pine (*Pinus sylvestris*) bark composition and degradation by fungi: Potential substrate for bioremediation. *Bioresource Technology* 2010; 101(7): 2203–2209. doi: 10.1016/j.biortech.2009.11.052
48. Szadkowska D, Auriga R, Lesiak A, et al. Influence of pine and alder woodchips storage method on the chemical composition and sugar yield in liquid biofuel production. *Polymers* 2022; 14(17): 3495. doi: 10.3390/polym14173495
49. Tarasov D, Leitch M, Fatehi P. Lignin–carbohydrate complexes: Properties, applications, analyses, and methods of extraction: A review. *Biotechnology for Biofuels and Bioproducts* 2018; 11: 269. doi: 10.1186/s13068-018-1262-1
50. Lourenço A, Pereira H. *Compositional Variability of Lignin in Biomass*. InTech; 2018. doi: 10.5772/intechopen.71208
51. De'Nobili MD, Bernhardt DC, Basanta MF, Rojas AM. Sunflower (*Helianthus annuus* L.) seed hull waste: Composition, antioxidant activity, and filler performance in pectin-based film composites. *Frontiers in Nutrition* 2021; 8: 777214. doi: 10.3389/fnut.2021.777214
52. Zhurka M, Spyridonidis A, Vasiliadou IA, Stamatelatou K. Biogas production from sunflower head and stalk residues: Effect of alkaline pretreatment. *Molecules* 2020; 25(1): 164. doi: 10.3390/molecules25010164
53. Papadopoulos AN, Kyzas GZ, Mitropoulos AC. Lignocellulosic composites from acetylated sunflower stalks. *Applied Sciences* 2019; 9(4): 646. doi: 10.3390/app9040646
54. Covino C, Sorrentino A, Di Pierro P, et al. Lignocellulosic fibres from enzyme-treated tomato plants: Characterisation and application in paperboard manufacturing. *International Journal of Biological Macromolecules* 2020; 161: 787–796. doi: 10.1016/j.ijbiomac.2020.06.077

55. Kehili M, Schmidt LM, Reynolds W, et al. Biorefinery cascade processing for creating added value on tomato industrial by-products from Tunisia. *Biotechnology for Biofuels and Bioproducts* 2016; 9: 261. doi: 10.1186/s13068-016-0676-x
56. Kamperidou V, Terzopoulou P. Anaerobic digestion of lignocellulosic waste materials. *Sustainability* 2021; 13(22): 12810. doi: 10.3390/su132212810
57. Sarker S, Lamb JJ, Hjelme DR, Lien KM. A review of the role of critical parameters in the design and operation of biogas production plants. *Applied Sciences* 2019; 9(9): 1915. doi: 10.3390/app9091915
58. Oduor WW, Wandera SM, Murunga SI, Raude JM. Enhancement of anaerobic digestion by co-digesting food waste and water hyacinth in improving treatment of organic waste and bio-methane recovery. *Heliyon* 2022; 8(9): e10580. doi: 10.1016/j.heliyon.2022.e10580
59. Kwietniewska E, Tys J. Process characteristics, inhibition factors and methane yields of anaerobic digestion process, with particular focus on microalgal biomass fermentation. *Renewable and Sustainable Energy Reviews* 2014; 34: 491–500. doi: 10.1016/j.rser.2014.03.041
60. Liu C, Yuan X, Zeng G, et al. Prediction of methane yield at optimum pH for anaerobic digestion of organic fraction of municipal solid waste. *Bioresource Technology* 2008; 99(4): 882–888. doi: 10.1016/j.biortech.2007.01.013
61. Gumisiriza R, Hawumba JF, Okure M. Hensel O. Biomass waste-to-energy valorisation technologies: A review case for banana processing in Uganda. *Biotechnolpgy for Biofuels* 2017; 10: 11. doi: 10.1186/s13068-016-0689-5
62. Steiniger B, Hupfauf S, Insam H, Schaum C. Exploring anaerobic digestion from mesophilic to thermophilic temperatures—Operational and microbial aspects. *Fermentation* 2023; 9(9): 798. doi: 10.3390/fermentation9090798
63. Sharma S, Tsai ML, Sharma V, et al. Environment friendly pretreatment approaches for the bioconversion of lignocellulosic biomass into biofuels and value-added products. *Environments* 2023; 10(1): 6. doi: 10.3390/environments10010006
64. Baruah J, Nath BK, Sharma R, et al. Recent trends in the pretreatment of lignocellulosic biomass for value-added products. *Frontiers in Energy Research* 2018; 6: 141. doi: 10.3389/fenrg.2018.00141
65. Shukla A, Kumar D, Girdhar M, et al. Strategies of pretreatment of feedstocks for optimized bioethanol production: Distinct and integrated approaches. *Biotechnology for Biofuels and Bioproducts* 2023; 16(1): 44. doi: 10.1186/s13068-023-02295-2
66. Maurya DP, Singla A, Negi S. An overview of key pretreatment processes for biological conversion of lignocellulosic biomass to bioethanol. *3 Biotech* 2015; 5(5): 597–609. doi: 10.1007/s13205-015-0279-4
67. Kucharska K, Rybarczyk P, Hołowacz I, et al. Pretreatment of lignocellulosic materials as substrates for fermentation processes. *Molecules* 2018; 23(11): 2937. doi: 10.3390/molecules23112937
68. Jędrzejczyk M, Soszka E, Czapnik M, et al. Physical and chemical pretreatment of lignocellulosic biomass. In: *Second and Third Generation of Feedstocks: The Evolution of Biofuels*. Elsevier; 2019. pp. 143–196. doi: 10.1016/B978-0-12-815162-4.00006-9
69. Abraham A, Mathew AK, Park H, et al. Pretreatment strategies for enhanced biogas production from lignocellulosic biomass. *Bioresource Technology* 2020; 301: 122725. doi: 10.1016/j.biortech.2019.122725.
70. Jönsson LJ, Alriksson B, Nilvebrant NO. Bioconversion of lignocellulose: Inhibitors and detoxification. *Biotechnology for Biofuels and Bioproducts* 2013; 6: 16. doi: 10.1186/1754-6834-6-16
71. Digman MF, Shinners KJ, Casler MD, et al. Optimizing on-farm pretreatment of perennial grasses for fuel ethanol production. *Bioresour Technol* 2010; 101(14): 5305–5314. doi: 10.1016/j.biortech.2010.02.014
72. Wyman C, Huber G. Biomass and America's energy future discussed. *Chemistry & Industry* 2009; 283(5): 17.
73. Xu Y, Liu K, Yang Y, et al. Hemicellulose-based hydrogels for advanced applications. *Frontiers in Bioengineering and Biotechnology* 2023; 10: 1110004. doi: 10.3389/fbioe.2022.1110004
74. Oriez V, Peydecastaing J, Pontalier PY. Lignocellulosic biomass fractionation by mineral acids and resulting extract purification processes: Conditions, yields, and purities. *Molecules (Basel, Switzerland)* 2019; 24(23): 4273. doi: 10.3390/molecules24234273
75. Kumar P, Barrett DM, Delwiche MJ, Stroeve P. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. *Industrial & Engineering Chemistry Research* 2009; 48(8): 3719–3729. doi: 10.1021/ie801542g
76. Banoth C, Sunkar B, Tondamanati PR, Bhukya B. Improved physicochemical pretreatment and enzymatic hydrolysis of rice straw for bioethanol production by yeast fermentation. *3 Biotech* 2017; 7(5): 334. doi: 10.1007/s13205-017-0980-6
77. Amin FR, Khalid H, Zhang H, et al. Pretreatment methods of lignocellulosic biomass for anaerobic digestion. *AMB Express* 2017; 7: 72. doi: 10.1186/s13568-017-0375-4
78. Badiei M, Asim N, Jahim JM, Sopian K. Comparison of chemical pretreatment methods for cellulosic biomass. *APCBEE Procedia* 2014; 9: 170–174. doi: 10.1016/j.apcbee.2014.01.030

79. Sun Y, Cheng J. Hydrolysis of lignocellulosic materials for ethanol production: A review. *Bioresour Technol* 2002; 83: 1–11. doi: 10.1016/S0960-8524(01)00212-7
80. Mudhoo A. *Biogas Production: Pretreatment Methods in Anaerobic Digestion*. Scrivener Publishing; 2012.
81. Hernández-Beltrán JU, Hernández-De Lira IO, Cruz-Santos MM, et al. Insight into pretreatment methods of lignocellulosic biomass to increase biogas yield: Current state, challenges, and opportunities. *Applied Sciences* 2019; 9(18): 3721. doi: 10.3390/app9183721
82. Zheng B, Yu S, Chen Z, Huo YX. A consolidated review of commercial-scale high-value products from lignocellulosic biomass. *Frontiers in Microbiology* 2022; 13: 933882. doi: 10.3389/fmicb.2022.933882
83. Donkor KO, Gottumukkala LD, Lin R, et al. A perspective on the combination of alkali pre-treatment with bioaugmentation to improve biogas production from lignocellulose biomass. *Bioresource Technology* 2022; 351: 126950. doi: 10.1016/j.biortech.2022.126950
84. Jiang D, Ge X, Zhang T, et al. Effect of alkaline pretreatment on photo-fermentative hydrogen production from giant reed: Comparison of NaOH and $Ca(OH)_2$. *Bioresource Technology* 2020; 304. doi: 10.1016/j.biortech.2020.123001
85. Kang X, Sun Y, Li L, et al. Improving methane production from anaerobic digestion of Pennisetum Hybrid by alkaline pretreatment. *Bioresource Technology* 2018; 255: 205–212. doi: 10.1016/j.biortech.2017.12.001
86. Pavlostathis SG, Gossett JM. A kinetic model for anaerobic digestion of biological sludge. *Biotechnology and Bioengineering* 1986; 28(10): 1519–1530. doi: 10.1002/bit.260281010
87. Fox MH, Noike T, Ohki T. Alkaline subcritical-water treatment and alkaline heat treatment for the increase in biodegradability of newsprint waste. *Water Science & Technology* 2003; 48(4): 77–84. doi: 10.2166/wst.2003.0226
88. He Y, Pang Y, Liu Y, et al. Physicochemical characterization of rice straw pretreated with sodium hydroxide in the solid state for enhancing biogas production. *Energy Fuels* 2008; 22(4): 2775–2781. doi: 10.1021/ef8000967
89. Wang LQ. *Different Pretreatments to Enhance Biogas Production* [Master’s thesis]. Halmstad University; 2011.
90. Alqaralleh RM. *Effect of Alkaline Pretreatment on anaerobic Digestion of Organic Fraction of Municipal Solid Waste* [Master’s thesis]. University of Ottawa; 2012.
91. Yang D, Zheng Y, Zhang R. Alkali pretreatment of rice straw for increasing the biodegradability. *American Society of Agricultural and Biological Engineers* 2009; 095685. doi: 10.13031/2013.26933
92. Zhao X, Cheng K, Liu D. Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis. *Applied Microbiology and Biotechnology* 2009; 82(5): 815–827. doi: 10.1007/s00253-009-1883-1
93. Sharma S, Tsai ML, Sharma V, et al. Environment friendly pretreatment approaches for the bioconversion of lignocellulosic biomass into biofuels and value-added products. *Environments* 2023; 10(1): 6. doi: 10.3390/environments10010006
94. Martin-Sampedro R, Revilla E, Villar JC, Eugenio ME. Enhancement of enzymatic saccharification of Eucalyptus globulus: Steam explosion versus steam treatment. *Bioresource Technology* 2014; 167: 186–191. doi: 10.1016/j.biortech.2014.06.027
95. Vaidya AA, Murton KD, Smith DA, Dedual G. A review on organosolv pretreatment of softwood with a focus on enzymatic hydrolysis of cellulose. *Biomass Conversion and Biorefinery* 2022; 12: 5427–5442. doi: 10.1007/s13399-022-02373-9
96. Thoresen PP, Matsakas L, Rova U, Christakopoulos P. Recent advances in organosolv fractionation: Towards biomass fractionation technology of the future. *Bioresource Technology* 2020; 306: 123189. doi: 10.1016/j.biortech.2020.123189.
97. Kuznetsov B, Malyar Y, Kuznetsova SA, et al. Isolation, study, and application of organosolv lignins (Review). *Journal of Siberian Federal University. Chemistry* 2016; 9: 454–482. doi: 10.17516/1998-2836-2016-9-4-454-482
98. Tan J, Li Y, Tan X, et al. Advances in pretreatment of straw biomass for sugar production. *Frontiers in Chemistry* 2021; 9: 696030. doi: 10.3389/fchem.2021.696030
99. Chin DWK, Lim S, Pang YL, et al. Effects of organic solvents on the organosolv pretreatment of degraded empty fruit bunch for fractionation and lignin removal. *Sustainability* 2021; 13: 6757. doi: 10.3390/su13126757
100. Mardawati E, Badruzaman I, Kasuma CAW, et al. Effect of organosolv pretreatment on delignification for bioethanol feedstock from oil palm empty fruit bunch (OPEFB). *IOP Conference Series: Earth and Environmental Science* 2018; 209: 012009. doi: 10.1088/1755-1315/209/1/012009
101. Viola E, Zimbardi F, Morgana M, et al. Optimized organosolv pretreatment of biomass residues using 2-methyltetrahydrofuran and n-Butanol. *Processes* 2021; 9(11): 2051. doi: 10.3390/pr9112051
102. Sar T, Arifa VH, Hilmy MR, et al. Organosolv pretreatment of oat husk using oxalic acid as an alternative organic acid and its potential applications in biorefinery. *Biomass Conversion Biorefinery* 2022. doi: 10.1007/s13399-022-02408-1
103. Amiri H, Karimi K, Zilouei H. Organosolv pretreatment of rice straw for efficient acetone, butanol, and ethanol production. *Bioresource Technology* 2014; 152: 450–456. doi: 10.1016/j.biortech.2013.11.038

104. Tsegaye B, Balomajumder C, Roy P. Organosolv pretreatments of rice straw followed by microbial hydrolysis for efficient biofuel production. *Renewable Energy* 2020; 148(C): 923–934. doi: 10.1016/j.renene.2019.10.176
105. Li P, Yang C, Jiang Z, et al. Lignocellulose pretreatment by deep eutectic solvents and related technologies: A review. *Journal of Bioresources and Bioproducts* 2023; 8(1): 33–44. doi: 10.1016/j.jobab.2022.11.004
106. Huijgen WJJ, Reith JH, de Uil H. Pretreatment and fractionation of wheat straw by an acetone-based organosolv process. *Industrial & Engineering Chemistry Research* 2010; 49(20): 10132–10140. doi: 10.1021/ie101247w
107. Park YC, Kim JS, Kim TH. Pretreatment of corn stover using organosolv with hydrogen peroxide for effective enzymatic saccharification. *Energies* 2018; 11(5): 1301. doi: 10.3390/en11051301
108. Salapa I, Topakas E, Sidiras D. Simulation and optimization of barley straw organosolv pretreatment. *Industrial Crops and Products* 2018; 113: 80–88. doi: 10.1016/j.indcrop.2018.01.018
109. Traviani R, Martín-Juárez J, Lorenzo-Hernando A, Bolado-Rodríguez S. Ozonolysis: An advantageous pretreatment for lignocellulosic biomass revisited. *Bioresource Technology* 2016; 199: 2–12. doi: 10.1016/j.biortech.2015.08.143
110. Sakthivel R, Harshini GV, Vardhan MS, et al. Biomass energy conversion through pyrolysis: A ray of hope for the current energy crisis. In: *Green Energy Systems*. Academic press; 2023. pp. 37–68. doi: 10.1016/B978-0-323-95108-1.00006-9
111. Kassim MA, Meng TK, Kamaludin R, et al. Bioprocessing of sustainable renewable biomass for bioethanol production. In: *Value-Chain of Biofuels*. Elesevier; 2022. pp. 195–234. doi: 10.1016/B978-0-12-824388-6.00004-X
112. Traviani R, Otero MDM, Coca M, et al. Sugarcane bagasse ozonolysis pretreatment: Effect on enzymatic digestibility and inhibitory compound formation. *Bioresource Technology* 2013; 133: 332–339. doi: 10.1016/j.biortech.2013.01.133
113. De Cassia Pereira J, Travaini R, Marques NP, et al. Saccharification of ozonated sugarcane bagasse using enzymes from *Myceliophthora thermophila* JCP 1-4 for sugars release and ethanol production. *Bioresource Technology* 2016; 204: 122–129. doi: 10.1016/j.biortech.2015.12.064
114. Onu P, Mbohwa C. Methodological approaches in agrowaste preparation and processes. In: *Agricultural Waste Diversity and Sustainability Issues: Sub-Saharan Africa as a Case Study*. Academic Press; 2021. pp. 37–54. doi: 10.1016/B978-0-323-85402-3.00009-7
115. Traviani R, Marangon-Jardim C, Colodette JL, et al. Ozonolysis. *Pretreatment of Biomass: Processes and Technologies*. Elsevier; 2015. pp. 105–135. doi: 10.1016/B978-0-12-800080-9.00007-4
116. Mulakhudair AR, Hanotu J, Zimmerman W. Exploiting ozonolysis-microbe synergy for biomass processing: Application in lignocellulosic biomass pretreatment. *Biomass and Bioenergy* 2017; 105: 147–154. doi: 10.1016/j.biombioe.2017.06.018
117. Garver MP, Liu S. Development of thermochemical and biochemical technologies for biorefineries. In: *Bioenergy Research: Advances and Applications*. Elsevier; 2014. 457–488. doi: 10.1016/B978-0-444-59561-4.00027-9
118. Patil R, Cimon C, Eskicioglu C, Goud V. Effect of ozonolysis and thermal pre-treatment on rice straw hydrolysis for the enhancement of biomethane production. *Renewable Energy* 2021; 179(C): 467–474. doi: 10.1016/j.renene.2021.07.048
119. Wang F, Li S, Sun Y, et al. Ionic liquids as efficient pretreatment solvents for lignocellulosic biomass. *RSC Advances* 2017; 7(76): 47990–47998. doi: 10.1039/C7RA08110C
120. Hou Q, Ju M, Li W, et al. Pretreatment of lignocellulosic biomass with ionic liquids and ionic liquid-based solvent systems. *Molecules* 2017; 22(3): 490. doi: 10.3390/molecules22030490
121. Moyer P, Kim K, Abdoulmoumine N, et al. Structural changes in lignocellulosic biomass during activation with ionic liquids comprising 3-methylimidazolium cations and carboxylate anions. *Biotechnology for Biofuels and Bioproducts* 2018; 11: 265. doi: 10.1186/s13068-018-1263-0
122. Usmani Z, Sharma M, Gupta P, et al. Ionic liquid based pretreatment of lignocellulosic biomass for enhanced bioconversion. *Bioresource Technology* 2020; 304: 123003. doi: 10.1016/j.biortech.2020.123003
123. Haykir NI, Zahari SMSNS, Harirchi S, et al. Applications of ionic liquids for the biochemical transformation of lignocellulosic biomass into biofuels and biochemicals: A critical review. *Biochemical Engineering Journal* 2023; 193: 108850. doi: 10.1016/j.bej.2023.108850
124. Amini E, Valls C, Roncero MB. Ionic liquid-assisted bioconversion of lignocellulosic biomass for the development of value-added product. *Journal of Cleaner Production* 2021; 326: 129275. doi: 10.1016/j.jclepro.2021.129275
125. Socha AM, Parthasarathi R, Shi J, et al. Efficient biomass pretreatment using ionic liquids derived from lignin and hemicellulose. *Proceedings of National Academy of Sciences* 2014; 111(35): E3587–E3595. doi: 10.1073/pnas.1405685111
126. Brandt A, Ray MJ, To TQ, et al. Ionic liquid pretreatment of lignocellulosic biomass with ionic liquid—water mixtures. *Green Chemistry* 2011; 13(9): 2489–2499. doi: 10.1039/C1GC15374A

127. Sriariyanun M, Kitiborwornkul N, Tantayotai P, et al. One-pot ionic liquid-mediated bioprocess for pretreatment and enzymatic hydrolysis of rice straw with ionic liquid-tolerance bacterial cellulase. *Bioengineering* 2022; 9(1): 17. doi: 10.3390/bioengineering9010017
128. Satlewal A, Agrawal R, Bhagia S, et al. Natural deep eutectic solvents for lignocellulosic biomass pretreatment: Recent developments, challenges and novel opportunities. *Biotechnology Advances* 2018; 36(8): 2032–2050. doi: 10.1016/j.biotechadv.2018.08.009
129. Kalhor P, Ghandi K. Deep eutectic solvents for pretreatment, extraction, and catalysis of biomass and food waste. *Molecules* 2019; 24(22): 4012. doi: 10.3390%2Fmolecules24224012
130. Zhang C, Xia S, Ma P. Facile pretreatment of lignocellulosic biomass using deep eutectic solvents. *Bioresource Technology* 2016; 219: 1–5. doi: 10.1016/j.biortech.2016.07.026
131. Scelsi E, Angelini A, Pastore C. Deep eutectic solvents for the valorisation of lignocellulosic biomasses towards fine chemicals. *Biomass* 2021; 1(1): 29–59. doi: 10.3390/biomass1010003
132. Mbous YP, Hayyan M, Hayyan A, et al. Applications of deep eutectic solvents in biotechnology and bioengineering—Promises and challenges. *Biotechnology Advances* 2017; 35(2): 105–134. doi: 10.1016/j.biotechadv.2016.11.006
133. Bajpai P. Processing of biomass by DESs. In: *Deep Eutectic Solvents for Pretreatment of Lignocellulosic Biomass*. Springer; 2021. pp. 29–54. doi: 10.1007/978-981-16-4013-1_4
134. Li W, Tan X, Miao C, et al. Mild organosolv pretreatment of sugarcane bagasse with acetone/phenoxyethanol/water for enhanced sugar production. *Green Chemistry* 2023; 25: 1169–1178. doi: 10.1039/D2GC04404H
135. Chen Y, Mu T. Application of deep eutectic solvents in biomass pretreatment and conversion. *Green Energy & Environment* 2019; 4(2): 95–115. doi: 10.1016/j.gee.2019.01.012
136. Wang W, Lee D. Lignocellulosic biomass pretreatment by deep eutectic solvents on lignin extraction and saccharification enhancement: A review. *Bioresource Technology* 2021; 339: 125587. doi: 10.1016/j.biortech.2021.125587
137. Arriaga S, Aizpuru A. Innovative non-aqueous phases and partitioning bioreactor configurations. *Advances in Chemical Engineering* 2019; 54: 299–348. doi: 10.1016/bs.ache.2018.12.004
138. Kumar N, Muley PD, Boldor D, et al. Pretreatment of waste biomass in deep eutectic solvents: Conductive heating versus microwave heating. *Industrial Crops and Products* 2019; 142: 111865. doi: 10.1016/j.indcrop.2019.111865
139. Fang C, Thomsen MH, Frankær CG, et al. Reviving pretreatment effectiveness of deep eutectic solvents on lignocellulosic date palm residues by prior recalcitrance reduction. *Industrial & Engineering Chemistry Research* 2017; 56(12): 3167–3174. doi: 10.1021/acs.iecr.6b04733