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BIOMASS PRETREATMENT AS A KEY PROCESS IN BIOETHANOL PRODUCTIONS: A REVIEW

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Abstract. Solid wastes like lignocellulosic materials have proven to be of immense benefit to the production of bioethanol and have given a headway towards the deviation from the traditional use of fossil fuel which is has been a long-time primary source of fuel and energy globally. The transformation of lignocellulosic wastes into bioethanol is of importance to the environment. The recalcitrant nature of this substance, owing to the presence of lignin which serves as a deterrent, making it hard to access cellulose and hemicellulose, which are later converted to bioethanol, has raised much concern for researchers. Various strategies for feed preparation for overcoming this problem have been identified by researchers in the literature, including chemical, physical, and physiochemical approaches with enzymes. This review aims to bring together recent advances made by researchers in different pretreatment methods in optimizing the production of bioethanol. The advantages, disadvantages and the specific conditions for these pretreatment methods are also discussed in this review. Embedded in this review is also a report of the usage of some of these feed preparation strategies and the amount of bioethanol that was obtained by each process using different feedstock.

Keywords: *Bio-alcohols, biofuels, biorefinery, environment, wastes, cellulose, pollution.*

Rezumat. Deșeurile solide, cum ar fi materialele lignocelulozice, s-au dovedit a fi de un beneficiu imens pentru producția de bioetanol și au făcut progrese către abaterea de la utilizarea tradițională a combustibilului fosil, care a fost o sursă primară de combustibil și energie la nivel global. Transformarea deșeurilor lignocelulozice în bioetanol este importantă pentru mediu. Natura recalcitrantă a acestor substanțe, din cauza prezenței ligninei, care servește ca un factor de descurajare, îngreunând accesul la celuloză și hemiceluloză, care sunt ulterior transformate în bioetanol, a stârnit multă îngrijorare pentru cercetători. Cercetătorii din literatură au identificat diverse strategii de preparare a hranei pentru a depăși această problemă, inclusiv abordări chimice, fizice și fizico-chimice, enzimatice. Această revizuire își propune să reunească progresele recente realizate de

cercetători în diferite metode de pretratare pentru optimizarea producției de bioetanol. Avantajele, dezavantajele şi condiţiile specifice pentru aceste metode de pretratare sunt, de asemenea, discutate în această recenzie. În această revizuire este inclus şi un raport despre utilizarea unora dintre aceste strategii de preparare a furajelor şi cantitatea de bioetanol care a fost obţinută prin fiecare proces folosind diferite materii prime.

Cuvinte cheie: *Bio-alcooli, biocombustibili, biorafinărie, mediu, deşeuri, celuloză, poluare.*

Introduction

The use of fossil fuels has proven to be unfriendly to the biosphere. The unfriendly nature has resulted into increased greenhouse gases in the atmosphere and an increase in the depletion of the ozone layer. Despite the depleting amount of fossil fuel, there is an increasing demand for fuel due to the increase in the number of industries and human activities dependent on energy [1]. Hence, there is a need to look for an alternative source of energy that is renewable and eco-friendly, which biofuels tend to offer. To save the world and the economy, a more eco-friendly source of fuel that is readily available at a cheaper rate needs to be provided. This subject has been the centre of energy research lately [2].

The use of biofuels as an alternative renewable and clean source of energy has attracted the attention of researchers all over the globe. Lignocellulosic biomass (examples of the biomass is in Figure 1 has proven to be promising. They include but are not limited to corn straw, sugarcane bagasse, cassava, rice straw. These parts of the plants are non-digestible by humans, which makes it better as there would be no competition for food. The use of this lignocellulosic feedstock also serves to recycle the waste, which is environmentally friendly [3 – 6]. Also, lignocellulosic materials are not available for bio-digestion due to the presence of residue (lignin) in lignocellulosic material, which limits fuel conversion and leads to low yield [7]. Hence there is a need for pretreatment of these materials to obtain a high yield of fuels.

Figure 1. Some Agro-wastes that could be used in bioethanol productions [8].

This paper focuses on reviewing the impact of the different pretreatment methods employed in the literature in bioethanol production using Nigeria biomass resources. This would aid in unveiling the most significant method that better promote the production of bioethanol in developing nations like Nigeria and to reveal areas where further studies are needed for the realization of biorefinery feasibility in developing nations.

Concept of Pretreatment

Lignocellulosic feedstocks are made up of a network of Cellulose, Hemicellulose and Lignin. Though promising, lignocellulosic feedstock offers a significant challenge due to recalcitrance. They are resistant to chemical and biological breakdowns making it hard for biofuel production. Due to this, pretreatment becomes very vital.
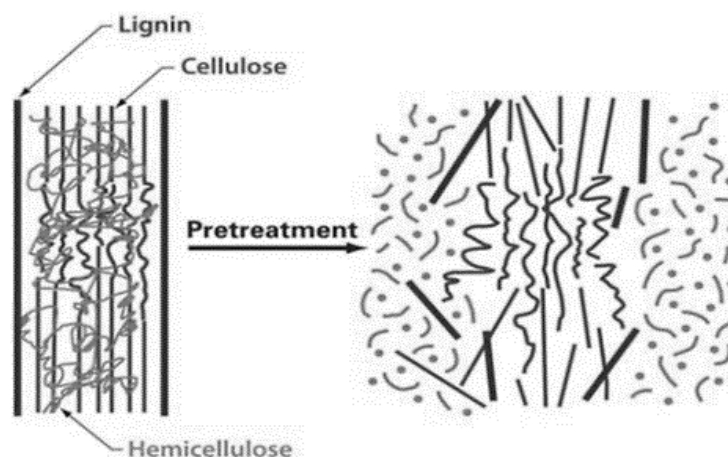

Figure 2. Effect of pretreatment on lignocellulosic biomass to liberate
cellulose and hemicellulose [9].

Pretreatment is defined as the process that clears away both the physical and chemical barriers that make feedstock recalcitrant and make it susceptible to enzymatic hydrolysis [10 - 11].

The concept of pretreatment is aimed at making feedstocks susceptible to further treatment by making cellulose and hemicellulose more accessible. This could be achieved through various means. Pretreatment could break down solid feedstock or even reduce the degree of crystallization of cellulose.

Lignin is extracted owing to its phenolic nature, which thereby makes the feedstock more digestible [12]. Figure 2 shows the effect of pretreatment on lignocellulosic biomass to liberate cellulose and hemicellulose.

From Figure 2 above, it can be observed that pretreatment is a critical step. It is important to find pretreatment methods that can give a high yield of bioethanol and, at the same time, be economical and eco-friendly.

Biomass Pretreatment Significances to the Production of Bioethanol in a Biorefinery

The chemical composition of feedstock is such that if not pretreated, bioethanol production would not be efficient.

Pretreatment increases the efficiency and efficacy of bioethanol production. This is necessary because the cost of production of bioethanol is dependent on the cost-effective measure or method of pretreatment as it forms a very vital part of the production process.

Pretreatment breaks down the strong association within the cell wall by bringing about physical, chemical, and biological changes to it. Because different feedstocks have a varied abundance of Cellulose, Hemicellulose and Lignin, their outcome differs. A suitable pretreatment method is one that is cost-effective, require minimal energy to run, does not denature cellulose and hemicellulose and does not produce by-products that inhibit the activity of microorganisms that are responsible for hydrolysis and fermentation [12].

With the aim of creating a very suitable method of pretreatment, several methods have been developed, each with its pros and cons. They can be categorized into physical pretreatment, mechanical pretreatment, chemical pretreatment, biological pretreatment and combined physical and chemical pretreatment.

Physical Pretreatment Methods

Physical pretreatment is the first line of action in the pretreatment process (Julie et al., 2018), which usually prepares feedstock for further treatment. This kind of pretreatment is sometimes referred to as mechanical pretreatment, which has been recorded to be the most widely used form of pretreatment [13]. In addition, this method breaks the biomass into smaller particles amiable by increasing the surface area, dissociating tissue, and disrupting the cell wall, which thereby aids in speeding up the rate of enzymatic hydrolysis. It also decreases the crystallization of biomass and reduces the degree of polymerization. Examples of these methods are milling, ultrasonication, microwave, and mechanical extrusion [2].

Milling

This method aids to reduce both the particle size and crystallinity of feedstock. It can reduce the size of biomass up to 0.2 mm. This type of physical pretreatment offers a significant advantage being physical. It does not produce inhibitors like furfural and hydroxyl methyl furfural (HMF) and therefore gives a high yield of bioethanol. However, its high energy demand makes it an uneconomical process on an industrial scale [13].

There are five different milling methods. Examples of such are ball, colloidal, hammer, vibrio-energy, and two-roll milling (pictorial view of milling forms in Figure 3). The choice of the milling process to employ is strongly dependent on the nature of the feedstock. However, it has been reported that the colloidal milling suit perfectly for wet feedstock, while hammer milling will suit best for dry feedstock like wastepaper. Although, literature has indicated that ball milling can be applicable for both the dry and wet feedstock. Milling enhances enzymatic hydrolysis [11] as it reduces the size of particles. This makes it easier for cellulose enzymes as cellulose is exposed.

A survey of the literature indicated that many studies have considered the exploration of a wide range of biomass resources, some of which includes cassava peels [15 – 17], cassava starch [18 – 23], sugarcane bagasse [21], [24 – 28], bark, corncob, stalk, husk, sweet potato peels [24], cassava pulp [20], banana pseudostem [29], and other solid agricultural residues [23]. Moreover, the studies indicated that the use of this pretreatment (milling) in the production of bioethanol yields 52.00 % (from cassava flours), 97.40 % (from cassava peels), 5.85 % (from cassava starch), 26.74 % (sugarcane bagasse, bark, corncob, stalk, and husk), 23.80 % (cassava peels), 47.99 % (sweet potato peels), 82.40 % (cassava pulp), 16.00 % (cassava), 9.03 % (sugarcane bagasse),67.00 % (sugarcane), 31 % (sweet potato peel), 14.46 g/cm^3 (41.00%) (cassava peel), 0.31 g/g (31.00 %) (cassava), 84.00 % (banana pseudostem), and 35.00 % (cassava effluent and solid agricultural residue), based on the report from the literature.
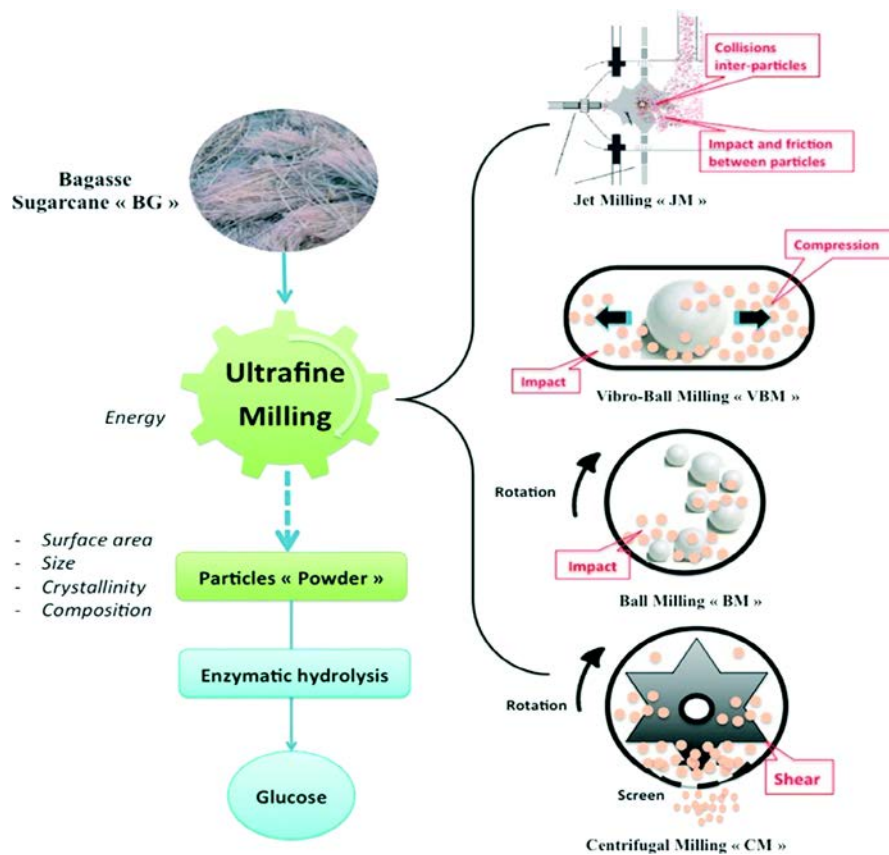
Figure 3. A pictorial display of the variety of milling biomass [14].

Ultra-sonication

Cavitation through high-frequency ultrasonic waves forms the working principle of this method. These approach forces lead to the separation of the complex network of the polysaccharide components of the feedstock, and a graphical illustration of the process is presented in Figure 4.

It also enhances the extraction of desired compounds like cellulose, hemicellulose, and lignin. This technique is carried out at 20 kHz and 200 kW for 10 minutes [13]. The works of Zhang et al. [30] employed the use of sweeping frequency ultrasonic pretreatment approach in the processing of okra into 16.7% (0.564 mg/mg) okra pectin content. Ultrasound-assisted microwave extraction (UAME) approach was similarly deployed by Sengar et al. [31] in the extraction of pectin from tomato processing waste, where 73.33% of extracted pectin yield was reported.
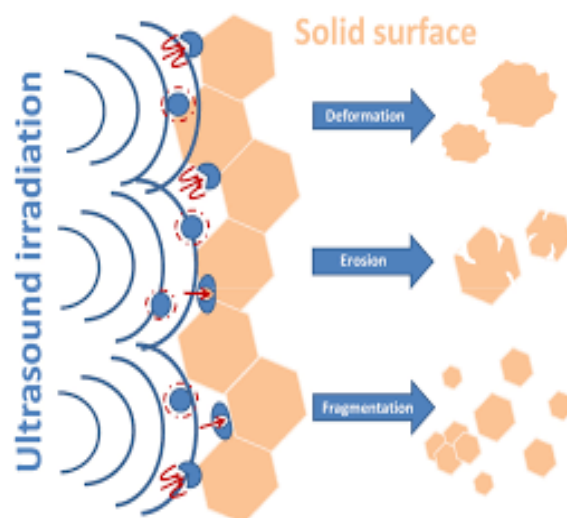

Figure 4. A demonstration of how the ultrasonic radiation impact the biomass in pretreating the materials [32].

Microwave

This method is commonly used due to its advantage. It has minimal energy requirement, short processing time, less inhibitor generation. This is carried out in closed containers as a high temperature is needed for optimal functioning. Penetration, reflection, and absorbance are associated with a microwave. It is from these attributes that the system for microwave pretreatment is built [2]. In microwave, the lignocellulosic structure is disrupted through di-electric polarization. The polarization causes a molecular collision, thereby generating heat energy that results in the disruption [33]. Examples of the studies that deployed the use of the microwave pretreatment method in the processing of calabash pulp juice [33], cassava [34], and cocoyam peel [35], where it was reported to have yielded 21.6 %, 20.49 %, 6g/100mL (9.40 %), and 50g/L (5.00 %), respectively.

Mechanical extrusion.

Extrusion is a process where feedstock is passed through a screw assembly called an extruder. The combined effect of high temperature and shear force caused by the blades in the barrel causes the disruption of the lignocellulosic structure [36]. Some of the advantages of this method include adaptability to modifications, the integrity of products being preserved, and a controllable environment. Moreover, there exist two types of extruders which are usually referred to as single and twin-screw extruders [2]. To enhance the activity of this process, chemicals like urea, Thiourea and sodium hydroxide can be added to the biomass [13], [37]. Other cases of studies that deployed the use of mechanical pretreatment/extrusion in the processing of sugarcane [38] and pineapple peels [39] to yield 9.20 cl/L (72.70 %) and 5.82 %v/v, respectively.

Chemical Pretreatment Methods

In practice, chemical pretreatment often comes next to physical pretreatment. The two main chemical pretreatments are acid and alkaline pretreatment. However, there are other methods like Ionic liquid and organic solvent pretreatment.

Alkali pretreatment

In this type of chemical pretreatment, alkali is added to the feedstock. This method causes swelling, which decreases the crystallinity and increases the specific area of the biomass. This further leads to the unfolding of lignin from polysaccharide moiety. Through this method, lignin is dissolved, and polysaccharides are exposed for further hydrolysis [12].

Compared to mechanical methods, the energy requirement of alkali pretreatment is low. However, it takes a lot of time to complete. It takes hours or days. The hydroxides of ammonium, sodium, calcium, and potassium are the commonly used base for alkali pretreatment. The setup for alkali pretreatment is a heating element, temperature controller, a tank, water jacket, CO_2 scrubber, manifold for water and air, pump, tray, and frame. A lime slurry is first prepared with a desired base and water. It is then sprayed of the feedstock and stored for hours or days [2]. The dissociation of lignin and the removal of acetyl groups, and ironic acid substitution in hemicellulose confer a great advantage to alkaline pretreatment. However, the difficulty in the recovery of the reagents used in this technique has proven to be disadvantageous and needs to be looked into. It is also observed that feedstocks with high levels of lignin are not favoured by this method [36].

A further survey of works reported in the literature on the deployment of alkali pretreatment method for the production of bioethanol from varying biomass like rice husk,

elephant grass, corn stover, rice straw, rice husk, groundnut shell, and a lot more [40 – 44]. Findings from the survey of the literature indicated that most of the studies that deploy alkaline pretreatment approach often use sodium hydroxide in the processing of the biomass into sugar and bioethanol, where it was reported to yield 6.25 % [Rice husk] [40], 78.00 % [Elephant grass stem] [41], 11.30 % [Corn stover] [42], 49.50 % [Rice straw] [43], 132.7 mg/mL [Cassaval peels] [45], 81 % [Sugarcan bagasse] [4], and 24.14 % [Groundnuts shell] [44].

Acid pretreatment

As the name implies, acids are used for the pretreatment of feedstock. A significant challenge to this method is the production of the inhibitory substance. Furfural, hydroxyl methyl furfural (HMF) and phenolic acid are produced in large amounts. However, measures have been developed to take care of that [36]. Acid pretreatment is of two types; they vary on the basis of duration and temperature. The first one has a short duration of 1 - 5 min but a high temperature of 180°C. The second has a high timeframe of 20 - 30 min and a temperature as low as 120°C [2]. Both organic and inorganic acids find use in this pretreatment. Inorganic acids like sulfuric, nitric, and hydrochloric acids are used in both their concentrated and diluted forms. However, concentrated acids are very corrosive and demand extra safety measures, which makes the process more expensive. The use of concentrated acid is reported to yield a high number of inhibitory compounds. Pretreatment with dilute acids is used on an industrial scale as it is suitably cost-effective with little or no number of inhibitory compounds. Organic acids like Oxalic acid, maleic acid is normally used in acid pretreatment. Maleic acid is reported to have more glucose and xylose yield [2].

A Survey of the literature on the pretreatment of biomass indicated studies had proven the viability of deploying acid treatment methods in the processing of sugarcane bagasse, rice husk, banana skin/peels, maize stalks, corncob, orange peels, cassava peels, cowpea shells, yam peels, and a lot more [5], [46 – 48]. The deployment of hydrochloric acid [for sawdust] [46], Sulphuric acid [for cassava peels] [45], sulphuric acid [for rice husk] (Mustafa et al., 2019), sulphuric acid [for rice stalk] [50], pretreatment yields 43.9%, 190.04 mg/mL, 25.35 %, and 5.06 % sugar yield, respectively.

Ionic liquids

Ionic liquids are liquids containing cations or anions. These liquids are known to be thermally stable, nontoxic, have high polarity, low melting point and less vapour pressure. The relationship between ionic liquid and feedstock is primarily affected by temperature, cations and anions and the duration of pretreatment [2]. Cations and anions both play significant roles in solubilizing cellulose and lignin. They do so by disrupting the intermolecular hydrogen bond between cellulose and the lignin network by competing for the same hydrogen bonds. While the cations are strictly organic in nature, the anions are both organic and inorganic. Imidazolium and pyridinium are examples of organic cations [36]. Another advantage of the ionic liquid is its recovery during the process. However, the use of this pretreatment is not compatible with cellulose activity [2].

Organic solvent

Organic solvents like acetone, methanol, ethylene glycol and ethanol are used in the pretreatment of feedstock. A catalyst aids this method of pretreatment. Some acids, bases and salts are added to the medium to either fasten delignification or regulate the temperature. In research conducted by Sidiras and Loanna [3], a cellulose concentration of

72% w/w and a lignin concentration of 59% w/w was obtained using acetone and sulfuric acid as catalyst.

This pretreatment type is widely used in extracting lignin from biomass. Lignin is a valuable substance of industrial use. The disruption of the bond between lignin and cellulose causes an increase in the surface area of cellulose. This makes it readily accessible to enzymes. As a result, a higher yield of bioethanol is produced. The recovery and reuse of solvents is an added advantage to this pretreatment. However, the chemicals are volatile and expensive. A high amount of energy is needed to recover and recycle the organic solvents, and they also are flammable [36]. The use of lime (organic catalyst) employed in the pretreatment of the sugarcane juice at temperature (35 C) and 5 hours yielded 19.30 % bioethanol [51]. Ethanoic acid and methanol pretreatment were employed in the processing of cassava peels [45] and cassava peels [52] into 51.50 mg/mL sugar and 331.79 mg/L glucose (including 45.3 mg/L rhamnoses and 46.52 mg/L xylose) yield.

Combined Chemical-mechanical Pretreatment Methods

This method combines both physical and chemical methods. It is also known as the physicochemical method. Examples of such kinds of this method include ammonia fibre explosion, steam explosion, and carbon dioxide explosion.

Steam explosion method

The steam explosion method is known for its little chemical use and low energy consumption. In this method, is exposed to high pressure saturated steam, after which pressure is reduced. This method results in an explosive decompression leading to the disruption of lignin and cellulose degradation. The steam is injected at a temperature of 160-260 0C and 0.69 and 4.83 MPa. The pressure is provided but for a few minutes. Carbon dioxide and sulfuric acid are used to decrease the time and formation of inhibitory substances and increase the efficiency of removing hemicellulose. Moisture content, particle size, temperature are factors that affect steam explosion. This technique is not very effective for softwood. [2]. One of the works that deployed the use of this approach includes Gayalai-Korpos et al. [53] whose studies employed the approach to pretreat sweet sorghum bagasse from which 58% cellulose were obtained resulting to a rise in the bioethanol yield.

Ammonia fibre explosion (AFEX)

Ammonia fibre expansion (AFEX) is known for being a thermochemical pretreatment that utilizes volatile ammonia as the main reactant for cellulosic biomass pretreatment [54]. The feedstock is treated with liquid ammonia at high temperatures and pressure. The pressure is then reduced. This process is similar to steam explosion. Owing to the volatile nature of ammonia, it is easily recovered and recycled. The process is usually carried out at a temperature of 90°C for about 30 min. Some of the works that deployed the use of the ammonia fibre explosion in the processing of biomass into bioethanol fuels include the report of the Bals et al. [55] that transforms switchgrass to bioethanol. Similarly, Feher et al. [56] deployed the use of aqueos ammonia pretreatment approach in their study to pretreat corn fibre which later yielded 79% bioethanol via the process.

Carbon dioxide explosion

This method is similar to steam and ammonia explosion and shares similar principles. High-pressure CO_2 reacts to carbonic acid, thereby improving the hydrolysis rate. The yield

gotten from this process is lower than that of steam and ammonia explosion [2]. It was further reported that CO_2 reacts to carbonic acid, thereby improving the hydrolysis rate. The yield is gotten from this process. Examples of studies that employed the use of this approach in their studies include Kim and Hong (2001), which employs the use of aspen and southern yellow pine; Puri and Mamers [58] employs the processing of wheat straw, bagasse, and Eucalyptus regnans woodchips; and Toscan et al. [59] employ the processing of wheat straw, bagasse, and Eucalyptus regnans woodchips; and many other feedstocks in the production of bioethanol.

Conclusions

The shift from fossil fuel to renewable sources of energy like biofuels is not without its challenges. The competition for food between the industries and humans has led to the use of solid waste and other cellulosic feedstocks. This approach helps recycle waste but is not sufficient in producing biofuel due to recalcitrance.

Pretreatment of feedstock is a way of optimizing the production of bioethanol from the feedstock. Different forms of pretreatment exist. They range from physical to chemical with varying strength. The most effective pretreatment type is the one that is cost-effective and gives a high yield of bioethanol.

More work needs to be done in order to optimize the production of bioethanol so that it can compete in production cost with its fossil fuel counterpart. We recommend that researchers consistently report their pretreatment type with the conditions used. And further studies are encouraged to consider the techno-economic evaluation and SWOT (Strength, Weakness, Opportunity, and Threats) analysis of the various biomass pretreatment methods reviewed in this report.

Conflict of Interest

The authors declare no conflict of interest.

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