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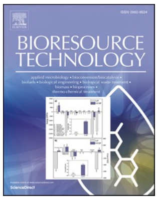

Review

Sustainable valorization of sugarcane residues: Efficient deconstruction strategies for fuels and chemicals production

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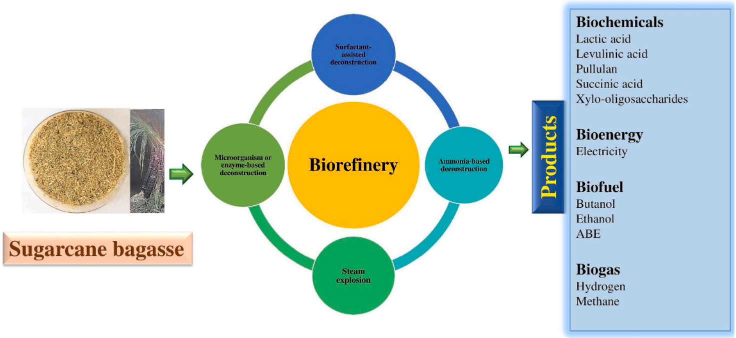
HIGHLIGHTS

- Chemical characterization of sugarcane bagasse is reviewed.
- Various deconstruction strategies for the synthesis of bioproducts are discussed.
- The review covers the major biofuels and biochemicals produced from sugarcane residues.

GRAPHICAL ABSTRACT



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ABSTRACT

The global climate crisis and the ongoing increase in fossil-based fuels have led to an alternative solution of using biomass for fuel production. Sugarcane bagasse (SCB) is an agricultural residue with a global production of more than 100 million metric tons and it has various applications in a biorefinery concept. This review brings forth the

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composition, life cycle assessment, and various pretreatments for the deconstruction techniques of SCB for the production of valuable products. The ongoing research in the production of biofuels, biogas, and electricity utilizing the bagasse was elucidated. SCB is used in the production of carboxymethyl cellulose, pigment, lactic acid, levulinic acid, and xylooligosaccharides and it has prospective in meeting the demand for global energy and environmental sustainability.

1. Introduction

The Intergovernmental Panel on Climate Change (IPCC) in their sixth assessment proceedings reported that compared to 1990, the year 2019 showed an increase in greenhouse gas (GHG) by about 55 % and 50 % from non-residential and residential buildings, respectively. The primary source of GHG carbon dioxide is fossil fuels which are used for the production of petroleum. In 2010, 14 % of global GHG was contributed by transportation (US EPA). To overcome this, electric powdered vehicles and biofuel are currently the best choices. Biomass (Algae, crops, and residues) can be used systematically using the biorefinery approach to compete for future demands such as food and fuels (Feed and Materials, 2007). Certain biomass dumped in the environment diminishes the quality of groundwater and the atmosphere. A 1.3 billion tons of solid waste is generated in a year, and by 2025, it is expected to reach 2.2 billion tons. In 2025, the cost of solid waste management will be $375 billion (Clark and Deswarte, 2015).

Limiting global warming, and fossil fuel use and establishing a sustainable environment, a biorefinery concept using the agricultural biomass or residues was implemented. It offers improved economic opportunities by exploiting various biomasses for the production of biofuels, biopower, and bioproducts such as antibiotics, pigments, and phenolic compounds (Menon and Rao, 2012). Biorefinery is a stepwise process with pre-treatment as the commencing step (Ferreira et al., 2016). Certain difficulties in the biorefinery concept are recognition among the already existing fossil-based market, recovery of the bioproduct, and composition of feedstock (Katakojwala and Mohan, 2021).

SCB is a heterogeneous feedstock used in biorefinery. It is a byproduct obtained after extracting juice from sugarcane (Martinez-Hernandez et al., 2018). 280 kg of SCB are generated from 1000 kg of sugarcane and globally 100 million tons of SCB are produced per year (Saelee et al., 2016). According to Heneigal et al, the top three SCB-producing countries are Brazil (31.16 metric tons), India (15.14 metric tons), and China (6.54 metric tons) (Heniegal et al., 2020). 10 % of the world's SCB are used by the paper industry and in India, 20 % of the paper is produced from SCB (Solomon, 2014). Recently, Ajala et al. gave a magnificent review on SCB as a feedstock for bioenergy production (Ajala et al., 2021).

Life Cycle Assessment (LCA) technique was employed to analyze the environmental impact of SCB electricity generation in Brazil. The impact was analyzed for the generation and transmission of electricity and the main impact identified was photochemical ozone and human toxicity (Lopes Silva et al., 2014). LCA was analyzed for the production of lactic acid (LA) from SCB in India. For the production of 1 kg of LA, the climate change was 4.62 kg CO_2eq, and the use of NaOH for pretreatment of the substrate causes a major environmental impact (Munagala et al., 2021). Amezcua-allieri et al. explored LCA for the generation of bioenergy from SCB in Mexico. They compared the environmental and economic impact of using SCB and fuel oil for the production of electricity. Later they found that the cost per unit for the production of energy using SCB and fuel oil are 5.5 USD/GJ and 14 USD/GJ, respectively. Similarly, the environmental impact index was more for fuel oil (2528 PEI/GJ for SCB and 20,200 PEI/GJ for fuel oil) and it can be concluded that SCB can be a good source for bioenergy production (Amezcua-Allieri et al., 2019). The present review focuses on the major pretreatments, deconstruction strategies, and a variety of bioproducts obtained from sugarcane biorefinery for ensuing potential advancements in future biorefinery.

2. Characteristics of sugarcane bagasse as a feedstock for fuels and chemical production

To find the optimal pretreatment method for turning biomass into fermentable sugars, enormous attempts utilizing numerous methodologies have been designed. SCB is a viable resource for the conversion to biofuels and biopower, and it is attracting substantial interest in biorefining applications, given sustainability concerns and the need to maximize the exploitation of bio resources. The biotechnological opportunities of SCB have been investigated for the production of a variety of chemicals, metabolites, alkaloids, and enzymes during the fermentation process, in the pulp and paper industry, and in biorefineries for the production of bioethanol, methane, and butanol. SCB is a waste product that is one of the most common remnants of the sugar and alcohol industries. SCB has unique benefits over other agro-based wastes such as maize stover and wheat straw due to its reduced ash level; as a result, it is a preferred choice for biorefining (Zhang et al., 2018b).

The composition of SCB makes it an attractive feedstock for the development of second-generation biofuels. SCB, like other lignocellulosic materials, has a limited nutritional value, which eliminates worries regarding the food vs fuel conflict. Sugarcane is a grass that belongs to the *Poaceae* family. The tissues of these plants are made up of cells with Type II cell walls, which means the cellulose fibers are encased in a glucurono-*arabino*-xylan matrix with a high hydroxycinnamate content (Gupta et al., 2022). Secondary cell walls comprising cellulose, hemicellulose (mostly glucuronoarabinoxylan), and lignin are formed between the primary cell wall and the plasma membrane as the sugarcane matures (Nasution et al., 2022). SCB is made up of holocellulose, which is made up of crystalline cellulose with intervening amorphous regions collected into microfibril bundles contained in an amorphous matrix of hemicellulose and additional cross-linked lignin. Pectin, extractives, and ashes are also present in small proportions in the biomass composition. Lignin works as a physical barrier, reducing cellulose and hemicellulose biodegradability (Nwajiaku et al., 2018).

Furthermore, SCB is a plentiful, renewable, and cost-effective feedstock, making it a versatile starting material for a variety of processes, including fermentation, biocatalysis, and chemo-catalysis, to produce value-added products such as biofuels, biopolymers, and other useful chemicals. SCB could be a feasible alternative substrate for bioethanol production, and biofuel for transportation could be a long-term solution for creating clean energy and reducing greenhouse gas emissions (Singh et al., 2022).

3. Major pretreatment parameters affecting fuels and chemicals production

Bioethanol production from SCB is composed of five stages such a biomass pretreatment, cellulose hydrolysis, fermentation, separation, and effluent treatment. SCB, which is made up of lignocellulosic components, has a more complicated intrinsic structure and lacks monosaccharides that microorganisms can access during the fermentation process. As a result, before introducing hydrolytic enzymes, a cost-effective pretreatment is required to break down the material by physicochemical processes. Prior to enzymatic saccharification of lignocellulose, pretreatment is the most important technique in a conversion scenario. Several pretreatment procedures have been developed to help with cellulose hydrolysis, including physical, chemical, physicochemical, and biological pretreatments (Rodríguez-Machín et al., 2022).

Chemical pretreatment procedures include acid, alkali, ozone, and solvent-based treatments, while physical preparation includes comminution and hydrothermolysis. Chemical pretreatments are essential and are typically carried out above the solvent's boiling point. Steam explosion and ammonia fiber explosion are examples of physiochemical treatments. Microorganisms and/or microbial enzyme systems are used in biological treatments. The fundamental purpose of these pretreatments is to break down the complex structure of SCB and its major components, such as celluloses, hemicelluloses, and lignin, into simple sugars that can be used in bioconversion processes (Thite and Nerurkar, 2019). Pretreatment enhances the accessibility of biomass components to the lignocellulolytic enzymes, resulting in maximum product recovery and improved economics of lignocellulosic bio refineries. The pretreatment processes should enhance the relative proportion of cellulose by reducing the hemicellulose and lignin contents for better conversion of cellulose during enzymatic hydrolysis. The most difficult aspects of pretreatment are determining the feed stock's composition and devising the optimum pretreatment approach for the feedstock in question. As a result, different pretreatment procedures must be used based on the biomass and the product of interest. The cost of operating a downstream unit can be reduced with appropriate pretreatment. The goal of effective lignocellulosic biomass pretreatment should be to boost the available surface area and decrystallize cellulose, partial depolymerization of cellulose and hemicellulose, solubilization of hemicelluloses and/or lignin, modification of the lignin structure, maximizes the enzymatic digestibility of the pretreated material, minimize sugar loss, and reduce capital and operating costs. In addition, a successful pretreatment must preserve the pentose fractions, prevent the need to reduce the size of biomass particles, and inhibit the development of toxic components that hinder fermentative microbe growth (Alokika et al., 2021).

4. Deconstruction strategies for fuels and chemicals production

Cellulose, hemicellulose, and lignin are all components of lignocellulosic plant cell walls. Lignocellulolytic enzymes are required for the biochemical conversion of cellulose (or hemicellulose) to mono-, di-, and oligo-saccharides. Microbes could ferment the sugars generated during hydrolysis to produce the desired product. Due to inherent biomass recalcitrance, complete and cost-effective conversion of lignocellulose biomass to their constituent saccharides remains a critical problem (Bu et al., 2021).

Efficient biomass deconstruction to sugars, lignin intermediates, and other monomers is central to achieving cost-competitive and sustainable biofuel production. The production of carbohydrates from SCB in a form that can be easily metabolized by fermenting microbes is the focus of those working on biomass deconstruction methods. The cellulose part has been the primary focus of most deconstruction methods because it offers glucose, which is a convenient substrate for fermentation (Torgbo et al., 2021). The lignin–hemicellulose shield must be broken apart to gain access to the cellulose, which is normally done chemically at high temperatures and pressures. In a separate saccharification phase, the exposed cellulose is hydrolyzed. Chemicals or enzymes can catalyze the saccharification process. The exploitation of pentoses, especially xylose, will enhance the economics of biofuel generation (Naik et al., 2021).

Because the solvents employed and reaction conditions have an impact on all downstream unit operations, the deconstruction method is frequently the driving element in the overall process architecture. SCB must be deconstructed by physical–chemical processes before being enzymatically hydrolyzed by lignocellulolytic enzymes to overcome its resistant nature. In addition, when compared to a single fermentation product, the recovery of non-fermentable components as co-products, particularly lignin, will open up new revenue streams. A wide range of physical, chemical, and combination approaches are now being researched to achieve these goals (Banu Jamaldheen et al., 2022). After enzymatic saccharification, proper pretreatment procedures can enhance the quantities of fermentable sugars, enhancing the overall efficiency of the process. Major deconstruction strategies used for the pretreatment of SCB are depicted in Fig. 1.

4.1. *Surfactant-assisted dilute acid deconstruction*

To make the process commercially feasible, appropriate pretreatment technologies must be developed and their optimization for various process parameters must be refined to reduce lignin hindrance and modify crystallinity, which improves enzymatic saccharification. Traditional pretreatment approaches, such as dilute acid and dilute alkali, release lignin into the solution during pretreatment, but they generate hydrophobic compounds that cyclically precipitate back on the biomass surface, obstructing enzymatic access to cellulose and hemicelluloses (Rodríguez-Machín et al., 2022). Dilute acid pretreatment could promote enzymatic saccharification by dissolving hemicellulose. Unfortunately, they could result in irreversible hemicellulose degradation and the generation of inhibitors such as acetic acid, formic acid, and furfural. Hereafter, preventing these hydrophobic molecules from redepositing on pretreated biomass will result in a higher yield of fermentable sugars (Zhuang et al., 2022). Adding non-ionic surfactants to the pretreatment process has recently been demonstrated to increase delignification and enzyme hydrolysis (Wang et al., 2018b; Zhang et al., 2018a).

Surfactants possess both hydrophobic and hydrophilic characteristics, capable to lower the surface tension between two phases during pretreatment. They can also extract hydrophobic compounds by forming an emulsion, rendering them unavailable for redeposition on the biomass surface, making it more hydrophilic. Surfactants have been found to bind to lignin and prevent enzyme adsorption which is ineffective. Surfactant-assisted pretreatment has been shown to be effective in enzymatic saccharification and ethanol fermentation in several studies. Surfactants can improve enzymatic digestibility by altering the substrate structure to make it more accessible to enzymes, stabilizing enzymes to avoid denaturation, reducing enzyme non-productive binding to lignin and other cellulase-active molecules, and rising positive interactions between substrates and enzymes (Nasirpour and Mousavi, 2021; Uma Maheswari et al., 2020). Rhamnolipids, bovine serum albumin, Tween 20, Tween 80, amino acids, PEG 4000, Triton X-100, 1-hexadecylsulfonic acid sodium salt, and *N*-hexadecyl trimethyl ammonium chloride are often used surfactants with the benefits in mild conditions and green surroundings. They have been proven to be efficient in lowering the quantity of lignin left in the pretreated material and speeding up enzymatic hydrolysis by enhancing cellulose accessibility (Kim et al., 2007). Nasirpour et al. proved the efficacy of surfactant inclusion during SCB pretreatment. The results showed that adding Tween 80 and PEG 4000 to SCB improves its enzymatic digestibility (Nasirpour et al., 2014).

The hybrid pretreatment procedure using surfactant and dilute acid was tried because it is recognized that surfactant can improve lignin solubility and thus removal. Sindhu et al. demonstrated the efficacy of surfactant-assisted acid pretreatment in enhancing the susceptibility of sugar cane tops to enzymatic hydrolysis. In terms of fermentable sugar yield, the study showed that Triton X-100-assisted acid pretreatment is superior to either dilute acid or dilute alkali in eliminating lignin and hemicelluloses (Sindhu et al., 2012). The effectiveness of surface-aided acid pretreatment for lignin removal was shown by Pandey et al. The study revealed that surface-aided acid pretreatment boosted ethanol fermentation efficiency and made bioethanol production more cost-effective (Pandey and Negi, 2015) Tong et al. investigated the impact of a fatty alcohol polyoxyethylene ether-based nonionic surfactant in dilute phosphoric acid pretreatment for fermentable sugar production and discovered that it had a significant impact on conquering biomass recalcitrance and promoting cellulose digestion, indicating that it has a wide range of applications in the biomass conversion process (Tong et al., 2022). According to a study reported by Baral et al., combining PEG 600 with the acid pretreatment with SCB doubled glucose release

(Baral et al., 2020).

4.2. Ammonia-based deconstruction

By cleaving the C—O—C linkages and other ether and ester bonds found in the lignin–carbohydrate complex, dilute ammonia pretreatment has demonstrated considerable efficacy in the delignification of grassy feedstocks. Dilute ammonia is more successful than acid or hydrothermal methods at removing lignin, with limited cellulose and hemicellulose solubilization. Because aqueous ammonia has better selectivity than other alkaline salts, it is non-polluting, non-corrosive, recoverable, and extensively used, it is a good pretreatment additive. Furthermore, ammonia-based pretreatment increases cellulose surface area, breaks crystalline structures, and results in better delignification with the little hazardous chemical generation, resulting in increased enzyme performance and microbial activity. Research showed the ammonia pretreatment strategy, results in cleaner production of products like sugars, biofuels, and sustainable waste management (Kim et al., 2008).

It was discovered that soaking in aqueous ammonia pretreatments at optimal temperature and dosage conditions led to improved lignin removal and increased sugar yields. It is an effective pretreatment method for recovering high pentoses and hexoses in biomass, resulting in greater sugar release and improved ethanol fermentation. Shi et al. developed a pretreatment based on aqueous ammonia and glycerol mixture that also focuses on ammonia recovery. SCB immersed in an aqueous ammonia-glycerol mixture resulted in significant lignin removal and fermentable sugar production. Simultaneously, roughly a third of the ammonia in the pretreatment liquid was recovered using distillation (Shi et al., 2019). Cao et al. utilized surfactants in combination with ammonium hydroxide for the pretreatment of SCB. Results indicated that the combined effect of non-ionic surfactants with ammonia during pretreatment enhanced lignin removal and retained most cellulose (Cao and Aita, 2013).

For fermentable sugar production, Ramadoss and Muthukumar, 2014, used ultrasound-aide ammonia pretreatment of SCB. The synergistic action of ultrasound and ammonia reduces byproduct generation, improves lignin removal, and promotes cellulose recovery (Ramadoss and Muthukumar, 2014). Yu et al. developed an SCB pretreatment approach using liquid hot water and aqueous ammonia. This method enhances lignin removal and enzymatic digestibility of glucan and xylan, as well as glucose recovery (Yu et al., 2013). Tsutsui et al. investigated the influence of ammonia pretreatment on SCB xylan recovery efficiency. The study found that pretreatment with anhydrous ammonia would be a good way to get SCB ready for enzymatic hydrolysis to extract xylooligosaccharides (Tsutsui et al., 2020). To improve the enzymatic saccharification and bioethanol production of SCB, Zeng et al. developed an aqueous ammonia-sodium sulfite pretreatment. Pretreatment solutions including aqueous ammonia and sodium sulfite had a synergistic effect on delignification and enzymatic saccharification (Zeng et al., 2021). Bala et al. reported that ammonia treatment dramatically reduced lignin and phenolic compounds while also increasing the saccharification of SCB. This is owing to ammonia's selectivity and its capability to ammonolysis lignin while also solubilizing hemicellulose during prolonged retention durations (Bala and Singh, 2019).

In the ammonia fiber expansion method, concentrated ammonia is utilized as a catalyst. This approach involves contacting the biomass with liquid anhydrous ammonia for a short time at low temperatures and pressures in the presence of different water loadings. The ammonia fiber expansion technique uses far less ammonia and water than those of soaking in aqueous ammonia or ammonia recycled percolation pretreatments (Rijal et al., 2014). Mokomele et al. reported a study focused on the co-digestion of ammonia fiber expansion treated SCB along with dairy cow manure. Here, ammonia fiber expansion increased the biomass nitrogen content and accelerated the biodegradability of SCB, resulting in higher methane yield and increased biogas methane content (Mokomele et al., 2019).

The low moisture anhydrous ammonia technique uses anhydrous ammonia to reduce chemical and water input with no inhibitor production during pretreatment. It does not necessitate any additional water washing procedures, making downstream processing more easily. The three major processes in this technique are ammoniation, pretreatment at the desired temperature/pressure, and evaporation/remaining ammonia removal. It allows simultaneous saccharification and co-fermentation of the glucan and xylan fractions, leading to higher ethanol production (Yoo et al., 2014). Utilizing SuperPro software, Rosentrater assessed the economic and environmental consequences of low-moisture anhydrous ammonia pretreatment for ethanol production from SCB (Rosentrater (2021)).

The extractive ammonia pretreatment method enables fractionation-based bio refining by using the liquid anhydrous ammonia at the high liquid to solid loadings. It allows for the selective extraction of lignin from lignocellulosic biomass and the conversion of resistant native cellulose I to cellulose III, a highly digestible allomorph. When compared to the ammonia fiber expansion approach, the cell wall alterations during this pretreatment contribute to enzyme reductions during saccharification (Da Costa Sousa et al., 2016). At low water loading, this process is carried out in a high-pressure stainless steel reactor. This process has three stages: ammonia loading and reaction, biomass extraction, and product recovery during solvent removal. This method preserves the functionalities of extracted lignin and has tremendous promise for chemical upgrading in biorefineries to value-added aromatic/phenolic compounds and lignin-derived fuels (Zhao et al., 2020).

4.3. Ionosolv deconstruction

For decades, scientists have been interested in employing ionic liquids to pretreat lignocellulose. Ionic liquids are salts made up of anions and cations of organic compounds that are loosely structured, resulting in a melting point below 100 °C, great thermal stability and polarity, and low vapor pressure. These solvents are effective delignification catalysts for bagasse. The degree of anion charge delocalization and the cation structure has a substantial impact on the physical, biological, and chemical properties of ionic liquids. Temperature, cations and anions, and pretreatment time all influence the interactions between ionic liquids and biomass.

Among many ionic solvents, 1-ethyl-3-methylimidazolium acetate is the most commonly employed for SCB because it is particularly good at dissolving cellulose. Polymerization and crystallinity were reduced as a result of it. Bian et al. examined the impact of ionic liquid pretreatment on cellulose enzymatic hydrolysis. Pretreatment resulted in effective cellulose disruption for subsequent enzyme hydrolysis, as shown by a high glucose conversion yield (Bian et al., 2014). 1-allyl-3-methylimidazolium chloride (Wang et al., 2018a), 1-butyl-3-methylimidazolium acetate (Kimon et al., 2011), 1,3-dimethylimidazolium dimethyl phosphate (Bahrani et al., 2015), and 1-butyl-3-methylimidazolium chloride (Chen et al., 2013) are some of the other solvents utilized for bagasse processing. Hashmi et al. reported a significant reduction in lignin content, decreased cellulose crystallinity, and improved glucan and xylan digestibility of SCB, after the 1-butyl-3-methylimidazolium acetate pretreatment (Hashmi et al., 2017). The efficiency of 1-ethyl-3-methylimidazolium acetate pretreatment in the delignification of SCB was established by Saha et al. the study also discovered that the pretreatment reduces bagasse crystallinity and increases reducing sugar production (Saha et al., 2018). Kimon et al. studied the dissolution of bagasse with 1-butyl-3-methylimidazolium chloride at high temperatures as a pretreatment process for saccharification and fermentation-based biofuel production and discovered that complete dissolution is not required for maximum saccharification yields at 150 °C (Kimon et al., 2011). These ionic solutions may remove up to 60 % of lignin from SCB while also lowering cellulose crystallinity. Nasipour et al.

investigated the efficacy of surfactant-assisted ionic liquid pretreatment of SCB for enzymatic hydrolysis. The efficiency of surfactant addition before ionic liquid pretreatment of SCB is demonstrated in this study, which shows that the addition significantly improves SCB enzymatic digestibility (Nasirpour et al., 2014).

4.4. Thermochemical deconstruction

When compared to mechanical and chemical methods, thermal pretreatment offers significant advantages, such as lower energy consumption and the creation of less hazardous chemicals and growth inhibitors. For the generation of liquid fuels from SCB, pyrolysis is an alternative to lignocellulose fermentation. Sugarcane is heated to extremely high temperatures and pressures during thermal pretreatment. Hemicellulose and lignin are successively solubilized at this high temperature. The solubility of hemicellulose in SCB is improved by combining thermal and chemical treatments (Scherzinger and Kaltschmitt, 2021). When SCB was processed using the hydrothermal technique, Boussarsar et al. found that greater hemicellulose solubilization occurred. In this method, the amount of sugar that was transformed into harmful byproducts was kept to a minimum (Boussarsar et al., 2009).

Liquid hot water pretreatment is a type of thermochemical pretreatment in which the biomass is pretreated at higher pressure without using any chemical. The water is kept in the liquid state at a higher temperature (140–220 °C) by increasing the pressure. The pressurized water when penetrates the biomass causes hydrolysis of the hemicellulose, increased surface area of biomass, hydration of cellulose, and removal of the lignin fraction of the biomass. Low cost and the non-requirement of any chemical are the advantages of this method. Combined liquid hot water and aqueous ammonia pretreatment enable to reduce the energy input and enhance the sugar recovery.

A study of bagasse pretreatment with a combination of hydrothermal and alkali $Ca(OH)_2$ revealed an increase in methane output and lignin breakdown when compared to raw bagasse (Mustafa et al., 2018). When comparing raw bagasse to hydrogen peroxide impregnation before hydrothermal processing, Ahmad et al. found a 118.6 % increase in methane output. Similarly, to overcome reluctance, SCB was saturated with the lime for the steam explosion. Ahmad et al. studied the effect of hydrogen peroxide impregnation before hydrothermal pretreatment and reported a 118.6 % increase in methane yield compared to raw bagasse (Ahmad et al., 2020). Similarly, SCB was impregnated with lime for the steam explosion to overcome recalcitrance. Lime was found to be an effective catalyst for increasing ethanol and methane output from pretreated bagasse, with lime recovered from the effluents by carbonation. Pretreatment with a hydrothermal or steam explosion followed by alkali showed promise and should be investigated further for biogas production from bagasse (Capecchi et al., 2015).

4.5. Hydrothermal deconstruction

Rocha et al. used Steam explosion (SE) for the pretreatment of SCB (190°C, 13 bar, 15 min) to remove hemicellulosic hydrolysate for the production of bioethanol (Rocha et al., 2012). SE (180°C, 5 min) carried out in the presence of phosphoric acid yielded a higher quantity of glucan (Pitarelo et al., 2016). Similarly, Saelee et al. performed thermal pretreatment (195^{O}C, 13 bar, 15 min) followed by enzymatic hydrolysis using xylanase to obtain cellulose nanofibrils from SCB and for the production of bioethanol (Saelee et al., 2016). SCB was initially treated with hot water (140-180^{O}C) followed by disk milling (Wang et al., 2018c). Liquid hot water (LHW) and NaOH pretreatment removed 42 % and 78 % of lignin, respectively. Combinative pretreatment such as LHW-NaOH and NaOH-LHW removed 76 % and 84 % of lignin, respectively. NaOH-LHW pretreatment gave the highest enzymatic digestibility (Gao et al., 2013).

Microwave-alkaline pre-treatment (450 W, 1 % NaOH) removed 90 % of lignin from SCB (Binod et al., 2012). Zhu et al. concluded that microwave-assisted pre-treatment is more effective than conventional thermal treatment. They obtained four times higher reducing sugars and good removal of lignin and hemicellulose than the conventional ones (Zhu et al., 2016). Organosolv and hydrothermal pre-treatment resulted in 62 % of lignin degradation which was confirmed by Confocal laser scanning microscopy and Field emission scanning electron microscopy (Espirito Santo et al., 2018). Mustafa et al. used the combination of hydrothermal and calcium hydroxide treatments for the production of biogas (Mustafa et al., 2018).

4.6. Ultrasonic deconstruction

Ultrasonic-assisted pretreatments have a very powerful impact on the removal of lignin than that of hemicellulose and cellulose. This delignification process can directly control the sugar yields. Ramadoss et al., investigated the effect of ultrasonic deconstruction using metal chlorides namely $AlCl_3$, $FeCl_3$, $MgCl_2$, $CuCl_2$, NaCl, $CaCl_2$, and KCl. The effectiveness of this method depends on the pretreatment conditions such as substrate dosage, sonication time, hydrogen peroxide concentration, molar ratio of the metal chloride to hydrogen peroxide, temperature, and particle size. The enzyme Cellulase has been found effective in the saccharification of hemicellulose and cellulose improving the solubility of cellodextrin deconstructed from cellulose and leading to a fast recovery of glucose. Ultrasonication does not directly lead to saccharification of the cellulose to sugars, but it enhanced the accessible surface area resulting in high yield. The effective removal of lignin was clear from the pits formation on the cell walls and the pretreated material become more fragile (Ramadoss and Muthukumar, 2014).

4.7. Biological deconstruction

The NaOH pretreated SCB was subjected to enzymatic hydrolysis using cellulase mixture under fed-batch conditions for 120 h. The 9.376 g/L, 56.03 g/L, and 129.50 g/L of cellobiose, xylose, and glucose were obtained with a total glucan conversion of 60 % (Gao et al., 2014). Similarly, enzymatic treatment using cellulase increased the saccharification from 1.93 % to 38.84 % after NaOH pretreatment (Thite and Nerurkar, 2019). Ultrasound-assisted alkaline pretreated SCB was hydrolyzed with cellulase and β-glucosidase to obtain a good sugar yield (Velmurugan and Muthukumar, 2012). Peroxyformic acid-treated SCB subjected to enzymatic hydrolysis using cellulase removed 59 % of lignin and 103.6 % of saccharification was obtained with a loss of 9.2 % cellulose (Bu et al., 2021). Mota et al. carried out alkaline pretreatment and enzymatic saccharification of SCB using Fractional Factorial design and Central Composite Orthogonal design. The optimized condition yielded 423 mg/g of sugar whereas the unoptimized and untreated SCB yielded 145.1 mg/g. The lignin content before and after optimization was 24.9 % and 8.7 %, respectively. Similarly, the glucose content before and after optimization was 16.7 and 19.2 mg/g, respectively (Mota et al., 2021).

LHW Pre-treated SCB was hydrolyzed using cellulase and hemicellulose. The maximum ethanol concentration was 29.9 g/L for 30 FPU/g enzyme loading (Wang et al., 2018c). Ramos et al. carried out the optimization of H_3PO_4 impregnated steam-treated SCB using enzymatic (Cellic CTec2) hydrolysis and achieved a sugar concentration of 76.8 g/L (Ramos et al., 2015). A 100 % conversion of glucan was obtained in glycerol pretreated SCB using Celluclast 1.5L, whereas the NaOH pretreated SCB gave 86 % of glucan conversion (Harrison et al., 2013).

To improve the enzymatic hydrolysis of SCB, Ling et al. performed pre-treatment using choline chloride and formic acid. The pre-treatment extracted 95.6 % hemicellulose and degraded 72.6 % lignin. Tween 80 was found to be the finest enzymatic additive, because it improved glucose production, reduced hydrolysis time by 24 h, and enzyme dosage by 10 FPU (Ling et al., 2021). Surfactants such as Tween 20, Tween 80, PEG 4000, and PEG 6000 along with ammonium hydroxide were used in the pretreatment of SCB followed by enzymatic hydrolysis using two enzymes (Novozyme 188 and Spezyme CP). The 66 % cellulose digestibility was obtained at an enzyme loading of 30 FPU/g glucan (Cao and Aita, 2013).

5. Bioproducts obtained from SCB

5.1. Butanol

Bioprocessing of cost-effective substrates and utilization of vegetable extract as a growth factor is a future aspect for biofuel research. An enzyme cocktail was used to saccharify the mixed substrates (wheat bran, SCB, and orange peel) into fermentable sugar. These sugars along with vegetable extract used as a fermentation medium gave a butanol production of 16.51 g/L (Mondal et al., 2022). Mariano et al. investigated the economic and technical aspects of butanol production in Brazilian sugarcane refinery and conveyed that engineered microorganisms reduced energy consumption and wastewater and increased butanol production by 59.1 % (Mariano et al., 2013). SCB pre-treated with dilute acid and oxidate ammonolysis followed by enzymatic hydrolysis produced 12.12 g/L of ABE (Li et al., 2017). List of some bioproducts obtained by utilizing SCB as the substrate is given in Table 1. Fermentation by *Clostridium beijerinckii* DSM 6423 using SCB hydrolysate and molasses produced 7.9 g/L of butanol and *Clostridium acetobutylicum* and *Clostridium beijerinckii* produced 0.072 g/g and 0.165 g/g of butanol, respectively (Travaini et al., 2016b; Vieira et al., 2021). SCB is used as a cell carrier and packed in a concentric annular basket and later *Clostridium beijerinckii* is immobilized on SCB. To recover isopropanol-butanol-ethanol from repeated batches, the *in-situ* vacuum product recovery technique was used and productivity of 0.35 g/L.h was achieved. An internal-loop boiling-driven fibrous-bed bioreactor concept was developed by inserting SCB-packed in annular basket in a vacuum fermentation. An advanced design of this bioreactor might help to combat the disadvantage of repeated batch such as cell degeneration (Ferreira et al. (2022)).

5.2. Ethanol

A novel pretreatment technique ‘Densifying Lignocellulosic biomass with Chemicals followed by Autoclave (DLCA)’ was used on SCB, wherein H_2SO_4 was used as a chemical reagent. Implementation of this new pretreatment technique gave higher fermentability and enzymatic digestibility. During simultaneous saccharification and co-fermentation, DLCA-pretreated SCB gave an ethanol yield of 234.09 g/kg SCB. This pretreatment gave higher amount of ethanol without any washing and detoxification (Shen et al., 2022). Cellulosic sugar syrup (CSS) produced from SCB was mixed with molasses to enhance ethanol production. No increase in ethanol was observed but gave 27 % lower COD level of spent wash. This might be due to increased dissolved oxygen level (Netsopa et al., 2022). The combined pre-treatment of SCB (SE and alkaline delignification) followed by fed-batch enzymatic hydrolysis increased ethanol production by 450 %. Ethanol production of non-delignified and lignified is 5.21 and 23.38 g/L, respectively (Wanderley et al., 2013). In a study, 94 % of ethanol conversion when SCB was treated at 180 °C followed by disk milling (Wang et al., 2018c). The autohydrolysis of SCB yielded 25 and 18 g/L of ethanol by separate hydrolysis fermentation and simultaneous hydrolysis fermentation, respectively (Neves et al., 2016). Xu et al. produced ethanol and succinic acid by co-fermentation. They developed a novel process for the complete utilization of xylose and glucose in SCB hydrolysate. 100 g of SCB was converted into 8.6 g and 8.7 g of ethanol and succinic acid, respectively. During co-fermentation, the carbon dioxide released by *S. cerevisiae* was recycled by *A. succinogenes* for the production of succinic acid. The recycling of CO_2 technique can be implemented in biorefinery for the reduction of

Table 1
Bioproducts obtained by utilizing SCB as substrate.

Sl. No.	Product	Pre-treatment technique	Microorganism	Yield	References
1	Acetic acid	HCl/H_2SO_4	*Lactococcuslactis* IO-1	7.87 g/L	(Laopaiboon et al., 2010)
2	Biohythane	HCl and H_2SO_4	NA	53.64 %	(Rena et al., 2020)
3	Butanol	HCl	Engineered *Clostridium beijerinckii* CC101	12 g/L	(Lu et al., 2017)
4	Butanol	H_2SO_4	Immobilized *Clostridium saccharoperbutylacetonicum*	43 % 2.5–2.9 g/L	(Chacón et al., 2021)
5	Formic acid	HCl/H_2SO_4	*Lactococcuslactis* IO-1	6.04 g/L	(Laopaiboon et al., 2010)
6	Ethanol	Hot water	Alcohol-active dry yeast	257 ± 5.51 mg/g	(Zheng et al., 2021)
7	Ethanol	H_2SO_4	*Kluyveromycesmarxianus*	0.65 g/L/h	(Lin et al., 2020)
8	Ethanol	$Na\ _2CO\ _3 \cdot 10(H_2O)$	*Saccharomyces cerevisiae*	7.27 ± 0.70 g/l	(Nosratpour et al., 2018)
9	Ethanol	Steam explosion	*Wickerhamomycessp*	9 g/L	(Bazoti et al., 2017)
10	Ethanol	Enzymatic (cellulase and cellobiase)	*Scheffersomycesshehatae*	8.13 g/L	(Chandel et al., 2014)
11	Ethanol	PEG 4000 Tween 80	*Saccharomyces cerevisiae D5A*	73 % 69 %	(Cao and Aita, 2013)
12	Ethanol	$NH_4OH–H_2O_2$	*Saccharomyces cerevisiae* and *Pichia stipitis*	0.42 g/g	(Zhu et al., 2012)
13	Ethanol	HCl/H_2SO_4	*Lactococcuslactis* IO-1	5.24 g/l	(Laopaiboon et al., 2010)
14	Gluconic acid	CH_3COOH	*Gluconobacteroxydans* ATCC 621H	340 g/kg	(Zhou and Xu, 2019)
15	5-HMF	Ultrasound-ionic liquid	NA	65.72 %	(Li et al., 2020)
16	Hydrogen	H_2SO_4 and NaOH	*Thermoanaerobacteriumthermosaccharolyticum* KKU-ED1	218 mL H2/L	(Saripan et al., 2021)
17	Hydrogen	NaOH	Clostridium sp.	93.4 mL/g-VS	(Kumari and Das, 2015)
18	D-Lactate	H_2SO_4	*E. coli* AV03	0.95 g/g	(Utrilla et al., 2016)
19	Lactic acid	HCl/H_2SO_4	*Lactococcuslactis* IO-1	10.85 g/L	(Laopaiboon et al., 2010)
20	Methane	NaOH	Consortia	221.8 mL/g-VS	(Kumari and Das, 2015)
21	Pullulan	NaOH	*Aureobasidium pullulans* LB83	20 g/L	(Terán Hilares et al., 2017b)
22	Succinic acid	Alkaline	*A. succinogenes*	41 g/L	(Chen et al., 2021)
23	Succinic acid	NaOH	*A. succinogenes*	80.5 %	(Chen et al., 2016)
24	Xylitol	NA	*Debaryomyceshansenii*	0.28 g/L/h	(Prakash et al., 2011)
25	Xylooligosaccharides,	Alkaline	Cellulase and Endo-β-1,4-xylanase	5.96 ± 0.09 g/g	(Xue et al., 2016)
26	Xylooligosaccharides	KOH	*Pichia stipitis*	5.29 g/L	(Bian et al., 2014)

greenhouse gases (Xu et al., 2021). Zhang et al. found that the enzyme feeding mode increased ethanol production and reduced enzyme loading. They obtained 83.25 g/L of ethanol from NaOH pretreated SCB (Zhang and Zhu, 2017). The 17.26 g/L of ethanol was produced via simultaneous saccharification and fermentation using SCB with alkali-assisted hydrodynamic cavitation and immobilized *Scheffersomyces stipites* (Terán Hilares et al., 2017a). Travaini et al. investigated the effect of different pre-treatment parameters on SCB using an L9$(3)^4$ orthogonal array. They pretreated SCB using ozone and later detoxified it with water. Among all the parameters, ozone concentration exhibited highest influence on sugar release and fermentation by *S. cerevisiae* yielding 80 % of ethanol (Travaini et al., 2016a). To overcome the problems (wastewater generation) caused by alkaline pre-treatment, Wang et al. performed fermentation using alkaline pre-treated bagasse by skipping the washing process. Cellulase hydrolyzed the pretreated SCB and attained 70.2 % hydrolysis efficiency and fermentation by *Saccharomyces cerevisiae* Y2034 yielded 67.5 % ethanol (Wang et al., 2019). Dias et al. carried out a comparative study between first, second, and integrated first and second-generation ethanol production from sugarcane, surplus SCB, and trash respectively. On the perceptive of economic and environmental analysis, integrated ethanol production gave better results since they share common fermentation and distillation equipment. The ethanol production for the second-generation increased from 158 L/ton to 181 L/ton and 335 L/ton due to progressed hydrolysis technologies and pentose fermentation, respectively (Dias et al., 2012). Similarly, Gubicza et al. carried out a techno-economic analysis of ethanol production from SCB using engineered *E. coli.* They found that feedstock and capital costs for ethanol production are 25 % and 45 %, respectively (Gubicza et al., 2016).

Enzyme cocktails can be employed in biorefinery approach to reduce the production cost since it depolymerize the lignocellulosic biomass. On-site produced enzyme cocktails (Cellulase, ligninases and hemicellulase) are used for saccharification of SCB pretreated by hydrothermal and alkaline delignification. Alkaline pretreated SCB yielded 60.80 % of ethanol (de Oliveira et al., 2022).

5.3. Hydrogen

Biohydrogen produced by a microbial consortium from raw and perchloric acid-pretreated SCB was 15.7 mM and 46.4 mM, respectively (Bu et al. 2021). Metal ions act as a catalyst for the production of hydrogen by increasing the activation energy and pre-exponential factor. An increase of 1–3 % was seen in the presence of NiO/CaO and a decrease of 3–6 % was seen in the presence of CuO/MgO (Kuan et al., 2013). NaOH pre-treated SCB when supplemented with 20 mM of $CaCO_3$ produced 4.89 mmol H_2/g by *Clostridium thermocellum.* $CaCO_3$ promoted the growth of microorganisms and biodegradation of SCB (Tian et al., 2015). Pre-treatment of SCB using UV irradiated nano-titanium dioxide enhanced the hydrogen production via fermentation. 1 g of nano-titanium dioxide with 120 min of UV irradiation produced 101.5 mL/g vS of hydrogen (Jafari and Zilouei, 2016). Cellulase obtained by graphene oxide treatment hydrolyzed the alkali pre-treated SCB and yielded 2870 mL/L of biohydrogen via fermentation by *Clostridium pasteurianum* and *Bacillus subtilis* (Srivastava et al., 2018). Nanocrystalline cellulose was produced from SCB, along with integrated co-production of lignin and hydrogen (Katakojwala and Mohan, 2022).

5.4. Methane

The residual liquid after fractionation of SCB produced 27.46 NL_{CH4} kg_{SB}^{-1} of methane during anaerobic digestion (Bittencourt et al., 2019). Arelli et al. used *Pseudomonas* with cellulolytic activity for bioaugmentation. They obtained 0.44 and 0.34 L/gVS of methane from bioaugmented and non-bioaugmented SCB, respectively (Arelli et al., 2021). Rabelo et al. obtained 72.1 L CH_4/kg when SCB was pre-treated with hydrogen peroxide followed by enzymatic hydrolysis (Rabelo et al., 2011). Baeta et al. found that mild autohydrolysis of SCB is favorable for the production of methane. Autohydrolysis at 170 ℃ for 35 min yielded 1.56 Nm^3 CH_4 kg $TOC^{-1}$and optimization using the Gompertz model gave a production rate of 2.6 mmol CH_4d^{-1} (Baêta et al., 2016).

5.5. Electricity

For a foreseeable future, a renewable source is required for electricity production. Using substrates such as corn stover, poplar sawdust, rice straw, SCB, and wheat straw, 1 metric ton of ethanol can be produced with 1.26 tons of lignin residue and 0.27 tons of methane after recovery of ethanol. 7,121–8,180 kWh of electricity are generated from one ton of ethanol by combustion of methane and lignin residue and it acts as a grid surplus (Liu and Bao, 2017). Integrating microbial fuel cell (MFC) and fermentation using SCB as substrate, 14.88 mW/m^2 and 8.70 mW/m^2 of electricity were generated via liquid and semi-solid state fermentation, respectively. SCB extract having 12000 ppm of glucose and incubated with 14 mg/L of biocatalyst *S. cerevisiae* for 72 h/cycle. For the first three cycles, media and yeast were replaced with fresh, whereas in the fourth cycle, yeast alone was not replaced. The highest value obtained in the first cycle was almost similar to the second and third cycles. In the fourth cycle, the voltage doesn't show any significant decrease in the absence of biocatalyst, because the biofilm directly converted SCB extract into electricity (Christwardana et al., 2021).

5.6. Other products

Xylan extracted from SCB using NaOH, when subjected to hydrolysis using endoxylanase yielded Xylooligosaccharides (Tseng et al., 2022). Solvents such as ethyl acetate and tri-*n*-butyl phosphate were used to extract L (+) lactic acid from the hydrolysate of SCB. This extraction yielded 59.63 ± 1.28 % of lactic acid and it was further enhanced to 85.95 ± 0.44 % using ammonium sulfate (Baral et al., 2021). Grewal et al. produced 0.52 g/g of lactic acid using *Lactobacillus brevis* by simultaneous saccharification and co-fermentation of SCB (Grewal and Khare, 2018). Carboxymethyl cellulose (CMC) was synthesized from SCB with a yield of 0.9457 and it was further converted into biodegradable film (Gupta et al., 2020). A thermally stable red pigment was produced by *Monascus ruber* Tieghem IOC 2225 using SCB hydrolysate as a carbon source (Terán Hilares et al., 2018). Liang et al. produced levulinic acid from pith-removed SCB using ethyl acetate extraction. The organic and aqueous layers yielded levulinic acid of 53.2 ± 0.3 % and 0.3 ± 0.1 %, respectively (Liang et al., 2021).

6. Present perspectives and future needs

Biorefinery can be defined as a framework which facilitates the utilization of renewable feed stock, mainly non-fossil fuel based feedstock, to churn out a range of potential market value products through various unit operations. It mainly aims to develop economically feasible and environmentally safe methods to convert renewable feedstock to products. The shift from fossil based feedstock to biomass or agro-industrial waste will result in reduced CO_2 emissions. Another advantage of biorefinery concept is to improve the usage of agro-waste and then to reduce the environmental load. By developing a method to convert low cost waste feedstock to high end value products based on biorefinery framework will result in carbon neutrality (Katakojwala and Mohan, 2021).

SCB, as mentioned before, is one of the potential feedstock which contains various pentose sugars and sugar acids. As SCB contains fermentable sugars abundantly, the conversion of these sugars to various platform chemicals can be employed (Konde et al., 2021). Previously, one of the major industry that have to be explored for biorefinery approach was sugar industries. Many of the researchers and industries found the importance and validity of byproducts from sugar industry to produce value added chemicals. The utilization of SCB comes under the second generation biorefinery.

Chatterjee and Mohan in 2021 studied the production of green hydrogen and bioethanol with reference to an biorefinery approach. They also included organic farming for the efficient utilization of segregated SCB. By implementing the closing the loop approach, the untreated SCB was utilized for bio-H_2 production and then the acid pretreated SCB for bio-H_2 and volatile fatty acid production. From the pretreated SCB, the unhydrolyzed feedstock was subjected for ethanol production through SSF (Simultaneous Saccharification and Fermentation). Then the remaining effluent from the bio-H_2 production was used as manure for plants. This study gives an idea about the second generation biorefinery approach with zero wastage of lignocellulosic waste discharge after the process (Chatterjee and Mohan, 2021). A feedstock for biodiesel production along with xylitol and xylanase from SCB was done by Kamat et al. in 2013. The acid-pretreated SCB hydrolysate was used for xylose production and the SCB residue was then used for xylanase production. The cell biomass from the above process were then extracted for oil and it was exploited in biodiesel production (Kamat et al., 2013).

The selection of the best possible scenario for the production of Furan-based compounds and alkanes from SCB was evaluated by Aristizábal et al. in 2015. From their study, it was found that by evaluating the raw material, economic, and environmental characteristics of different scenarios, ethanol, furfural and octane production from SCB and coffee cut-stems were the best option to be considered for the biorefinery process (Aristizábal et al., 2015). Very recently, nanocellulose, lignin and biohydrogen production using SCB as feedstock was done by Katakojwala and Mohan. They have developed a multi-product as well as resource efficient biorefinery with zero liquid waste discharge. The life cycle analysis of the process gave satisfactory values (Katakojwala and Mohan, 2022).

For zero waste biorefinery, chemically pretreated as well as fermented SCB were compared to find out the efficacy of its composting to attain the sustainable usage of SCB. From that study, they concluded that usage of chemically pretreated as well as fermented SCB were resulted in improved biodegradation (Ansari et al., 2021). Co-production of *xylo*-oligosaccharides and glucose from SCB through recyclable furoic acid-assisted pretreatment was employed by Dai et al. in 2021. They have used furoic acid as the catalyst for the sugar extraction as well as for the further saccharification process (Dai et al., 2021).

The efficiency in utilizing SCB as the feedstock was investigated by Restrepo-Serna et al. in 2018. Through simulation, energy and exergy assessment, the best process method with lesser energy loss can be identified and selected (Restrepo-Serna et al., 2018). Furthermore, more development on these studies are required.

7. Conclusion

The lignocellulosic biorefinery system having multiple products with zero waste disposal seems to be the best for a bioprocess. Many studies have been carried out based on SCB as the feedstock and most of them were successful to bring out an efficient scenario for the second-generation biorefinery approach by incorporating different pretreatment methods. Furthermore, more analysis reports and energy assessment has to be carried out in the processes to evaluate the environmental impact as well as industrial applicability.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

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