Discover Materials

Review

Enhancing Biogas Generation: A Comprehensive Analysis of Pre-Treatment Strategies for Napier Grass in Anaerobic Digestion

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Abstract
Grass is being explored as a potential feedstock for biogas production since it consumes less water than other crops and may be grown on non-arable soils without displacing the food crops directly. The feedstock's features, particularly its intricate lignocellulosic structure, limit the amount of biogas produced. Various pretreatment techniques are being researched to prevent disruption of the grass's structural integrity during the anaerobic digestion process. This article aims to review the knowledge of recent pretreatment techniques that are used for lignocellulosic biomass. The chemical composition of an energy crop (Napier grass) from various literature sources is evaluated and tabulated. Techniques for pretreatment are divided into physical, chemical, thermal, physicochemical, biological, and combined categories. Alkaline chemical pretreatment on Napier grass showed enhancements in methane yield up to 70%, demonstrating its potential as an effective strategy for improving biogas production efficiency. The pretreatment method can serve as an effective alternative for enhancing biogas and methane yields from lignocellulosic biomass in both full-scale and pilot-scale bio-methanation projects.

Keywords Biogas · Napier grass · Anaerobic digestion · Pretreatment · Methane · Energy crop

1 Introduction

The world's commodity markets make considerable use of coal, natural gas, petroleum, and crude oil as energy sources, fuels, and chemicals. However, because fossil fuels take millions of years to develop on a global scale, their sources are finite and susceptible to depletion when utilized [1]. Research into the generation of alternative fuels from bio-resources has been sparked by the continuous consumption of fossil fuels and the impact of greenhouse gases on the ecosystem [2]. In this context, biomass energy has emerged as one of the most promising prospects for the future of renewable energy sources [3]. A renewable and green energy source is biogas. The energy used to produce biogas is obtained from

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the Sun through photosynthesis by plants, much like all other renewable energy sources as shown in the modified Fig. 1 [4]. It is mostly composed of carbon dioxide (CO_2) and methane (CH_4), which can be purified to produce feed gas, liquefied to produce methanol, compressed to make vehicle fuel, and purified to produce methane for its use in producing heat or power [5]. Biogas can be produced through anaerobic digestion of agricultural waste, sewage sludge, energy crops, animal manure, and food waste [6, 7].

Anaerobic digestion is a useful technique for reducing waste by producing biogas and can be used to turn waste into energy that can be utilized [8]. To create monomers such as long-chain fatty acids, sugars, and amino acids, complex organic materials like protein, lipids, and carbohydrate polymers (starch and cellulose) must be hydrolyzed [9]. This is the first step of the anaerobic digestion process known as hydrolysis. During acidogenesis (second phase), these monomers are subsequently fermented to create volatile fatty acids (butyric acids, lactic acid, and propionic acid) [10]. These volatile fatty acids are consumed by bacteria in the third phase, called acetogenesis, where they produce carbon dioxide (CO_2), hydrogen (H_2), and acetic acid. The final step is the production of methane (CH_4) by methanogenic organisms that consume H_2, acetate, and CO_2. This phase is known as methanogenesis [11]. The process of anaerobic digestion is shown in Fig. 2a and b. Anaerobic digestion is completed at various ranges of temperatures such as psychrophilic (10–25 °C), mesophilic (30–40 °C) or thermophilic (50–60 °C). Recently, numerous nations have used anaerobic digestion with great success for things like waste management and energy production efficiency of anaerobic digestion processes using a single fuel, however, is often limited by their inability to create biogas on a large scale. Utilizing a single substrate also has drawbacks, including low pH, unsuitable carbon-to-nitrogen (C/N) ratios, and high ammonia concentrations [13]. Consequently, the co-digestion of mixed substrates for biogas production has recently drawn more attention [14]. Widespread usage of anaerobic co-digestion has increased the biogas output of digesters [15]. The anaerobic co-digestion of animal manure along with different alternative biomasses has been studied in several published articles to increase the rate of production of biogas [3, 16, 17]. Anaerobic digestion results in the recovery of methane (CH_4) as a major product in the gas phase at the end of the co-digestion process. More methane production may still be possible using volatile fatty acids in the liquid phase and the solid by-products resulting from the production process. Decrease the amount of crystalline cellulose, enhance the cellulose's surface area, and eliminate lignin structure in the solid residues, pretreatment is needed [18]. This increases the availability of fungal or bacterial enzymes that hydrolyze hemicellulose and cellulose into fermentable sugars [19].

One of the most abundant and renewable resources for producing biofuels, biochemicals, and other useful products is lignocellulosic biomass, which is composed of cellulose, hemicellulose, and lignin. However, processing it effectively is challenging due to its complex structure. Although the cellulose and hemicellulose are densely packed beneath a layer of lignin, enzymes and microorganisms are unable to break them down and release fermentable sugars. Pretreatment methods are used as a critical step to improve the digestibility and accessibility of lignocellulosic materials in order to get these obstacles. Pretreatment techniques are intended to enhance the biomass's porosity, decrease cellulose crystallinity, decrease lignin, and compromise the structural integrity of lignocellulose. These methods fell into the following four

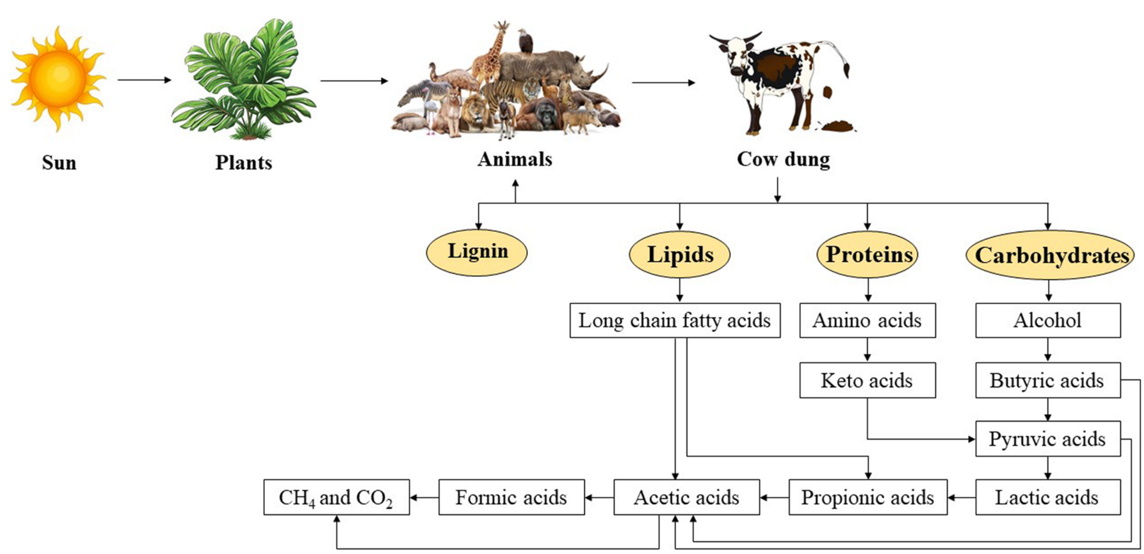
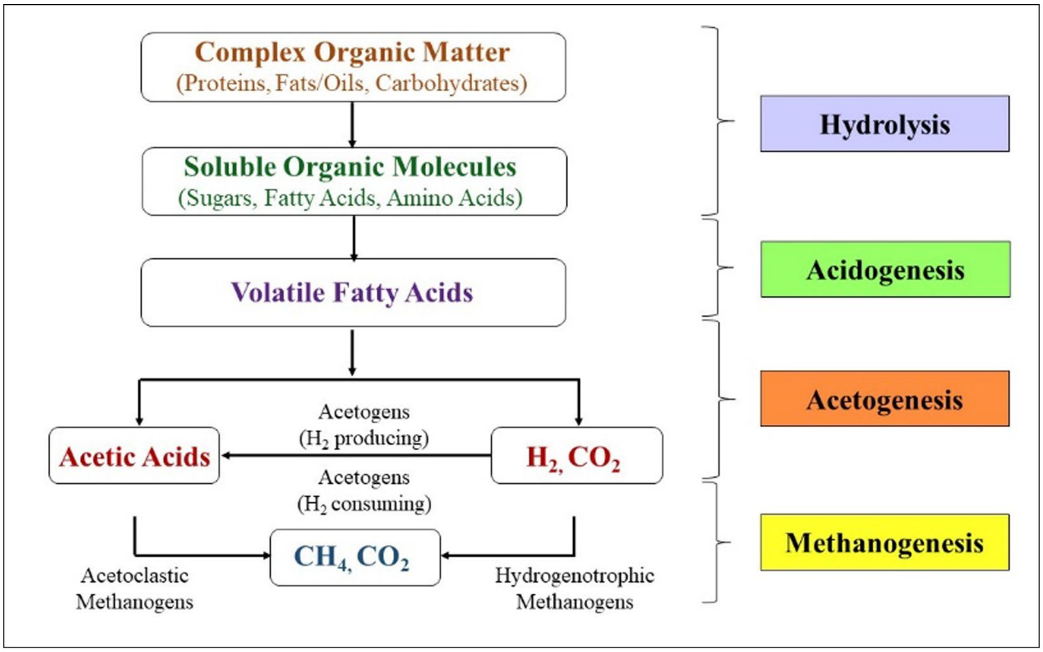
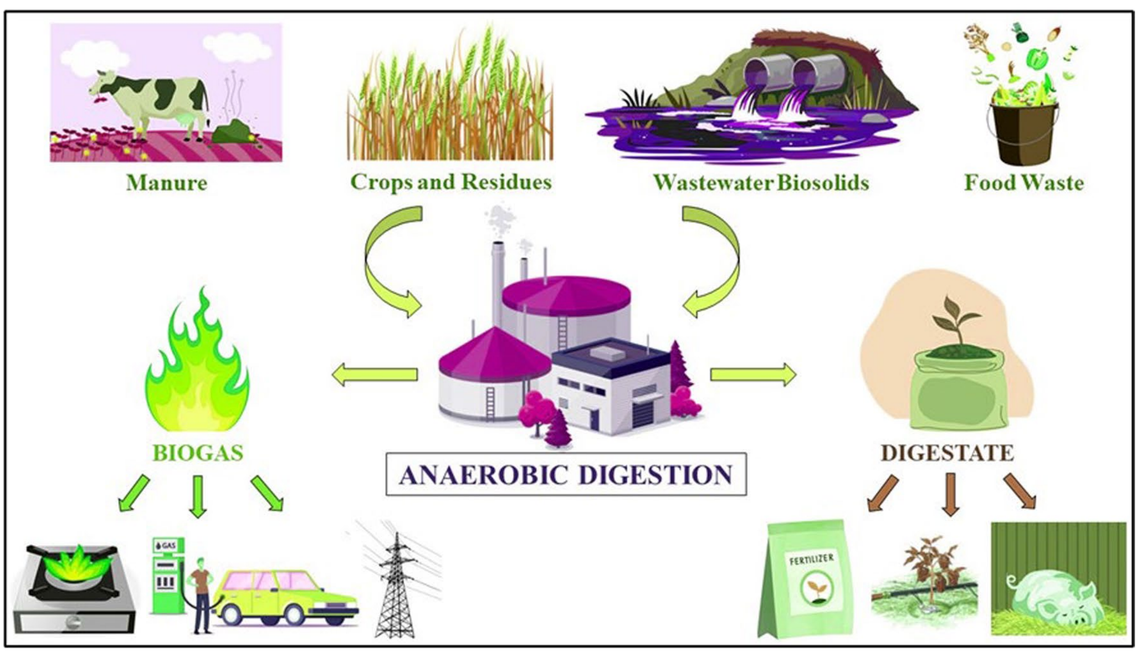


Fig. 1 Biogas production scheme



(a)



(b)

Fig. 2 Anaerobic Digestion Process [(**a**) Steps and Products, (**b**) Working and Applications]

general categories: physicochemical (such as steam explosion or ammonia fiber explosion), chemical (such as acid hydrolysis or alkaline pretreatment), biological (such as microbial or enzymatic treatments), or physical (such as milling or grinding). A number of variables, such as the classification of biomass, final product, and economic viability, influence the choice of pretreatment technique.

This study aims to review and evaluate recent information on pretreatment methods for lignocellulosic biomass on the basis of different parameters as shown in Fig. 3. This study highlights the effectiveness of pretreatment methods in degrading lignin, cellulose, and hemicellulose, and links compositional changes to improvements in methane yield,

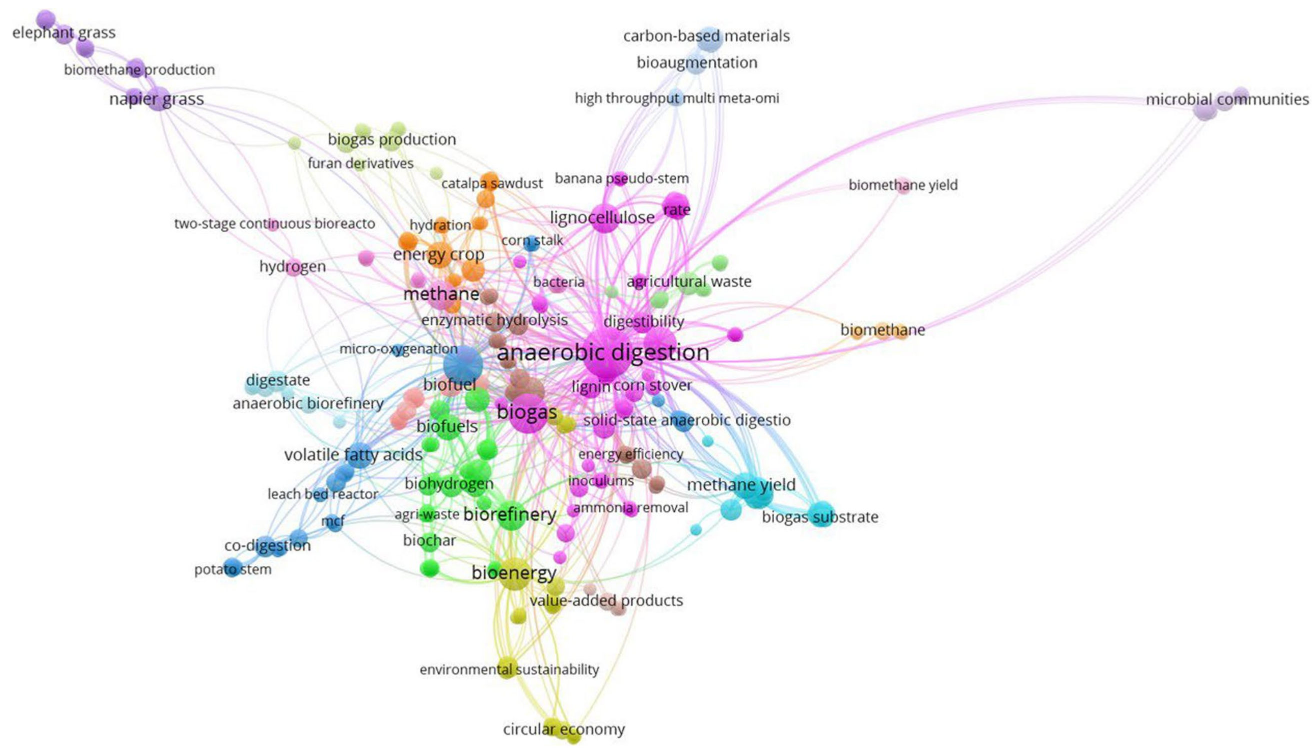


Fig. 3 Parameters of review process

offering a valuable comparison of their efficiency. However, the study identifies several gaps, including the limited analysis of combined pretreatment strategies for synergistic effects, lack of discussion on economic feasibility, scalability, and environmental sustainability, and insufficient exploration of the underlying mechanisms driving lignocellulose degradation. Additionally, it overlooks geographical variations in Napier grass composition, lacks emphasis on novel biological approaches like genetic engineering or enzyme-based methods, and fails to address the practical applicability of the reviewed methods at an industrial scale. These gaps underscore opportunities for future research to optimize pretreatment processes and enhance the sustainable use of Napier grass in biogas production.

2 Napier grass as a substrate

Energy crops, forestry waste, and farm debris are examples of lignocellulose biomass, which is becoming more popular as a feedstock for biogas. This is a reliable and long-term resource. Several perennial grasses can be used as biogas feedstock, such as *guinea, ruzi, para, and Napier grass*. The most valuable of these grasses is Napier grass *(Pennisetum purpureum)*. Figure 4, shows a picture of Napier grass which is a kind of grass cultivated primarily for grazing. The production of Napier grass is about 150 MT/Acre/Year [1, 20]. Hybrid Napier grass is also known as Elephant grass or Ryegrass in Africa, Europe and Asia. It is being explored as an energy novel alternative crop that can be used to produce biofuel. Because it is perennial, high in green biomass, and resistant to pests, Napier grass has been valued. Due to more celluloses & hemicelluloses which are degradable content around 80 to 92%, it is more useful in anaerobic digestion and methane generation. Napier grass is cultivated in conventional agricultural system as a result it is easily harvested & collected for utilization as an animal fodder and can be used as a substrate for biomethane production. The growth characteristics and biomass yield of Napier grass vary across geographical regions due to differences in climate, soil conditions, altitude, and management practices. Thriving in tropical and subtropical climates, Napier grass grows best at temperatures between 25 and 35 °C, with optimal rainfall of 750–2500 mm annually. It requires fertile, well-drained soils with a pH of 5.5–7.5. While high solar radiation promotes photosynthesis, growth may be stunted in shaded areas or at higher altitudes with cooler temperatures. Regional variations are also influenced by irrigation, fertilization, and harvesting frequency, which can mitigate challenges like erratic rainfall or nutrient-poor soils. For instance, regions like tropical Africa and Southeast Asia yield high biomass due to favourable climates. Arid or nutrient-deficient areas like parts of South Asia

Fig. 4 Napier Grass

require enhanced management practices to optimize productivity [19, 21]. Napier grass is primarily composed of three principal constituents: lignin, cellulose, and hemicellulose as depicted in the Fig. 5. Once harvested, Napier grass can be cultivated for up to 7 years. It has a strong growth rate, can resist drought well, and recovers quickly from rainfall. It also adapts effectively to tropical and subtropical regions [22].

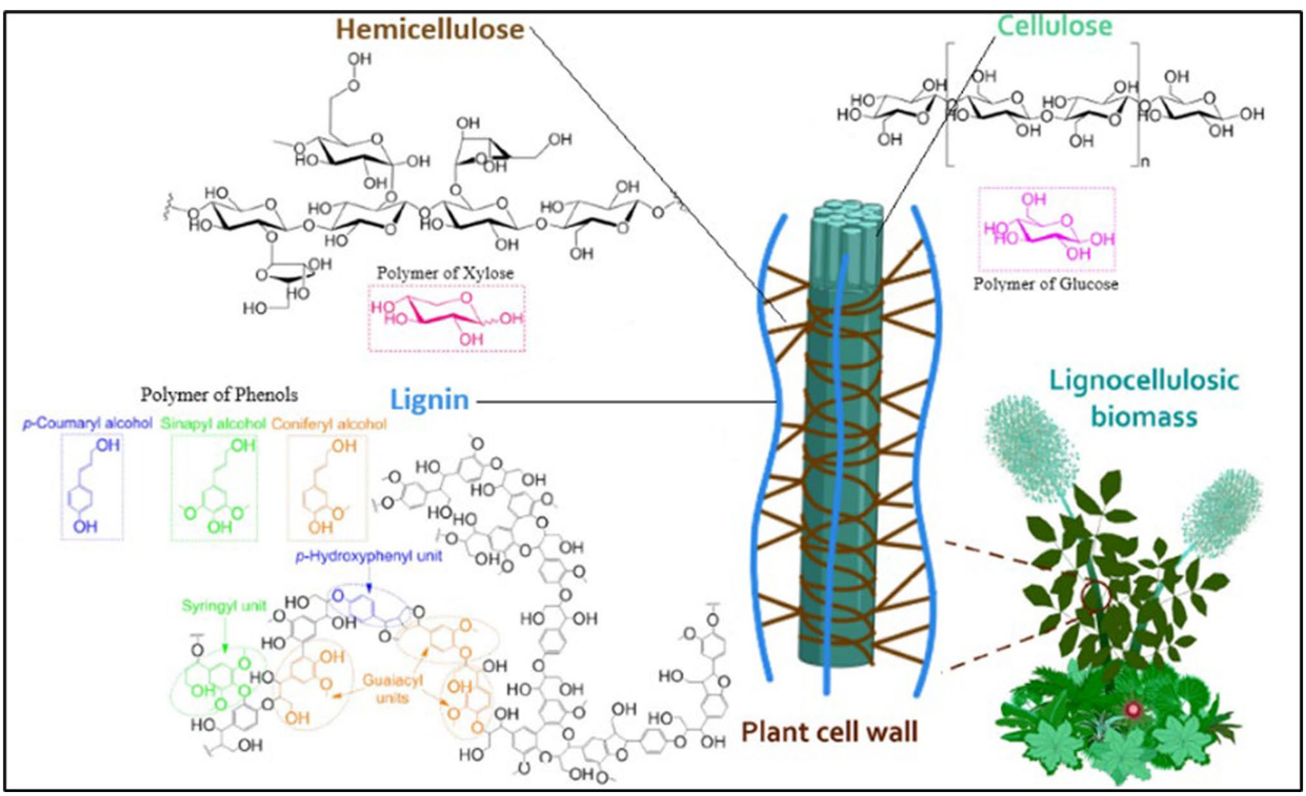


Fig. 5 Structure of Lignocellulosic Biomass (Reproduced with permission from [23] copyright Elsevier BV

There have been several studies where Napier grass is used as a feedstock in biomass for increased biogas yield as tabulated in Table 1. It presents the composition of lignocellulosic biomass, showing variations in lignin, cellulose, hemicellulose, total carbon (C), total nitrogen (N), and the carbon-to-nitrogen (C/N) ratio across different harvesting days and sources. Lignin content ranges from 8.27 to 32.04%, with lower values favouring bioenergy applications due to higher digestibility. Cellulose, critical for glucose yields in biofuel production, varies widely from 22 to 84.56%, while hemicellulose ranges from 4.36 to 34.12%, contributing to overall sugar yields. Total carbon (10–49.93%) reflects the energy potential, with higher values suitable for combustion or gasification. Nitrogen content (0.44–2.67%) indicates protein levels, where low nitrogen is ideal for bioenergy to avoid fouling. The C/N ratio (9.10–58.15) highlights biomass suitability for composting or anaerobic digestion, with higher ratios suggesting slower decomposition. These variations emphasize the importance of selecting appropriate harvesting periods, such as 30–45 days, to balance lignin, cellulose, and hemicellulose for specific applications like biofuel, composting, or paper production, as supported by the referenced studies. One another research considered the possibility of producing biogas from dry anaerobic digestion of Napier grass using a batch experiment [1, 12, 24, 25].

3 Pretreatment

The internal structure of lignocellulosic biomass is intricate. It has several major constituents, including lignin, cellulose, and hemicellulose, each of which has an intricate structure. To supply the microorganisms in the reactor with a larger target surface area and accelerate the breakdown process, the grass must be adequately prepared before anaerobic digestion [33]. Pretreatment techniques are required to: (i) improve the cellulose and hemicelluloses' accessibility to the enzymes and thereby their degradability; (ii) prevent the breakdown or destruction of the carbohydrates; (iii) prevent the generation of potential inhibitors; (iv) be economical and energy efficient; (v) have as few adverse environmental consequences as possible [34].

The various methods of pretreatment of lignocellulosic biomass classified in this study are illustrated in Fig. 6.

The references included in Fig. 7 a, b and c were carefully chosen from peer-reviewed journals, conference proceedings, and authoritative review articles published in reputable scientific databases such as Scopus, Web of Science, and PubMed. The selection was based on the relevance of the studies to the various pretreatment techniques for lignocellulosic biomass, including physical, chemical, physicochemical, and biological methods. Priority was given to studies that demonstrated innovative approaches, high effectiveness in enhancing enzymatic digestibility, or addressed challenges related to scalability and sustainability.

Table 1 Chemical Composition of Napier Grass in Literature

Harvesting days	Lignin (%)	Cellulose (%)	Hemicellulose (%)	Total carbon C (%)	Total nitrogen N (%)	C/N ratio	References
–	32.04	34.25	17.36	49.93	2.02	24.72	[14]
–	30.23	29.48	17.32	45.36	0.78	58.15	[19]
30–45	10–33	25–43	15–53	49.93	2.05	24.35	[20]
45	11.08	84.56	4.36	11.37	0.44	25.84	[24]
45	30.40	36.34	34.12	44.19	2.00	22.10	[25]
–	21.67	32.26	19.73	–	–	–	[26]
–	–	–	–	10	2.26	17.64	[27]
–	–	–	–	10	2	5	[28]
–	24	22	24	–	–	–	[29]
–	21.6	47.1	31.2	–	–	–	[30]
60	8.27	36.81	26.16	24.3	2.67	9.10	[31]
–	–	–	–	43.9	2	21.95	[32]
–	–	–	–	44.2	2	22.1	[32]
–	–	–	–	44	1.9	23.16	[32]

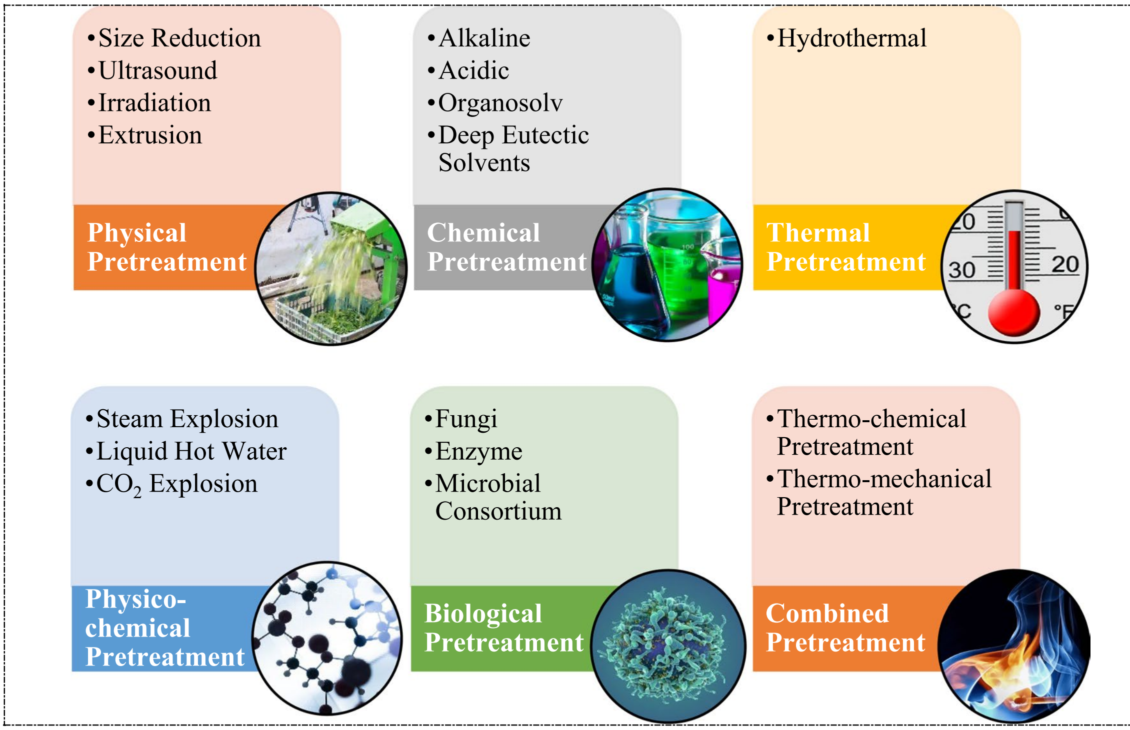


Fig. 6 Pretreatment Methods for Lignocellulosic Biomass

3.1 Physical pretreatment

Physical pretreatment emphasizes pretreatment techniques that exclude the use of external substances like water, chemicals, or microbes [33]. The physical pretreatment techniques of size reduction, ultrasound, irradiation, and extrusion are examined in this literature.

3.2 Size reduction

Reducing the substrate's particle size is the goal of size reduction. The outcome revealed that the biomass's specific surface area increases and its level of polymerization decreases. Before the subsequent pretreatment, most pretreatments call for a varying size reduction degree of the collected feedstock. Lignocellulosic biomass that degrades more quickly may only require size reduction or milling as a pretreatment method. Biomass that is compact and difficult to manage can be treated by crushing, milling, and grinding. The biomass's size, mechanical characteristics, and moisture content all influence the grinding technique [35]. Hammers, knives, screw shredders, and scissors are the most typical tools for crushing or grinding. A rotor with mounted hammers that push up the feedstock into a breaker plate, shredding it and releasing it via screens, is the basic part of a hammer mill. A hammer mill was effectively employed to handle various biomasses, including wheat straw and corn stover [33–36]. In one study, mechanical pretreatments applied to decrease complex cellulose particle size. This also increase the substrate's specific surface area available to bacteria improved the biogas yield. According to a survey, there is a substantial correlation between the biogas generation rate and particle size. The raw materials with the smallest particle sizes created the most biogas from agricultural waste. In another study, Napier grass leaves were dried, and then the leaves were crushed using a grinder and sieved through 10, 35, and 60-number mesh. This ultimately improved the yield of biogas and methane [11, 37]. However, Chang et al. discovered that neither the rate nor the yield of hydrolysis was significantly impacted by biomass particles smaller than 0.4 mm [38, 39]. The various grinding techniques include ball grinding, rod grinding, hammer grinding, grinding, and colloid grinding, depending on the type of motorized equipment used. The kind of grinding technique utilized, the length of processing, and the biomass type employed

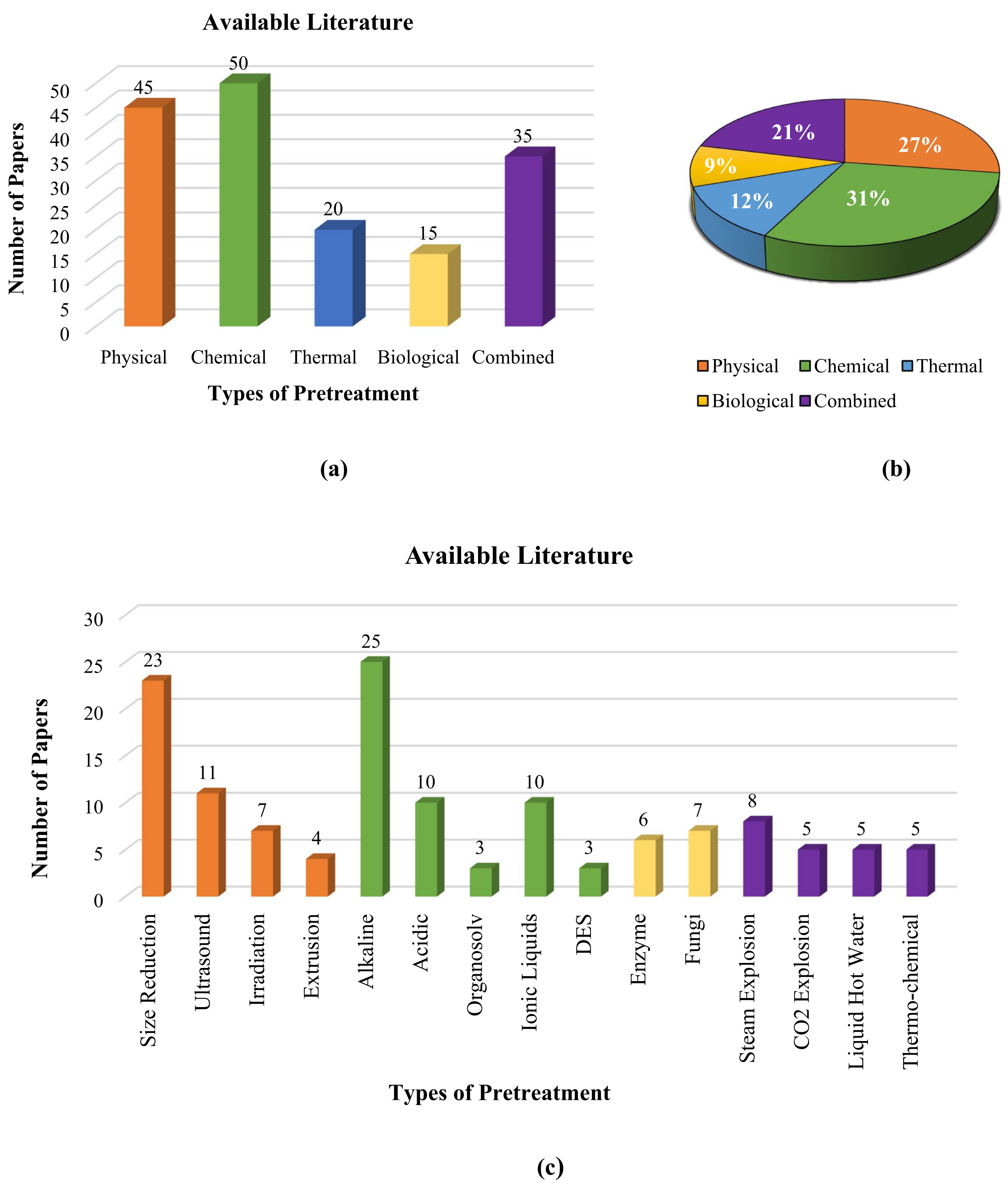
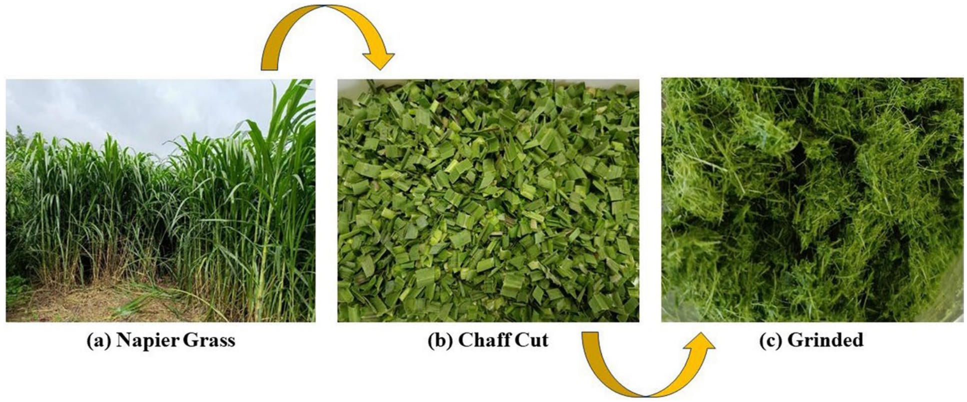


Fig. 7 Available Literature Based on Web of Science, Scopus, and PubMed on Various Pretreatment Methods of Lignocellulosic Biomass (**a**) Data Based on Various Types (**b**) Percentage-Based Data (**c**) Data Based on Various Sub-Types

Fig. 8 Size Reduction on Napier Grass (Napier Grass—Chaff cut—Grinded)



all affect the decrease in crystallinity and particle size [38, 40]. Figure 8 depicts size reduction pre-treatment (chaff cut and grinding) on Napier grass.

When Bai et al., examined the efficiency of rod-milling and hammer-milling as pretreatments for pyrolysis of wheat straw. Rod-milling for a suitable duration of 60 min produced a significant reduction in size and a decrease in overall crystallinity [41]. Because of the significant decrease in size and crystallinity, wheat straw showed excellent surface contact and volume of pores. Additionally, the kinetic study revealed that rod milling wheat straw before pyrolysis results in a lower thermal degradation temperature than hammer milling, which improved pyrolysis efficiency. However, the high energy needs and significant initial investment in mechanical equipment associated with milling pre-treatment are among its main drawbacks [38, 41].

3.3 Ultrasound

Pre-treatment using ultrasound is based on the cavitation theory and uses ultrasonic energy. The intricate network structure of lignocellulosic biomass is split apart by cavitation-generated shear stresses, which facilitates the extraction of desirable components like lignin, cellulose, and/or hemicellulose as illustrated in the modified Fig. 9 [38, 42]. The biomass, such as sludge particles from waste-water treatment, is mechanically destroyed and disintegrated by ultrasound [43]. The frequency, the duration, the amount of energy, and the properties of the sludge all have an impact on the ultrasound pretreatment. This treatment works by disassembling the microbial cell structure and removing the internal part from the cells. Full-scale sewage sludge plants that employ ultrasonication have shown a 50% increase in biogas output. Ultrasound is the name given to acoustic energy that emerges as waves with a frequency that is higher than that detected by human ears [44]. By creating cavitation inside the cells and in areas where there is liquid vapour, microbubbles are created by the higher frequencies of the sonic waves. Cavitation generates velocity or pressure shockwaves and micro-turbulence dynamics. Due to the very high local pressures and temperatures that are caused by cavitation, which also create extremely strong shear forces in the fluid and cause reactive radicals such as (H^+ and OH^-) to form, biomass's hydrolysis speeds up, which causes volatile fatty acids, to be more easily produced and converted into methane. According to Schwede et al., contradictory to expectations, samples of the microalgae Nannochloropis salina with greater

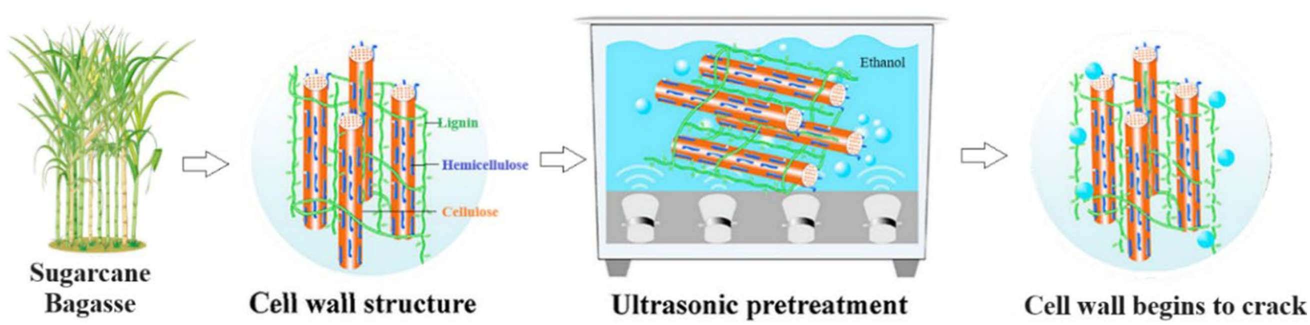


Fig. 9 Ultrasound Pretreatment of Sugarcane Bagasse

VS degradations produced less specific biogas. The author notes that this may be a symptom of the potential loss of volatile organic matter after cell destruction by ultrasounds [33, 34, 45, 46]. Liyakathali et al. found that temperature and sonication time enhanced the enzymatic digestion of energy cane bagasse, but the frequency of ultrasonic waves had no effect on it [38, 47]. Cherpozat et al. investigated pre-treating wood chips with ultrasonic technology to produce bio-oil. The experiments conducted were under various settings for the applied power (125, 250, 500, and 1000 Watt), treatment time (0.5, 1, and 1.5 h), and frequency (40, 68, and 170 kHz). They determined that a power of 1000 Watt and frequency combinations of 170 kHz for 0.5 h and 40 kHz for 1.5 h produced 12% higher output of bio-oil than untreated wood [38, 48]. However, extended ultrasonication may have negative effects due to particle collision and agglomeration. Another study found that pretreatment with ultrasound on sugar beet shreds that were before enzymatic hydrolysis produced cellulose yields of 780 mg/g, which were 3.7 times greater than the samples that were untreated [49].

The investigations mentioned above conclusively show that ultrasonication is a useful pretreatment method since it may contribute to the disruption of various lignocellulosic biomass sources. Using ultrasound to hydrolyse biomass can speed up the process by up to 80%, which is helpful for the generation of biofuels [50]. To improve the process parameters for large-scale applications, however, in-depth research is required due to the process's high energy requirements [38, 51].

3.4 Irradiation

For many years, lignocellulosic biomass has been pretreated using microwave irradiation, a novel heating technique, with an applied electromagnetic field. Ooshima et al. conducted the first study on microwave irradiation pretreatment, and ever since, this method has been regarded as practical because of various factors, such as the ease of use, energy efficiency, minimum inhibitor formation, and high heating capacity in a brief amount of time [38, 52, 53]. High-energy electron radiation, such as gamma rays or microwave energy, is employed in irradiation as a pretreatment technique. The techniques can damage the cell wall, reduce cellulose crystallinity, and enhance the amount of surface that is accessible. The breakdown of cells in wastewater sludge resulted in a 22% increase in biogas output because of irradiation pretreatment. The specific methane production of microwave-pretreated Pennisetum hybrid reduced from 189.7 mL/g VS corresponding to the initial substance to 163.6 mL/g VS after 3 min of pretreatment [34, 54]. Similar results have been observed with switchgrass, where the application of microwave pretreatment technology accelerated the pace of methane synthesis without significantly affecting the total amount of CH_4 generated. It also reduced the time taken to reach the 80% threshold by 4.5 days [55]. High-pressure microwave irradiation and atmospheric microwave irradiation are the two types of microwave irradiation treatments available. In closed reactors, the temperatures at which high-pressure irradiation pretreatments are performed range from 150 to 250 °C [56]. A research investigation on the irradiation pretreatment of Panicum species and Miscanthus species revealed that after treatment, the materials were 7–10% more soluble in subcritical water than the untreated raw materials. The samples in this experiment were pretreated at various temperatures, and for Miscanthus species and Panicum species, respectively, the optimal conditions were 60 °C and 120 °C at 1600 Watt [38, 57]. In a different study, Hyacinthus species were pretreated with microwaves to increase the methane generation from anaerobic digestion. The maximum methane yield was achieved with this approach, which was 38.3% higher than the substrate that underwent water heating pretreatment. The maximum methane yield was achieved with this approach, which was 38.3% higher than the substrate that underwent water heating pretreatment [38, 58]. A modified schematic illustration of microwave irradiation pretreatment on rice husk is shown in Fig. 10.

Fig. 10 Microwave Irradiation of Rice husk

3.5 Extrusion

One of the most popular physical pretreatment techniques used on lignocellulosic biomasses is extrusion. This method's foundation is a tight barrel with one or two spinning screws that are equipped with temperature control [59]. The lignocellulose's refractory structure is broken when raw materials are fed into the barrel at over 300 °C. This is because the barrel's revolving screw blades create shear pressures in addition to the high temperatures. The two main types of extrusion machines are single-screw, which are built from a single solid component, and twin-screw extruders, which are composed of small pieces called screw elements arranged in a cylindrical form. The breakdown of lignocellulosic biomass is significantly influenced by the design of the screw. The design of the screw, speed of the screw, and temperature of the barrel are a few of the variables that affect the extrusion preparation [38, 40, 59]. Erick Heredia-Olia et al. studied the various process variables of sweet sorghum bagasse extrusion pretreatment, followed by enzymatic hydrolysis and the generation of bioethanol. Using surface response methods, they ran the process under several settings and found that the 200-rpm speed of the screw, 30% moisture content of the feedstock, and 100 °C barrel temperature were the best extrusion parameters, producing 70% of total sugars upon enzymatic hydrolysis. This paper described how moisture content and temperature combine to affect extruder shear stress, which increases the cellulose fibre disintegration and increased enzyme contact surface and porosity [38, 60]. In their investigation of the twin-screw extruder's pretreatment of straw and bagasse from sugarcane, Moro et al. optimized several variables, such as the kind of additives, biomass: addition proportion, number of extrusions passes, barrel temperature, screw velocity, and screw configurations. Additives, such as glycerol, ethylene, water, etc., were loaded in varied amounts during the pretreatment process. By adding two additional screw configurations to the extruder, the effect of extrusion was regulated, and an enzymatic hydrolysis yield of glucose of 68.2% was discovered. This study demonstrated that the extrusion pretreatment solely is a more effective method for producing 69% glucose from olive tree pruning than extrusion-assisted alkaline pretreatment [38, 61, 62]. There haven't been any studies done on Napier grass using extrusion pre-treatment as of yet.

3.6 Chemical pretreatment

One of the most promising pretreatment techniques for biomass is chemical pretreatment [63, 64]. An acid reagent or an alkali reagent is the substance that is used in this process the most often. Chemical pretreatment's primary objective is to solubilize polymers, which favours the biomass's availability of carbohydrates for enzymatic saccharification [65].

3.7 Alkaline pretreatment

The chemical pretreatment technique known as alkali pretreatment works by solubilizing lignin in an alkali solution and has received extensive research [38]. In alkali pretreatment, bases such as sodium hydroxide (NaOH), ammonia (NH_3), and lime ($Ca(OH)_2$) are used to solubilize the lignin content [66, 67]. The most successful of these was discovered to be sodium hydroxide [68]. The intermolecular ester linkages between hemicelluloses and lignin are broken during the alkali pretreatment process by a saponification reaction. As a result, pieces of hemicellulose and lignin are solubilized in an alkali solution, bringing cellulose into contact with the enzymes [38, 69]. While still preserving a high cellulose percentage, alkaline pretreatments are efficient at removing lignin. Alkali pretreatment can inflate the fibres, enhancing the surface area that is accessible. Additionally, it has the potential to reduce the crystallinity weaken the bonds between carbohydrates and lignin, and disturb the lignin structure. A crucial factor to consider when pre-treating substrates with alkali is that the biomass itself uses some of the alkali, necessitating the use of stronger alkali reagents to achieve the necessary anaerobic digestion increase [27, 70, 71]. Lignin removal has been demonstrated to be more successful with alkaline pretreatment [33, 72, 73]. Although often seen as economically unappealing, chemical pretreatment technology can be employed on lignin-rich biomass would be indigestible otherwise. Alkali-pretreated biomass's remaining alkali may be able to avoid a pH drop during the acidogenesis phase [33, 57, 74]. A modified schematic illustration of alkaline pretreatment on Napier grass is shown in Fig. 11.

Napier grass biomass was pretreated with 2% NaOH. After two days of incubation with 2% NaOH (w/v) at room temperature, the biomass (insoluble portion) was removed and rinsed using tap water till a neutral pH was obtained. After being dehydrated to eliminate free water, the pretreated biomass was put in plastic bags sealed and kept at a temperature of 4 °C. The results showed that high-yield biogas was produced from pretreated substrates at a rate that

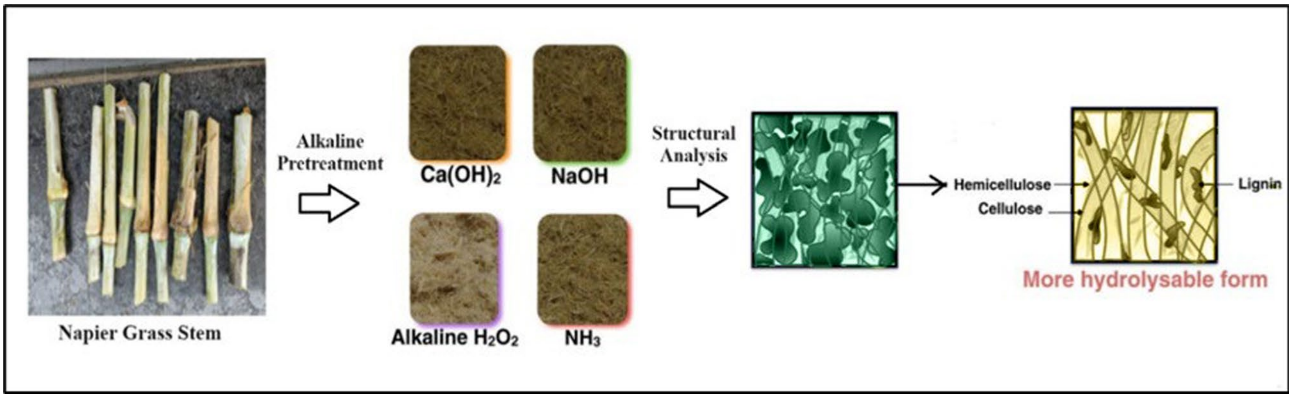


Fig. 11 Alkaline Pretreatment of Napier Grass (Reproduced with permission from [75]) copyright Elsevier BV

was three times more than that of an untreated fermenter. Talha et al. enhanced the alkaline pretreatment of filter mud and sugarcane bagasse to enhance bio-methanation. The outcomes revealed an increase in the methane output of 82.20% and removal of lignin by 86.27% using 1% NaOH at 100 °C for 3 h [1, 76].

In another study, alkali pretreatment was applied in batch mode on Napier grass. Immerse three kilograms of biomass, 1, 2, and 3% sodium hydroxide (NaOH) solutions were made. Alkali hydrolysis was applied to this reaction mixture during 24, 48, and 72 h. The linkages between lignin, cellulose, and hemicellulose have been released by an alkali pretreatment. A percentage of the lignin and hemicellulose components were probably degraded during pretreatment, creating a soluble material that gave the hydrolysis process easier access to the material. After alkali pretreatment, the substrate porosity for the pretreated substance increases, which may promote microbial interaction and facilitate hydrolysis, which is the first stage of biogas fermentation. The study's findings made it abundantly clear that samples prepared with NaOH produced higher biogas yields than samples pretreated with hot water or untreated (raw) [77]. Additionally, the results showed that using 1% NaOH in a 24 h biogas reaction produced greater alkali pretreatment values. Additionally, 1% of NaOH and a 24 h reaction time may be preferable to save both time and cost. According to research on the alkaline pretreatment of rice straw to form biomethane, 1% sodium hydroxide at ambient temperature for three hours substantially decreased the hemicellulose and lignin contents while leaving the cellulose unaffected. Compared to rice straw that hadn't been treated, this resulted in a more than 34% rise in methane yield [25, 78]. Alkali hydrolysis was conducted by Rekha et al. for two hours at temperatures between 70 °C and 90 °C using various sodium hydroxide solution concentrations. Each condition's Soluble Chemical Oxygen Demand (SCOD), biogas, and methane yields were measured. It was noticed that the pretreatment that was conducted at a temperature of 80 °C instead of 70 °C resulted in a relatively greater methane and biogas output following anaerobic digestion. Similar findings showed that pretreatment performed at greater temperatures did not result in significant differences. This showed that the SCOD, biogas, and methane production are more dependent on the alkali content and the timing of the hydrolysis. Shen et al. showed the effectiveness of pretreatment using sodium hydroxide to improve the anaerobic digestion process. They improved the vinegar residue pretreatment conditions and obtained a greater methane yield of 205.86 mL gvs^{-1} at 3% sodium hydroxide concentration, which was 53.99% more than the vinegar residue that was untreated [12, 79]. Similar studies were conducted with sodium hydroxide concentrations ranging from 0.3% (w/v) to 0.9% (w/v) throughout an extended treatment duration of up to three hours. It was noted that samples pretreated for one hour emitted much less biogas and methane after anaerobic digestion than those pretreated for two hours. However, it was noted that despite the samples being treated for 3 h, there was no appreciable increase in biogas generation. The ideal alkali pretreatment parameters for the production of maximum methane and biogas yield were found to be 0.6% (w/v) of NaOH for 2 h at 80 °C. To maximize the process's alkali concentration, an alkali pre-treatment step was then carried out solely at 80 °C for 2 h. The crystallinity and lignin content of the cellulose in silage and grass can be largely destroyed by the alkaline pretreatment, according to Wipa et al.'s evaluation. An enhancement in porosity and internal surface area, a deterioration of bonds between lignin and other polymers, a reduction in crystallinity and polymerization and structural swelling are all effects of alkali pretreatment. Thus, lignin can be eliminated chemically using an alkaline solution, producing cellulose that can be used as a substrate by methanogens. Grass biomass was pretreated with calcium hydroxide at various loading rates, and the results showed that methane production is improved when the lime content is higher. At 52 °C, the methane yield increased by 4% for a lime concentration of 0.8% and by 14% for a lime concentration of 9.2%.

The best outcome, however, was at 10 °C and a 7.5% loading rate, along with a 37% increase in methane output [19, 25, 80]. When Rabelo et al. investigated the effects of lime and alkaline peroxide on sugarcane bagasse, they discovered that lime loading of 0.04 g per kilogram per hour at 70 °C for 37 h produced the highest glucose production of 200 mg per kilogram. However, compared to peroxide pretreatment, lime pretreatment requires a prolonged residence time and higher temperatures [38, 81]. The digestion process is sped up by the pretreatment by eliminating lignin, according to an investigation on the use of lime to pretreat corn cob residue to increase biogas yield. The study also found that treated corn cob produced two times as much biogas as untreated corn cob [38, 82, 83].

According to the investigations, alkali pretreatment is a useful method for eliminating lignin and increases the exposure of carbohydrates for usage in the next operations. Alkali pretreatment is further preferable for lignocellulosic biomasses with a lower lignin content, which includes grassland crops as well as agricultural waste. This technique's recovery of added alkalis, which necessitates further research, is a significant drawback [38].

3.8 Acidic pretreatment

One of the most performed pretreatment processes for lignocellulosic biomass is acidic pretreatment. Based on the hemicellulose and cellulose's glycosidic bonds' acid sensitivity, lignocellulosic biomasses are subjected to acid pretreatment. Long hemicellulose and cellulose chains are broken down into sugar monomers by the hydronium ions resulting from the acid catalyst [38, 84]. Pretreatments with weak or strong acids, such as hydrochloric acid, sulfuric acid, or nitric acid, have been conducted at high temperatures. Regarding the pretreatment of lignocellulosic biomass, sulfuric (H_2SO_4) and hydrochloric (HCl) acids are the most utilized. These acids start the linking bond and solubilize the hemicellulose during this process. Both lignin and hemicellulose are soluble at higher acid concentrations, but acid recovery is necessary. To obtain the desired neutral pH, neutralization before anaerobic digestion is significant, as lignin is not solubilized but rather redistributed at low acid concentrations [34, 63, 85]. Acid pretreatment can be applied at moderate temperatures (100 °C) in the form of concentrated acids (30–70%) or else at remarkably high temperatures between 100 and 250 °C as diluted acids (0.1–10%). Although pretreatment with concentrated acids can significantly speed up the sugar conversion (by > 90%), most concentrated acids are highly poisonous and corrosive, necessitating considerable operational and maintenance expenditures. It is reported that diluted sulfuric acid (H_2SO_4) is often used to treat lignocellulosic biomass before usage. Prepare wild rice grass, also known as "Zizania latifolia" for enzymatic hydrolysis, the effects of pretreatment with alkalis and diluted acids were examined by Sahoo et al. The findings showed that 0.4% sulfuric acid (H_2SO_4) with 10% biomass loading released 163 mg of sugar per gram of biomass, but 1% NaOH treatment only produced 92 mg. This indicated that pretreatment with dilute acid is a more useful method than alkali pretreatment for this grass [38, 86]. Acid pretreatment is also influenced by the properties of lignocellulosic biomass. Studies on the impact of acidic pretreatment on various maize stem sections for bioethanol generation have been conducted. They saw that the cob had the maximum content of sugar, producing glucose (94.2%) and ethanol (24.0 gL^{-1}) after pre-treating the flower, stem, husk, cob. and leaf with 2% H_2SO_4 at a temperature of 121 °C for 60 min [38, 87]. Amnuaycheewa et al. investigated the effects of pre-treating rice straw with organic acids on enzymatic hydrolysis along with the biogas yield. They examined the effects of different acids such as citric ($C_6H_8O_7$), acetic ($C_2H_4O_2$), hydrochloric (HCl), and oxalic ($C_2H_2O_4$) while optimizing the pretreatment conditions. Pretreatment with oxalic acid under the ideal conditions of 5%, 30.86 min, and 135.91 °C produced the highest amount of sugar (213.4 mg/500 mg of pretreated sample) during enzymatic saccharification, according to the results [38, 88]. Concentrated acid is quite efficient at hydrolyzing cellulose, but the process is expensive and energy-intensive. A more cost-effective option for pre-treating lignocellulosic biomass is diluted acid, which can hydrolyse as much as one hundred percent of the hemicellulose to its component sugars. Furfural and hydroxymethylfurfural are examples of inhibitory byproducts that may be produced because of a strong acidic pretreatment. Thus, pretreatment with strong acids is avoided in favour of pretreatment with diluted acids combined with thermal techniques [33, 85, 89]. Figure 12 shows a modified schematic illustration of acidic pretreatment on wheat straw.

3.9 Organosolv (organic solvent) pretreatment

In this process, lignocellulosic biomass is pre-treated with organic solvents to break down the internal connections between hemicellulose and lignin, leaving behind a fairly pure residue of cellulose as illustrated in modified Fig. 13. Solubilization as well as delignification of hemicellulose throughout the process increase cellulose's pore capacity and surface area, which improves the availability of enzymatic hydrolysis and saccharification [38, 91]. To pretreat

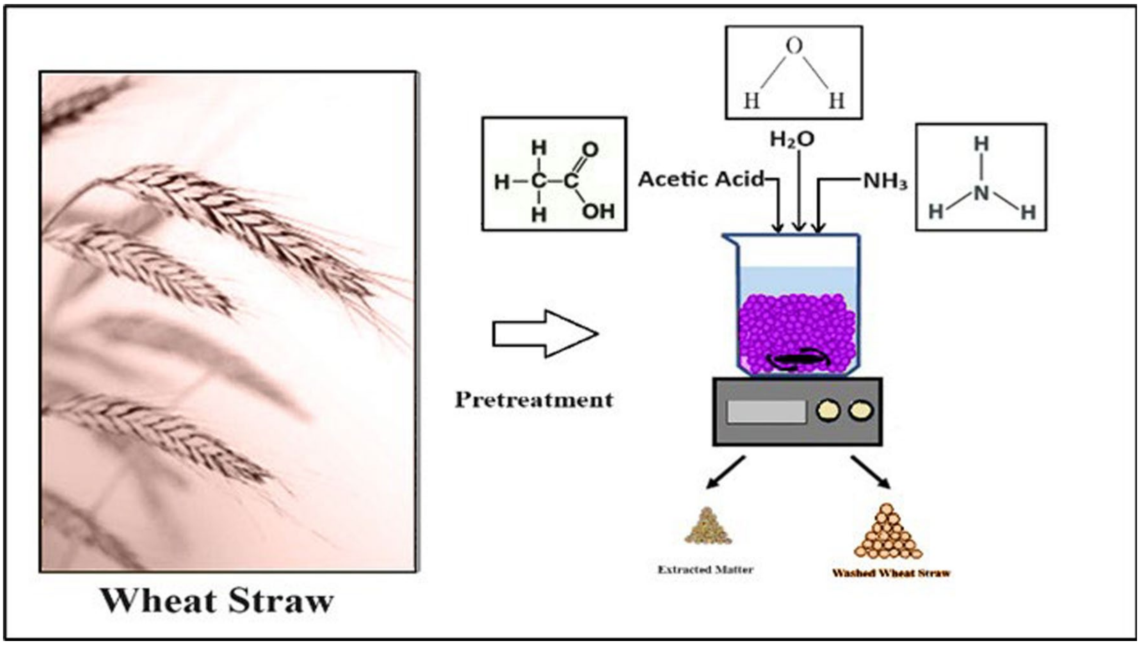
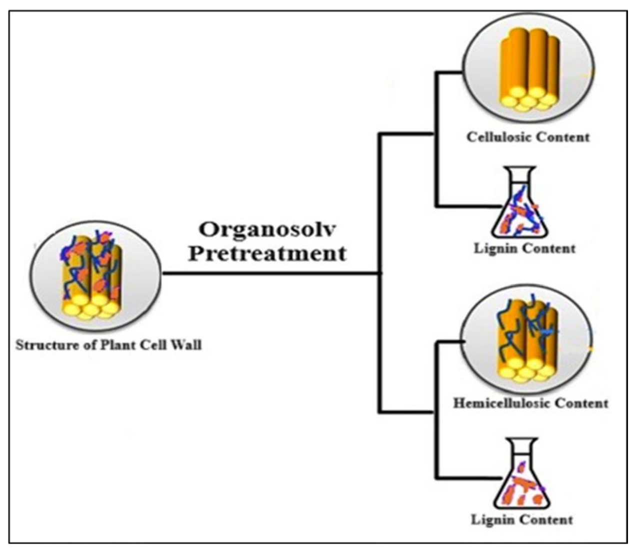


Fig. 12 Acidic Pretreatment on Wheat Straw (Reproduced with permission from [90]) copyright Elsevier BV

Fig. 13 Organosolv Pretreatment of Lignocellulosic Biomass



different lignocellulosic biomass, several organic solvents such as acetone, ethanol, organic acids, methanol, organic peracid, and ethylene glycol have been used. A catalyst is often added to the procedure to either lessen the pretreatment temperature or increase the delignification rate. As catalysts, typically, mineral acids (hydrochloric acid, phosphoric acid, and sulfuric acid), bases (ammonia, sodium hydroxide, and lime), and certain salts are employed [38, 92]. It's inherent benefits, such as the simplicity in solvents recovery by the process of distillation. The ability to recycle the solvents into the pretreatment process, and the utilization of lignin of good-quality separate from the process can be used as by-products in industries. This pretreatment presents itself as one newly developed pretreatment process.

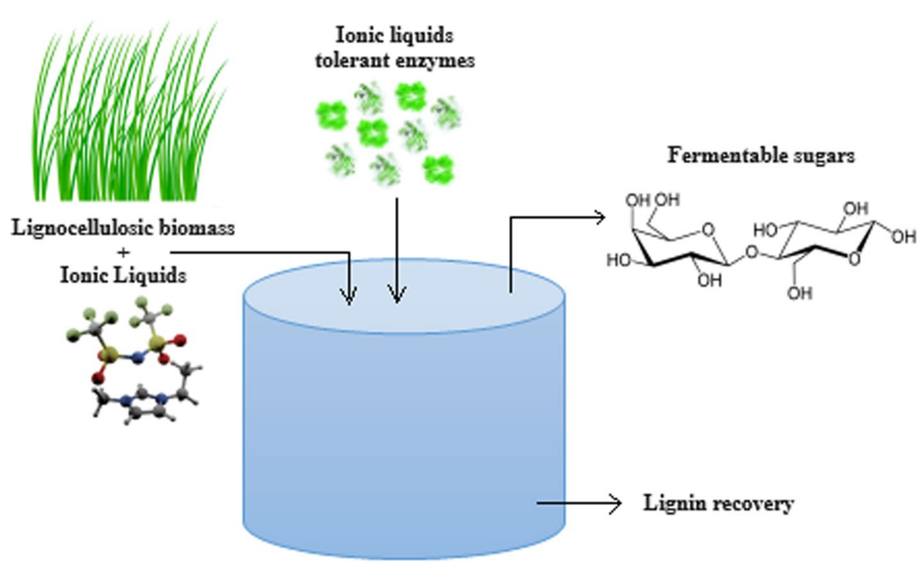
A few significant drawbacks to the organosolv pretreatment do exist, though. Since most organic solvents are expensive, it is necessary to recover them as much as possible, which requires a lot of energy. Additionally, because organic solvents are highly flammable and volatile, pretreatment must be performed under strict controls [38, 92].

3.10 Ionic liquids pretreatment

This pretreatment of lignocellulosic biomass has since gained popularity because of Swatloski et al.'s proposal to use ionic liquids as cellulose solvents. Ionic liquids are a relatively recent class of anions-based solvents and cations-based solvents having a melting point of < 100 °C [93]. Anions comprise both organic and inorganic ions, whereas cations are typically organic, including aliphatic ammonium, imidazolium, sulfonium, pyridinium, and alkylated phosphonium ions [38, 94]. Most ionic liquids can be recovered and used again. They have the impressive benefits of minimal vapor pressure, non-toxicity, non-volatility, large thermal and chemical stability, and most crucially, their cations and anions may be adjusted [95]. These explain why ionic liquids are often called as "green solvents". Several forms of ionic liquids are imidazolium-based ionic liquid ($[(C_3N_2)X_n]+$), pyrrolidinium-based ionic liquid ($[C_4N)X_n]+$, pyridinium-based ionic liquid ($[(C_5N)X_n]+$), phosphonium-based ionic liquid $[PX_4]+$, ammonium-based ionic liquid $[NX_4]+$, sulfonium-based ionic liquid $[SO_3]+$,etc. Imidazolium salts are most often employed in all the aforementioned ionic liquids [38, 96]. Investigations were conducted by Stanton et al. into how different imidazolium-based ionic liquids affected the properties and composition of microcrystalline cellulose and silk bio-composite films. These findings demonstrated that the anion composition of ionic liquids is closely related to the interaction between molecules in the films [97]. Using response surface methods, Smuga-Kogut et al. pretreated rye straw with 1-ethyl-3-methylimidazonium chloride and discovered that 2 h, a temperature of 120 °C, and 1 ml per kilogram of the dry matter rye straw produced the maximum sugar production. Pretreatment increased the yields of reducing sugars after enzymatic hydrolysis, three times more than untreated straw [38, 98]. The pretreatment of lignocellulosic compounds was also strongly influenced by the use of ionic liquids other than imidazolium salts, as demonstrated by the pretreatment of bagasse powder with choline acetate. As compared to composites made of the untreated bagasse powder, increasing the elastic moduli from 2.0 GPa to 2.6 GPa and the tensile strength from 35 to 40 MPa [99]. A modified schematic illustration of ionic liquid pretreatment on lignocellulosic biomass is shown in Fig. 14.

There is currently no research on Napier grass that has been pre-treated with ionic liquids. Despite having unique chemical characteristics, ionic liquids have two significant drawbacks: they are costly and hazardous to enzymes and microbes. For commercially viable large-scale applications, additional research on these features with inexpensive recovery technology and their toxicity to enzymes is still needed.

Fig. 14 Ionic Liquids Pretreatment of Lignocellulosic Biomass



3.11 Deep eutectic solvents pretreatment

In recent years, there has been a lot of interest in the pretreatment of lignocellulosic biomass utilizing deep eutectic solvents (DES). Two or three components that are regularly linked together by hydrogen bonds to produce a lower melting point eutectic combination than the sum of their melting points make up a novel class of ionic fluids known as DESs. The majority of the time, they are liquids at less than 100 °C [38, 100]. A quaternary ammonium salt is combined with a hydrogen bond donor or a metal salt to produce the majority of DESs that may form a complex with the quaternary ammonium salt's halide ion [38, 101]. Choline chloride (ChCl), a non-toxic, biodegradable and inexpensive organic salt, is combined with low-risk hydrogen bond donors such as urea, polyols, carboxylic acids, and glycerol in the majority of deep eutectic solvents. An investigation on the pretreatment of corn stover utilizing various deep eutectic solvents that had the same halide salt, ChCl, discovered that ChCl: Formic acid was the best solution for butanol fermentation. These findings revealed that ionic liquids are inferior to deep eutectic solvents with acidic hydrogen donors and can also boost lignin and hemicellulose removal more effectively [38, 100, 102]. As per authors best knowledge, no research has been conducted on Napier grass pre-treated with deep eutectic solvents.

3.12 Thermal pretreatment

The process of thermal pretreatment involves solubilizing the biomass in the pretreatment system by using heat [33]. Thermal pretreatment is useful in degrading lignin and hemicellulose as depicted in the modified Fig. 15. In general, there are three different types of thermal pretreatment: thermal treatment (temperature equal to 100 °C under atmospheric pressure), hydrothermal treatment (temperature greater than or equal to 100 °C with gradual pressure release after the treatment), and thermal treatment along with steam explosion (temperature greater than 100 °C with abrupt pressure drop after the pretreatment). The two most critical variables that significantly impact this pretreatment procedure are reaction time and temperature [33, 103]. Most of the time, laboratory-scale jacketed reactors, pressure cookers, or autoclaves are used for thermal pretreatment. Heat breaks up the hydrogen bonds in the crystalline complexes of lignin as well as cellulose, due to which the biomass grows and the surface area that is available increases. Most thermal pretreatments are done in laboratory-scale jacketed reactors, pressure cookers, or autoclaves. Chemical introduction can be combined with thermal pretreatment; typically, the effectiveness of the pretreatment is improved by the presence of an acid or an alkali. Another benefit of thermal pretreatment is the sanitization of the feedstock, which is conducted by using high temperatures to destroy microorganisms. This effect is especially helpful if the biomass remains stored and is not used immediately after the pretreatment [33, 72, 104, 105]. After 30 min of water vapour pretreatment, thermally pretreated Pennisetum hybrid had a rise in the yield of methane from 189.7 mL/g VS corresponding to raw material to 198.3 mL/g VS. Hemicellulose and lignin have both proven to be solubilized by thermal pretreatments, both under low and high pressure. There is no necessity for chemical addition in strict thermal pretreatment and this is a major benefit.

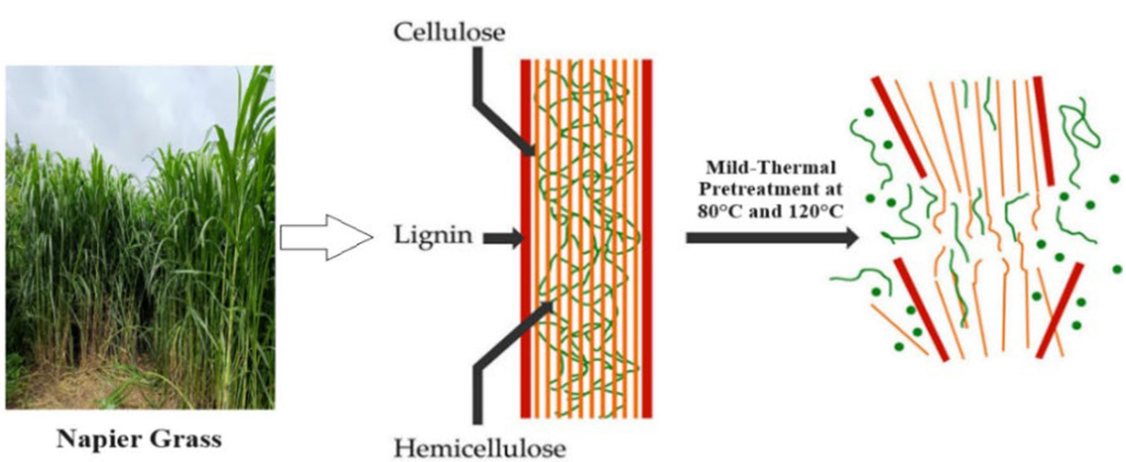


Fig. 15 Thermal Pretreatment of Napier Grass/ Rice Straw

The potential generation of phenolic chemicals, as well as hydroxymethyl furfural and furfural, that are decomposed products of sugars and lignin, respectively, is a disadvantage of pretreatments at high temperatures [33, 105].

3.13 Hydrothermal pretreatment

Chettaphong et al., performed hydrothermal pretreatment (HTP) in batch mode [33]. 200 g (dry weight) of processed Napier grass sample was combined with two litres of distilled water. The hydrothermal pretreatment was conducted in triplicates at 125, 150, 175 and 200 °C. Each experiment involved heating the high-pressure vessel to the desired temperature over a range of times, holding it there for 15 min, and then allowing it to cool to roughly 80 °C before opening the lid. After the pretreatment, a 200-mesh screen with a 0.09 mm aperture size was used for segregating the solid fractions and liquid fractions. As a control, a sample of dried Napier grass which was ground was immersed in distilled water with a solid–liquid ratio of 1:10 w/w at a room temperature of 25 ± 2 °C. Napier grass digestibility and methane output were greatly impacted by the pretreatment temperature. In this batch test, biomass that had been through hydrothermal pretreatment at 175 °C produced about 35% more methane than unpretreated biomass. Both inoculum evaluated for anaerobic digestion of biomass that was pretreated hydrothermally were hindered by the generation of considerable amounts of degradation products of biomass, especially furfural as well as hydroxymethyl furfural, that were produced during hydrothermal pretreatment of Napier grass at 200 °C. Significant amounts of soluble organics in hydrothermally processed slurry led to speedy acidification of the digester during semi-continuous anaerobic digestion operation, [34, 54, 106].

3.14 Physico-chemical pretreatment

3.14.1 Steam explosion

The most efficient and popular pretreatment technique, known as steam explosion, involves applying lignocellulosic biomass to a combination of mechanical and chemical stresses. This technique involves heating biomass to a temperature of 160–260 °C and subjecting it to a saturated steam at high pressure (0.69–4.83 MPa) to allow molecules of water to permeate into the substrate structure. The pressure is then dropped to allow the molecules of water to explode during their escape. When pressure is suddenly released, bulk lignocellulosic biomass explodes into broken strands as shown in Fig. 16. The method is also known as autohydrolysis because during the treatment, the breaking down of hemicellulose into monomers of xylose releases acetic acid, that catalyses the hydrolysis of hemicelluloses [107]. It was discovered that steam explosion required nearly 70% less energy to achieve the same reduction in particle size than typical mechanical methods [108]. When compared to the alternative pretreatment techniques, the steam explosion had many benefits, including reduced chemical use, no recycling expenses, 100% sugar recovery, great energy efficiency, and minimal environmental impact [109]. Several variables, including moisture content, residence duration, temperature of steam, and biomass size, have an impact on this process. Without using any chemicals, steam explosion can be applied directly to milled lignocellulosic biomass [38, 110]. To produce biogas,

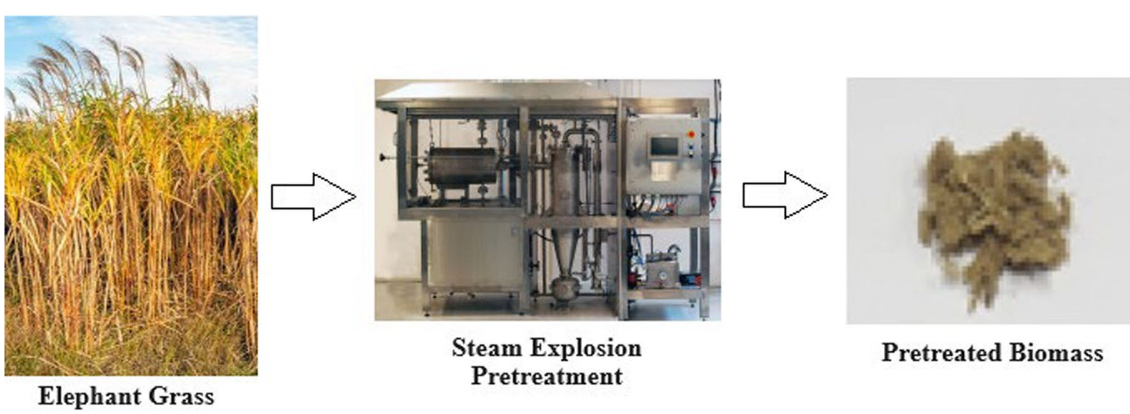


Fig. 16 Steam Explosion Pretreatment of Elephant Grass (Reproduced with permission from [113]) copyright Elsevier BV

steam explosion pretreatment at 140–220 °C was given to corn stover. The methane output was raised by 22% after the 2 min pretreatment at 160 °C, however, inhibitors were formed under the intense pretreatment conditions [111]. Using the response surface approach, Guerrero et al. examined the relationship between residence time and temperature of acid-impregnated steam explosion of the stem of the banana. A higher yield of glucose of 91% was obtained at the ideal conditions of 2.2% sulfuric acid (H_2SO_4) (v/v), 170 °C and, 5 min [38, 112].

3.14.2 CO_2 explosion

Supercritical CO_2 can mass transfer between a 'gas-like' and a 'liquid-like' solvating strength, which allows it to diffuse between spaces like gas and dissolve materials like liquid [114]. Higher-level structures containing lignin and hemicellulose are broken down by CO_2 molecules that enter biomass under intense pressure. The breakdown of hemicellulose is catalysed by carbonic acid, which is created when CO_2 is dissolved in water. This is one of the reasons why the pretreatment method does not effectively remove moisture from biomass. On the contrary, when compressed gas is released, it disrupts the biomass's dense matrix structure, making the cellulose fibres more accessible [38, 115]. According to a study, adding water and ethanol as co-solvents during the pretreatment step of a supercritical CO_2 explosion can considerably reduce lignin and improve the enzymatic breakdown of corn stover [116, 117]. Using supercritical CO_2, Benazzi et al. demonstrated a single-step method for hydrolysing bagasse from sugarcane and produced a 60% yield of fermentable sugars [118]. Under ideal conditions of a temperature of 170 °C and 20 MPa, the enzymatic hydrolysis of maize stalk and cob was enhanced by 13.4 and 75%, by combining pretreatment with ultrasonic energy and supercritical CO_2, respectively. Supercritical CO_2 is an appealing pretreatment option for lignocellulosic biomass because of its low cost, minimal environmental impact, non-flammability, lack of toxin production, and ease of recovery. However, a significant obstacle to its industrial application is the high cost of building an experimental setup that can withstand the extreme pressures of CO_2 pretreatment conditions [38, 119].

3.14.3 Liquid hot water

Pretreatment with liquid hot water (LHW) is quite identical to the steam explosion pretreatment, except for the fact that LHW utilizes water under pressure of up to 5 MPa and at 170–230 °C. In contrast to the steam explosion, quick pressure release is not necessary for LHW, and pressure is merely applied to stop water from evaporating. By releasing the acetyl groups from hemicellulose and eliminating lignin, LHW hydrolyses hemicellulose as well as increasing the visibility of the cellulose fibers [38, 120]. Using enzymatic hydrolysis at a temperature of 180 °C for half an hour, Hongdan et al. adjusted the process variables (residence time and temperature) in the LHW pretreatment of bagasse sugarcane and acquired 90% glucose recovery [121]. Another study that looked at the impact of the alkaline catalyst on rice straw pretreatment with LHW found that rice straw pretreated with LHW in the presence of sodium hydroxide (NaOH) had a noticeably higher glucose yield than the rice straw that was pretreated with liquid hot water when NaOH was not present. The second investigation on the impact of promoters of alkali and acid during the LHW pretreatment of rice straw reports that the introduction of these promoters alters the physical structure of the biomass that was pretreated, reducing the necessary temperature of the liquid hot water and boosting the

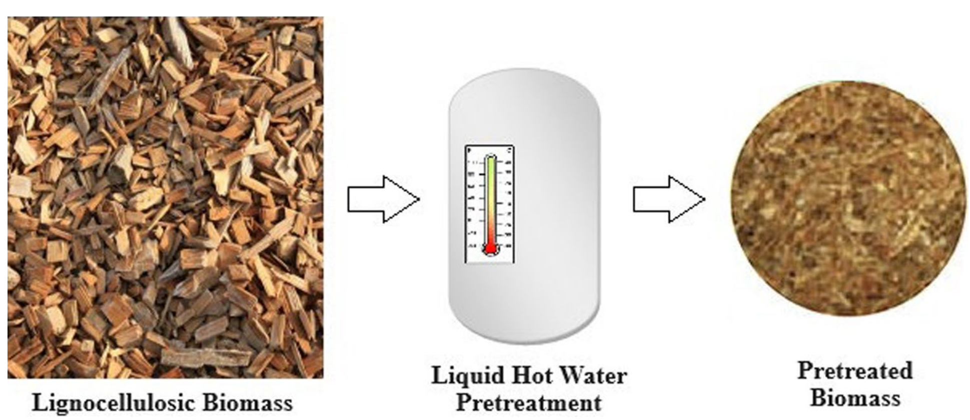


Fig. 17 Liquid Hot Water Pretreatment of Lignocellulosic Biomass (Reproduced with permission from [124]) copyright Elsevier BV

Fig. 18 Fungal Pretreatment of Energy & Industrial Crops (Reproduced with permission from [133]) copyright Elsevier BV

digestibility of enzymes [38, 122, 123]. Figure 17 shows the pretreated biomass after liquid hot water pretreatment on lignocellulosic biomass.

The pretreatment with LHW has several benefits because it doesn't need a catalyst or chemicals, nearly no harmful compounds are formed, and the solvent cost is minimal for large-scale applications. However, because there is a lot of water used, the process requires a lot of energy.

3.15 Biological pretreatment

Before enzymatic saccharification, lignocellulosic biomass can be treated using a low-cost, environmentally friendly method called biological pretreatment [125]. Microbes and enzymes are used in this pretreatment to break down chemical components and liberate fermentable sugars from the biomass. This method is promising because it uses less energy and does not cause the creation of inhibitors [33, 38, 126, 127]. Two primary processes, fungal and enzymatic activities, are the types of biological pretreatment for the production of biogas [128].

3.15.1 Fungi

Since they can break down cellulose, hemicelluloses, and lignin, fungi are ideally suited for use in these applications as depicted in Fig. 18. Fungi called white-rot, soft-rot, and brown-rot are employed to break down the lignin and hemicelluloses in lignocellulosic biomass [33, 38, 129]. While brown-rot fungi primarily target lignin, soft-rot fungi, and white-rot fungi target cellulose. White-rot fungi were proven to be more effective in breaking down lignocellulosic biomass. White-rot fungi, a subclass of basidiomycetes, are known to first degrade lignin while mostly leaving hemicellulose as well as cellulose unaltered. At the time of this pretreatment, biomass is injected with fungi at room temperature and left for many weeks. These biological pretreatment techniques have the benefits of low energy usage and chemical-free operation. There are downsides, though, like the fact that some cellulose and hemicelluloses break down with the lignin over the prolonged incubation period. Popular brown rot fungi employed in this procedure to pretreat biomass include *Laetiporus suiphureus*, *Gleophylium sepiarum*, and *Fomitopsis pinicola*. For pre-treating rice straw, white-rot fungi and brown-rot fungi were used, and the treatments resulted in an improvement in methane generation of 46% and 31%, respectively [34, 130]. Due to the higher yield of sugar integrated with enzymatic saccharification, white-rot fungi are mostly involved with biological pretreatment [38, 131]. While some white-rot fungi can specifically destroy polysaccharides while concurrently degrading lignin, this results in a breakdown of carbohydrates [132].

3.15.2 Enzyme

Another method of biological pretreatment is enzymatic hydrolysis. A larger methane output can be produced by preferentially breaking down the cellulose into sugars during the enzyme pretreatment. Though enzymes already exist in the digesters since they are created by microbes that aid in digestion, an enzyme or combination of enzymes could be introduced to speed up the decomposition of biomass. The most often employed enzymes for feedstock made from lignocellulosic materials are those that break down cellulose, hemicellulose, and starch. Since enzymes are considerably safer compounds than chemicals, enzymatic hydrolysis pretreatment can be used as a substitute to energy-intensive chemical, mechanical, and thermal methods of pretreatment. Biological pretreatments require a lot of space and time. Typically, they need up to 10 to 14 days of residence, after which a larger reactor volume is needed. If there is a large amount of resistant chemicals, biological pretreatment is capable of being used alone or in collaboration with other pretreatment techniques. Enzymatic degradation is significantly influenced by two groups of ligninolytic enzymes: phenol oxidase laccase (Lac) and peroxidases, which include manganese peroxidase (MnP), lignin peroxidase (LiP), and versatile peroxidase (VP) [19, 33, 134]. There haven't been many investigations done using ligninolytic enzymes as a pretreatment approach before AD. It has been used to extract the enzymes peroxidase, manganese, laccase, and lignin peroxidase from white-rot fungi. These ligninolytic enzymes use mediators, a low molecular weight reactive chemical, to attack and destroy the lignin because they are too large to work directly on the lignin. The subsequent AD of degraded biofibres benefited from the pretreatment of laccase along with steam explosion. When those biofibres were only pretreated with laccase, however, no enhancement was observed. The grass was pretreated with the ligninolytic fungus *Phanerochaete flavido-alba* before it was subjected to anaerobic digestion. Even though the pretreatment decreased every single lignocellulosic fraction, including lignin, cellulose, and hemicellulose, biogas generation was equivalent for inoculated and non-inoculated substrates. However, the authors did not explain this finding. For wood fibre, the same treatment is efficient [34, 135].

3.15.3 Microbial consortium

Wen et al., pretreated Napier grass with three microbial consortia, MC1, WSD-5 and XDC-2 for varying lengths of time: 3, 7, 13, 17, and 21 days. The thermophilic bacterium *Clostridium straminisolvens,* which largely breaks down cellulose, makes up MC1. Coprinus cinereus is the most prevalent fungus and *Ochrobactrum sp*. is the most prevalent bacteria in the fungal and bacterial populations found in WSD-5. Mesophilic bacteria from genera Pseudomonas, Clostridium, Alcaligenes, and Bacteroides made up the majority of XDC-2. With the potential exception of pretreatment on the 21st day with the XDC-2 consortia and MC1, the biogas production for pretreated grass was greater than that for untreated samples. Maximum methane yields were 1.39, 1.49, and 1.32 times higher for pretreatment samples of MC1, WSD-5, and XDC-2 than for untreated samples [33, 136].

3.16 Combined pretreatment

Solubilize particulate organic matter, various pretreatment techniques use distinct processes. So, pretreatment techniques in combination have also been investigated to increase biogas output even more and speed up the kinetics of the anaerobic digestion process [137, 138].

3.17 Thermal and chemical pretreatment (thermo-chemical pretreatment)

The AD of organic components of waste from municipalities that had been pretreated with a combination of microwaves of high temperature and pretreatment with hydrogen peroxide was studied by Shahriari et al. [139]. Numerous studies on the use of microwaves to treat biomass, for example, palm biomass, have been published [63, 140, 141]. The standard approach with microwave-assisted chemical-based pretreatment of empty fruit bunches was compared by Akhbar et al. and they discovered that the latter resulted in a higher lignin removal rate (up to 72%). The fractionation of biomass and biofibre may be aided by the introduction of chemicals like acid or alkaline during the microwave pretreatment process [63, 142].

Table 2 Comparison of some of the pretreatment techniques on Napier grass in literature

Pretreatment	Process	Feedstock	Composition (after pretreatment)	Results (gas production)	Variation	References
Physical	Chopping	25:25:100 (cow dung: grass: water)	Volatile solid reduction up to 50%	524.3 Lit	31.37% methane content	[11]
	H_2SO_4 microwave C/N = 3.42, pH = 7	Hydrolysate Napier Grass Slaughterhouse Wastewater	Lignin content reduced from 32.04% to 22.9%, Cellulose content reduced from 34.25% to 29.9% Hemicellulose content reduced from 17.36% to 13.0%	299.69 ml CH_4/L	2.11 times higher methane yield	[14]
Chemical	2% NaOH	Napier Grass	Lignin content 24.11% Cellulose content 40.05% Hemicellulose content 26.23%	220 ml/day	45.61% increase in methane yield	[1]
	0.6% NaOH, 90 °C, 2 h	Napier Grass Anaerobic Sludge Inoculum	Total Solid 93.87% Volatile Solids 83.50% Total Organic carbon 43.80%	0.158 m^3 CH_4/kg TS	70% increase in methane yield	[12]
	1% NaOH, 24 h	Napier Grass	Total Solid 99867 mg/lit Volatile Solids 81700 mg/lit	179.38 L/kg VS	9.33% increase in biogas yield	[25]
	Native Potash pH = 6.8, 31 °C	Napier Grass Microorganism	Total Solid 31.60% Volatile Solids 93.70% Ash Content 2.00%	850 ml/kg VS	64% methane content	[28]
Thermal	Boiled 100 °C, 1 h	Napier Grass	Total Solid 79983 mg/lit Volatile Solids 69917 mg/lit	155.91 L/kg VS	4.9% decrease in biogas yield	[25]
	HTP- 175 °C	Napier Grass	Volatile Solids 96.90% Cellulose 48.50% Hemicellulose 11.3% Lignin 14.7%	248.20 ml CH_4/gm VS	35% higher methane yield	[106]
Biological	Microbial Consortium: MC1 (21 day treatment)	Napier Grass	Lignin degradation 37.50% Cellulose degradation 19.90% Hemicellulose degradation 29.9%	259 ml/gm VS	39% increase in methane yield	[33, 136]
	Microbial Consortium: WSD-5 (21 day treatment)	Napier Grass	Lignin degradation 35.50% Cellulose degradation 22.0% Hemicellulose degradation 40.0%	279 ml/gm VS	49% increase in methane yield	[33, 136]
	Microbial Consortium: XDC-2 (21 day treatment)	Napier Grass	Lignin degradation 31.50% Cellulose degradation 17.70% Hemicellulose degradation 38.80%	247 ml/gm VS	32% increase in methane yield	[33, 136]

3.18 Thermal and mechanical pretreatment (thermo-mechanical pretreatment)

Reduced biomass particle size as well as increased surface area are achieved through mechanical pretreatment in combination with microwave pretreatment. Wett et al. investigated the breakdown of sludge that has been processed for 1 h at 19–21 bar of pressure and temperatures of 160–180 °C. At steady state, the combined pretreatment enhanced biogas output by 75%, and by improving the sludge's dewatering properties, the disposal cost decreased by 25%. However, enhanced protein hydrolysis resulted in a 64% rise in the reactor's ammonia content [143].

Table 2 summarizes various pretreatment methods for Napier grass and other feedstocks, highlighting their effects on composition and biogas production. Physical pretreatments like chopping and microwave-assisted hydrolysis reduce volatile solids by up to 50% and lignin, cellulose, and hemicellulose contents significantly, enhancing methane yield by up to 2.11 times. Chemical pretreatments using NaOH (0.6–2%) or native potash effectively degrade lignin (up to 24.11%) and improve methane yields by 45.61–70%, with NaOH pretreatment achieving a notable increase in volatile solid degradation and methane content. Thermal methods like boiling and hydrothermal processing (HTP) at 175 °C further reduce volatile solids and enhance cellulose accessibility, yielding 35% higher methane in some cases. Biological treatments involving microbial consortia degrade lignin (31.50–37.50%) and hemicellulose (29.9–40.0%), leading to biogas yields of 247–279 ml/gm VS and methane increases of up to 49%. Overall, the table demonstrates the effectiveness of combined pretreatments in optimizing biogas production, with chemical and biological methods showing the highest improvements in methane yield and feedstock digestibility.

The study does not address regional and climatic variations in Napier grass composition, which significantly influence pretreatment outcomes. Furthermore, while biological pretreatments are discussed, the paper does not incorporate recent advancements in genetic engineering or enzyme-based approaches that hold promise for sustainable and cost-effective solutions. Despite its valuable insights, the paper would benefit from addressing these practical considerations to make its findings more relevant for large-scale, real-world applications in biogas production.

4 Interpretations

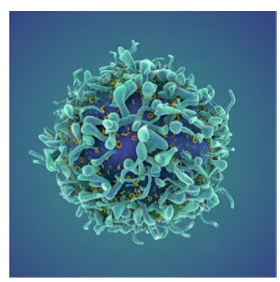
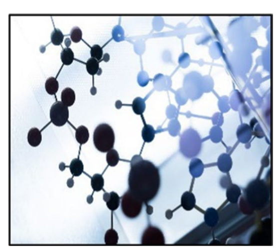
Since there is limited information about the pretreatment of grass for the production of biogas that is currently accessible, comparing approaches is difficult because most reported studies used various pretreatment settings on various grass species. For the process to be profitable, the energy balance of pretreatment methods must be positive. The most crucial consideration when choosing a pre-treatment method is its economic efficiency. Pretreatment methods that demand less energy typically have less of an influence on the output of methane and biogas than methods that need more energy Table 3. Advantages and Disadvantages of Pretreatment Methods on Lignocellulosic Biomass.

It was noted from the literature that physical pretreatment on Napier grass has so far increased methane content by about 31.37%. By adopting chemical pretreatment, the methane yield enhancements ranged from 9 to 70%, and through thermal pretreatment on Napier grass, the methane yield improvements were 35%. Whereas, when Napier grass was subjected to biological pretreatment, methane yield improvements of 30–50% were possible when using various microbial consortiums and the ensiling procedure.

5 Challenges

The primary determinant of the appropriate pre-treatment approach is economic efficiency. In general, pre-treatment methods requiring less energy have less of an effect on the output of methane and biogas than methods requiring more energy. In contrast, the cultivation area that is accessible figures out the potential of bioenergy sources based on energy crops, and in growth scenarios, the amount of bioenergy produced from energy crops increases over time. In the medium and long term, the energy crop sector has great potential, especially if innovative solutions could find to balance land use such as efficiently managing land resources and addressing competing needs for meeting future energy demands. There is growing concern that as biofuel production expands, food costs may rise in parallel with fuel prices as food and biofuel production from energy crops struggle for the same agricultural lands. This would have the effect of making food and the resources needed to manufacture it more costly, possibly out of reach for the underprivileged. A wide range of environmental problems may also result from the production and processing of

Table 3 Advantages and Disadvantages of Pretreatment Methods on Lignocellulosic Biomass

Pretreatment		Reference
Physical Pretreatment Advantages: -Enhances the surface area -Biomass is easier to manage -Increases the reactor's efficiency Disadvantages: -High demand of energy -High expense of maintenance -Limited enzyme digestibility -Sensitive to inert materials		[23, 33]
Chemical Pretreatment Advantages: -Easy operation -Low demand of energy -Solubilization of hemicellulose -Lower requirements of pressure and temperature Disadvantages: -Chemicals expenses -Environmental pollution -Potential inhibitory compounds -Need for a corrosion-resistant reactor and piping -Neutralization before downstream digestion		[33, 59, 144, 145]
Thermal Pretreatment Advantages: -High solubilization of biomass -High increase in methane yield Disadvantages: -Energy-consuming -Expanded biomass -Potential recalcitrant compounds -High-pressure reactor with a specific design		[33, 144, 146, 147]
Biological Pretreatment Advantages: -Low demand of energy -No inhibitory compounds -Simple equipment -Simple operating conditions -No pollution -No need for the chemical recovery and treatment Disadvantages: -Requires efficient bacteria -Slow and less effective process -Huge area required -Enzyme expenses -Longer pretreatment time -Loss of carbohydrates -Low downstream yields		[146, 147]
Physico-chemical Pretreatment Advantages: -No need for size reduction -Higher sugar recovery -Increase solubilization of lignin and hemicellulose -Production of hemicellulose and glucose is higher Disadvantages: -Energy consumption is high -High cost -High water demand -Suitable for low lignin content biomass		[144, 146, 147]

bioenergy sources. These include loss of biodiversity, harmful particle emissions, overfertilization, and acidification of agricultural soil, among other additional burdens. Since the use of energy crops and bioenergy has not yet been shown to be economically feasible, political structuring will be necessary before these technologies can be expanded. In the nexus of energy, environmental, agricultural, scientific, and economic policy, the goal of increasing the use of agricultural products as renewable energy sources thus poses a significant question and challenge. A cost–benefit analysis of different pretreatment methods for Napier grass highlights the economic and practical considerations of each approach. Physical methods, such as chopping and microwave-assisted hydrolysis, involve moderate equipment costs but can be energy-intensive, with microwave treatments enhancing methane yield by up to 2.11 times, making them viable for small-to-medium setups with access to renewable energy. Chemical pretreatments, like NaOH or native potash, effectively degrade lignin and boost methane yields by up to 70%, but their high chemical and wastewater handling costs make them suitable for industrial-scale operations with robust budgets. Thermal methods, including boiling and hydrothermal processing (HTP), achieve significant cellulose degradation and a 35% increase in methane production, but their high energy demands limit cost-effectiveness unless low-cost heat sources are available. Biological pretreatments, using microbial consortia, are environmentally friendly and relatively low-cost, with methane yield improvements up to 49%, but their long treatment times (21 days) may challenge scalability for industrial use. For small-scale setups, biological pretreatment offers the best balance of cost and sustainability, while medium-scale operations could benefit from combining physical and biological methods. Large-scale facilities may prefer chemical pretreatments, complemented by thermal methods powered by renewable energy, to maximize efficiency and methane yield. Incorporating energy recovery and life cycle assessments is essential to fully evaluate the economic and environmental feasibility of these methods.

6 Conclusion and future perspectives

Numerous pretreatment techniques have been proposed recently to facilitate the deconstruction of lignocellulosic biomass. The choice of the most practical pretreatment method relies on the kind of lignocellulosic biomass being used because lignin, cellulose, and hemicellulose composition differ. The main pretreatment methods and how they affect the separation of intricate components of the different lignocellulosic sources are covered in this paper. This paper reviews current knowledge on pretreatment techniques on lignocellulosic biomass as well as pretreatment techniques used to enhance biogas from an energy crop (Napier grass). The study seen that most pretreatment methods can increase the biogas production from grass by various percentages of about 50%. Also, through the alkaline chemical pretreatment on Napier grass, methane yield enhancements were up to 70% and thus this method can be an effective alternative for improving the yield of biogas and methane from the lignocellulosic biomass in full scale & pilot scale bio-methanation projects.

Despite the pretreatment method's drawbacks, more research is required to get around them and develop more effective solutions that can be scaled up and used in industry. A common drawback of all procedures is their high energy requirements. A comprehensive analysis is necessary to determine the optimal utilization of each appliance for the respective approach. Further research is also needed on hydrolysis and partial acidification at a controlled pH, followed by improved screening methods, which can drastically improve the biogas yield from grass. New substances and enzymes can be researched for chemical and biological treatments to improve efficiency while lowering toxicity and pre-treatment time. Multi-objective optimization can be used to specify the pretreatment parameters to create higher biogas output with a positive energy balance.

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Declarations

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