Review Article

A Review of Sugarcane Biorefinery: From Waste to Value-Added Products

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Abstract
The sugarcane industry is one of the agricultural sectors for the production of commodity products that can generate sugars along with byproducts such as straw, bagasse, and molasses. When subjected to effective processing, these byproducts of sugarcane cease to be categorized as waste, as they can be converted into resources rich in carbon for use in biorefineries. Numerous conversion technologies consisting of thermochemical, biochemical, and chemical processes of biorefinery are also applied to produce high-value products, either from 1st Generation (molasses feedstock) or through integrated 1st Generation and 2nd Generation configurations (molasses and sugarcane lignocellulose feedstock). This review focuses on recent progress in techniques for maximizing the value of sugarcane, encompassing aspects, such as sugarcane processing, pretreatment methods, and the fermentation of sugar derivatives to six value-added products, namely ethanol, xylitol, butanol, polyhydroxyalkanoates, biogas, and nanocellulose. Furthermore, this review encompasses an examination of the economic and environmental repercussions associated with sugarcane biorefinery. It also explores advancements using cutting-edge technology to address obstacles in industrial production.

Keywords: Bioeconomy, Biorefinery, Fractionation, Pretreatment, Sugarcane, Valorization

1 Introduction

The increasing global population has an impact on the increment of energy demand, coupled with decreasing fossil sources. Addressing this environmental issue has been a considerable commitment now in the spotlight. Considering this issue, renewable energy has become a central policy supported by governments in almost every country around the world. Consequently, the promotion of bioenergy has emerged as a key energy strategy in many nations [1]. The basic concept of biorefinery, well-known as sustainable bio-based production, is converting biomass into fuels, heat, electricity and value-added products in the same context as producing fossil resource-based chemical production through petroleum refinery [2]. To achieve the goal of producing high-value products from low-value raw materials, the biorefinery is a crucial factor in the future generation of energy and chemical products, contributing to waste reduction through sustainable approaches [3]. The concept of the biorefinery is associated with the concept of the Bio-Circular-Green Economy (BCG) model, including bioeconomy, circular economy and green economy [4]. The European Union (EU) and the governments of many countries have followed and implemented this model that is oriented towards harnessing the growth potential of the bioeconomy. In the first decade of the 21st century, the Organisation for Economic Co-operation and Development (OECD) has taken bioeconomy as an international policy concept for developing new products and markets through advancements in biotechnology [5], [6].

Table 1: Annual records of the top ten sugarcane producers

Country	Sugarcane Products (million tons)	Harvested Area (million ha)
Brazil	715	9.97
India	405	5.16
China	107	1.14
Pakistan	88.7	1.26
Thailand	66.3	1.50
Mexico	55.5	0.81
Indonesia	32.2	0.45
Australia	31.1	0.36
U.S.A.	30.0	0.38
Guatemala	27.8	0.24
Worldwide	**1,859**	**26.4**

Currently, 2nd generation (2G) biorefinery, using non-edible biomass as raw materials, has gained interest from R&D sectors and industries because it reduces the debates of competition for food and feed supplies. Lignocellulose biomass is a representative biomass because it is the most abundant biomass in the world. Among the lignocellulosic biomass, sugarcane processing plays a vital role in producing bioethanol and sugar, since sugarcane contains a high proportion of biomass that is readily converted to fermentable sugars [1], [4]. In addition, sugarcane wastes also possess nutrient contents, such as cellulose, hemicellulose, lignin, minerals, amino acids, etc., that have the potential to be used as input materials in the biorefinery process [3]. The worldwide production of sugarcane amounted to about 1,859 million tons across a harvested area totaling 26.4 million ha in 2021. Brazil held the position of the leading sugarcane producer globally, followed by India, China, Pakistan, Thailand, Mexico, Indonesia, Australia, the United States, and Guatemala (Table 1) [7], [8]. Until now, sugarcane biorefining technology has gone through two generations. In the first generation (1G), it typically utilized food crops as feedstock resources and reached the commercialization stage. This led to the production of fuels and commodity chemicals, specifically products like sugar-ethanol-electricity [4], [9]. Nevertheless, the 1G production has led to competition for feedstock resources, affecting both the energy and food industries, and resulting in higher food prices [10]. Consequently, agricultural wastes, which are mostly lignocellulosic biomass consisting of cellulose, hemicellulose, and lignin, are primarily used in 2G for producing high-value bioproducts and biochemicals [9], [10]. However, 2G has not yet reached commercial competition due to initial technical challenges, scaling issues, and production costs [11]. To overcome the roadblocks of 1G and 2G along with the more advanced technology, other methods of sugarcane biorefineries have been proposed, such as the integration of 1G and 2G ethanol production. This can be achieved by combining sugarcane mills with ethanol plants, and butanol production combined with sugar and the first-generation ethanol process [4]. The establishment of integrated sugarcane biorefineries aims to fully utilize sugarcane and its byproducts, namely bagasse, molasses, sugar cane trash, and others, in the production of sugar, ethanol, and bioelectricity.

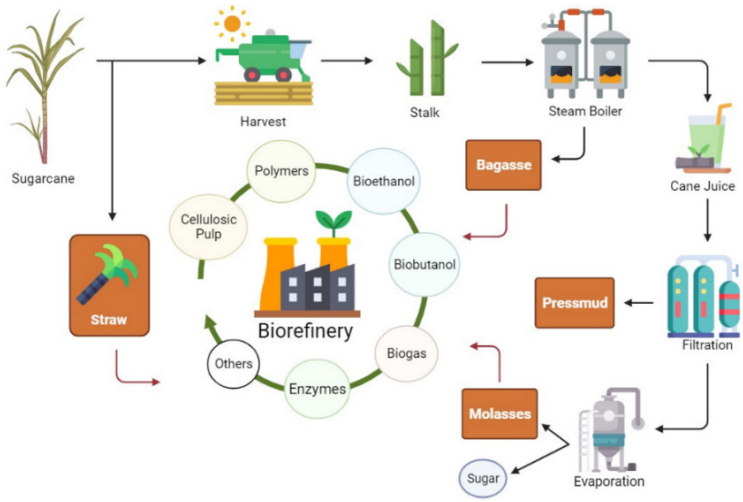

Figure 1: Overview of sugarcane processing and sugarcane biorefinery.

This review showcases the considerable potential of sugarcane byproducts, specifically straw, bagasse, and molasses, in acquiring a range of enhanced-value products. These include ethanol, xylitol, butanol, polyhydroxyalkanoates, biogas, and nanocellulose, benefitting from recent advancements in pretreatment methods, enzymatic hydrolysis, and the fermentation process. Additionally, the review delves into an analysis of the economic and environmental consequences linked to sugarcane biorefinery. It further investigates how cutting-edge technology can be leveraged to overcome challenges in industrial production.

2 The Potential of Sugarcane as a Raw Material in Biorefinery

Sugarcane mills play a crucial role in the agricultural sector, and their production policies and legal regulations can vary based on geographical settings and the specific products they aim to produce. In the sugar production process, alongside sugar as the primary product, various byproducts, such as sugarcane straw (SCS), sugarcane stalk, sugarcane bagasse (SCB), sugarcane molasses (SCM), etc., are generated through the sequential processing of sugarcane [12], [13]. Sugarcane industries typically involve a seven-step process, which includes harvesting, cleaning, chopping, juice extraction, purification, evaporation, and crystallization. Figure 1 illustrates that after harvesting, the primary product is not only sugarcane stalk but also the valuable byproduct of SCS, comprising around 60% dry leaves and 40% green tops [1]. Normally, sugarcane stalk is washed and taken to prepare the broth through a series of milling operations, typically involving four to seven milling units that use shredders or crusher rollers. Following the extraction of the broth, sugarcane juice is separated from the fibrous byproduct known as SCB. This SCB is then directed to the energy plant within the production facility [14], [15]. Removing the impurity of sugarcane juice is conducted by heating and adding an alkaline agent such as lime (calcium hydroxide). In the purification process, significant particles precipitate and create a soft brownish mass known as press mud. The processed sugarcane juice is concentrated using multi-effect evaporators to solidify sucrose. The resulting residual solution, known as SCM and separated through massecuite, is rich in sugar and does not re-enter the sugar production process [15]. SCM retains residual sucrose along with elevated levels of reducing sugars, specifically glucose and fructose. It can be employed as a raw material for ethanol production through the process of fermentation.

From harvesting 1000 kg of sugarcane, around 140 kg of SCS is obtained (based on a dry basis). After passing the sugarcane process (Figure 2), sugar production constitutes about 92% of the total cane output [13]. Additionally, byproducts, such as SCB (275 kg), filter cake (25 kg), press mud (35 kg), and SCM (35 kg) are obtained [13], [16]. The structural

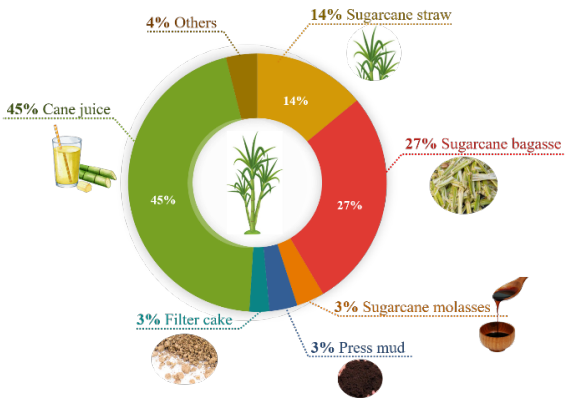

Figure 2: The primary products and byproducts of sugarcane processing.

arrangement of these components' cellulose, covered with lignin, and hemicellulose is complex and serves to prevent chemical and biological degradation [1]. Holocellulose, comprising cellulose and hemicellulose, is a desired feedstock for biofuel and chemical production. The composition of sugarcane SCS shows varying proportions: cellulose (32.4–44.4%), hemicellulose (24.2–30.8%), and lignin (12.0–36.1%). In contrast, SCB exhibits slightly different proportions: lignin (14–23%), hemicellulose (19–33%), and cellulose (26–47%) [3]. These findings align with the results reported by A. Aguiar *et al*. [1], who noted that SCS contains lignin (12–31%), hemicellulose (20–30%), and cellulose (31–45%), while SCB comprises lignin (17–32%), hemicellulose (20–32%), and cellulose (32–45%) [17]. The composition of SCS is in line with SCB due to the similar characteristic structure of biomass, resulting in comparable proportions of cellulose, hemicellulose, and lignin. On the other hand, SCM still contains some fiber from sugarcane, making it a potential biomass source, like SCS and SCB. SCM typically comprises of cellulose (26–47%), hemicellulose (19–33%), and lignin (1–5%) [3].

Generating substantial waste from the production of ethanol and sugar necessitates the implementation of appropriate waste disposal and recycling methods. Since the byproducts of the sugarcane process contain high levels of polysaccharides, namely cellulose and hemicellulose, as mentioned earlier, it has the potential to produce high-value products other than sugar and ethanol utilizing technological advancements [15]. Consequently, the sugarcane industry can serve as a cost-effective precursor to the biorefinery facilities, due to its abundant resources. Integrated sugarcane biorefineries are designed to maximize the utilization of both the raw material as sugarcane and its byproducts, such as SCB, SCS, SCM, etc. in the production of sugar, bioethanol, and bioelectricity [3]. Even though SCB holds significant potential for the production of second-generation biofuels, it is still sent to boilers for steam generation, typically at a rate of approximately 2 kg of steam per kg of SCB [12], [16]. This steam is subsequently employed to drive turbines for electricity generation, with the expended steam being reintegrated into the industrial process [16]. Currently, the SCM produced in the sugar mill is marketed at a relatively inexpensive price for use in animal feed and the production of ethanol [12]. It is also conveyed through pipes to an associated distillery unit where processing is carried out to yield 99.5% pure alcohol. This alcohol is considered an alternative product for gasoline, with an assumed substitution ratio of 0.85, so-called E85 gasohol [16]. It can serve a dual role as both a component in livestock feed and a raw material of ethanol production [14]. The manufacturing process of 99.5% ethanol from SCM involves fermentation, distillation, and dehydration stages. The blending of filter cake from the sugar mill with stillage can meet organic fertilizer standards, rendering it suitable for sale in Thailand as it serves as a soil conditioner for plantations [14].

3 Sugarcane Conversion in Biorefinery

In the past half-decade, there has been an increased focus on the circular bioeconomy, which is a new economic model involved the sustainable and resource-efficient utilization of biomass in integrated, multi-output production chains, such as biorefineries [18]. This approach not only incorporates the use of residues and wastes but also aims to optimize the value of biomass over time through cascading. The growing attention to the circular bioeconomy underscores the importance of comprehensively addressing economic, environmental, and social aspects within the industrial sector [19]. In this context, the biorefinery serves as a strategic mechanism to achieve the goals of a circular bioeconomy. A biorefinery in the circular bioeconomy aligns with zero waste generation because it utilizes sustainable and clean technologies, producing green

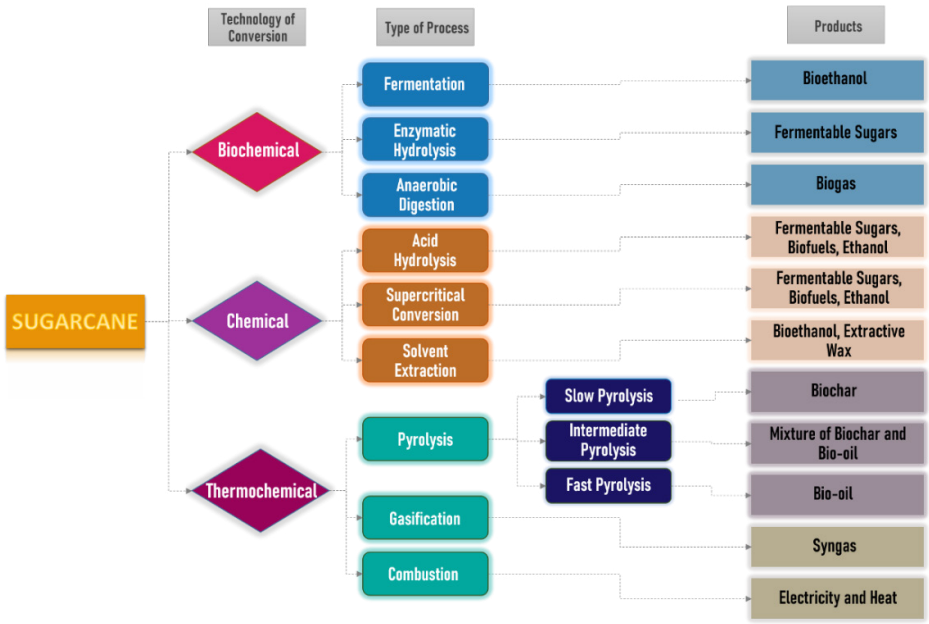

Figure 3: The routes of biorefinery for lignocellulose conversion to chemicals and fuels.

energy and motivating industries to manufacture environmentally friendly products with low carbon and water footprints [20], [21]. As a result, the idea of a biorefinery plays a crucial role in maximizing biomass conversion to achieve the objectives of the bioeconomy, aligning with the principles of a 'zero waste' society [22], [23]. The concept of a biorefinery can be applied in various settings, from small scale facilities using agricultural waste in isolated rural areas to large factories efficiently utilizing waste from nearby industries and municipalities through biological processes [22]. The utilization of renewable biological resources in biorefinery is significant for the production of diverse high-value bio-based products. These products can be broadly classified into three categories: 1) biofuels like bioethanol and biodiesel, 2) bio-energy encompassing power and heat, and 3) bio-based chemicals and materials like polylactic acid and succinic acid [19], [22]. Lignocellulosic biomass, a readily abundant and extensively researched source, is fractionated into lignin, hemicelluloses, and cellulose within the biorefinery. Lignocellulosic fractionation requires the integration of optimized technologies, along with life cycle analysis and economic assessment, to achieve a more valuable and sustainable economy [24]. To produce these sustainable high-value bio-based products, biorefinery requires efficient conversion technologies consisting of thermochemical, biochemical, and chemical processes [23].

In order to refine the sugarcane wastes, which are mainly composed of cellulose embedded in an amorphous matrix of hemicelluloses and lignin, it requires two major steps [20], [23]. The first step involves the depolymerization of sugarcane through various pretreatment processes to enhance accessibility and increase the efficiency of subsequent processes. Following the pretreatment stage, lignin can be utilized in the production of adhesives and bio-based components [24]. The second step involves integrated biorefining, encompassing various conversion processes, such as biochemical, chemical, and thermochemical methods, to generate value-added products as alternatives to fossil-derived products (Figure 3).

3.1 *Pretreatment process*

Sugarcane residues as feedstock resource is known for its recalcitrance to enzymatic hydrolysis because its fibers are composed of sclerenchyma and sheathed within cell walls that are thick and lignified [24]. As a result, the conversion process necessitates a

pretreatment stage to improve cellulose accessibility. This involves removing lignin and hemicelluloses, reducing cellulose crystallinity, and enhancing the materials' porosity [25]. The pretreatment procedure should have the capability to: 1) increase sugar generation or the potential for sugar formation through enzymatic hydrolysis; 2) safeguard against the degradation of carbohydrates; 3) prevent the production of byproducts that could impede hydrolysis and fermentation in downstream processes; and 4) ensure cost-effectiveness [25].

The pretreatment process can be categorized as mechanical (or physical), chemical, and biological, which can change the composition and structure of biomass and may also produce unwanted byproducts interfering with the bioconversion process [26]. In biochemical pathways, these sugarcane materials undergo conversion into bio-based products employing enzymes, bacteria, or engineered organisms, utilizing various technologies, namely alcoholic fermentation, anaerobic digestion, and photobiological hydrogen production [27], [28]. The difficulties linked to biochemical conversion technology include factors like size reduction, reduction of crystallinity, deactivation of cellulase, and the yeast's tolerance to ethanol [28].

Various pretreatment methods have been developed from lab-scale research and their pros and cons were demonstrated (Table 2). Physical pretreatment plays a vital role in improving enzymatic hydrolysis by enlarging surface area, pore size and declining crystallinity and degree of polymerization of cellulose [21], [29]. Physical pretreatment, such as mechanical grinding, pyrolysis, irradiation, and ultrasound, microwave irradiation, is extensively employed because it is a key step for bulky size reduction of lignocellulose biomass to appropriate size for handling in the further processes. Mechanical grinding can decrease the crystallinity of cellulose through various techniques, such as chipping, grinding, and milling [30]. Pyrolysis, a thermal degradation process, functions without the presence of an oxidizing agent at elevated temperatures, typically ranging from 500 to 800 °C [31]. Additionally, pyrolysis offers flexibility in production and marketing due to its saturation in design and technology.

Chemical pretreatment methods include different agents, such as acid, alkali, organic solvent, deep eutectic solvent (DES) and ionic liquid (IL) [32]. The acid pretreatment consists of dilute-acid pretreatment, which entails processes at high temperature with low acid concentration. Furthermore, there is concentrated-acid pretreatment, involving operations at low temperature with high acid concentration [33]. Alkali reagents cause the cleavage of side chains in esters and glycosides, leading to changes in the structure of lignin, swelling of cellulose, and hemicelluloses' decrystallization and solvation [26], [34]. The hydroxyl derivatives of sodium, potassium, calcium, and ammonium salts are among the most frequently employed alkali reagents for these processes [35]. Organosolv pretreatment is appropriate for the subsequent enzymatic hydrolysis process through deconstruction and removing lignin to expose the cellulose fibers [26]. This pretreatment uses several aqueous organic solvents, such as ethyl alcohol, methyl alcohol, 1,2-ethanediol, dimethyl ketone, glycerol, tetrahydrofurfuryl alcohol, etc., to biomass under defined conditions of temperature and pressure [36], [37].

Recently, there has been considerable attention given to the utilization of ILs in biomass pretreatment [38]. The broad application of these ILs across diverse lignocellulosic feedstocks is largely attributed to their unique capability to dissolve the entire lignocellulosic matrix [26]. The commonly used ILs in pretreatment processes are those recognized as effective solvents for cellulose extraction and fractionation. The most known ILs used for this purpose include 1-allyl-3-methylimidazolium chloride (Amim-Cl), 1-butyl-3-methylimidazolium chloride (Bmim-Cl), and 1-ethyl-3-methylimidazolium acetate (Emim-Ac), [38]. While IL pretreatment proves to be an efficient method for treating lignocellulosic biomass, it faces several challenges that need to be tackled, including high costs, complications in recycling and reusing, elevated viscosity, etc. [26], [39]. Due to their comparable properties, DES is considered a novel subclass of ILs [40]. DES is prepared under medium temperature by two or more components, involving a hydrogen bond acceptor (HBA), such as quats, alcohols, acid amides, etc. [41] and a hydrogen bond donor (HBD), such as carboxamides, carboxylic acids and polyols [42]. While DES is recognized for its effectiveness in delignification, it also exhibits the capability to remove hemicellulose through proton dissociation [32].

Biological pretreatment involves operating under low energy and standard environmental conditions, however, it comes with drawbacks such as a relatively

low hydrolysis yield and extended treatment durations [43]. Lignin and hemicellulose components of lignocellulosic biomass are degraded by various fungi, namely, brown-, white-, and soft-rot fungi [44]. Notably, white-rot fungi stand out as highly efficient microorganisms in the biological pretreatment [26]. Normally, microorganisms can degrade the fractions of lignin and hemicellulose. However, it is only capable of slightly degrading cellulose components due to its greater resistance to biological breakdown [45].

Table 2: Various pretreatment methods for lignocellulose conversion and their advantages and disadvantages

Pretreatment Method	Active Mechanism	Effect	Advantage	Disadvantage	Ref.
Hot water autohydrolysis	High temperature and pressured water	Hemicellulose extraction and cellulosic fraction separation	Low water consumption, highly proficient in the extraction of hemicelluloses, eco-friendly process, reduced equipment corrosion and reduced xylose degradation, a more streamlined and cost-effective procedure, high yield	Hydrolysate is complex and the Liquid-solid ratio (LSR) is large	[46]–[48]
Thermo-mechanical	Mechanical grinding	Disrupt the crystalline arrangement of cellulose	Minimize particle dimensions and enhance the ratio of surface area to volume	High demands of thermal energy, high capital cost	[49]
Ultrasound-assisted	Ultrasonic	Chemical bond disintegration	Lignin removal with great efficiency and environmental friendliness	High capital cost	[50]
Microwave	Microwave	Chemical bond disintegration	No requirement for reagent	High capital investment and safety	[50]
Organosolv pretreatment	Acetone, glycerol	Remove lignin from lignocellulosic biomass	High yields and selectivities on cellulose, high purity, high thermal stability	The use of low boiling point solvents is restricted due to their high volatility and flammability. Significant energy dissipation occurs when using solvents with low boiling points.	[51]
Acid pretreatment	Dilute/ concentrated forms, e.g. H_2SO_4, HCl, H_3PO_4, HNO_3	Hydrolyzed cellulose and hemicellulose	High sugar yield, efficient acid recovery, low cost, ready availability of acids, and the ability to breakdown hemicelluloses and lignin.	Demands a substantial quantity of poisonous and corrosive acid, inhibitor formation	[52], [53]
Alkaline pretreatment	Dilute/ concentrated forms, e.g. NaOH, NH_3, H_2O_2	Removing the lignin from the biomass, removing acetyl groups and uronic acid substitutions on hemicellulose	Easily treat at room temperature	Produce black liquor, necessary to perform acid neutralization after reaction, generation of large volume wastewater	[54]
Organic solvent	Ethanol, methanol, 1,2-ethanediol, glycerol, CH_3COOH, and CH_2O_2	Lignin extraction	Enhanced yields and conversion rates of cellulose, high purity, easy recovery and reuse	High cost, environmental pollution, flammable and explosive	[55], [56]
Ionic liquids	[BMIM][Cl], [EMIM][AcO] and [EMIM][DEP]	Cellulose fibril separation, lignin removal	Solvents are recyclable and could be reused, Eco-friendly, thermally stable, non-volatile, and non-flammable	Some types are viscous, poor biodegradability and relatively high cost, inhibitory effect on cellulase	[55], [57]
Deep Eutectic Solvent	ChCl:MA (1:1), ChCl:Gly (1:2) and ChCl:LA (1:5)	Lignin extraction	High DES recovery, efficient lignin removal, economical, less toxic, biodegradable	The multitude of potential combinations of components in DES complicates the task of characterizing and generalizing their properties	[58], [59]
Biological treatment	Fungi, bacteria, microbial	Lignin degradation, cellulose and hemicellulose disintegration	Low energy consumption, without chemical reagent, environmentally friendly	Requires long reaction times, inconsistency in pretreatment efficiency	[60]

3.2 *Enzymatic hydrolysis*

Glucose, derived from cellulose through pretreatment and acid hydrolysis or enzymatic hydrolysis, serves as a carbon source suitable for the fermentation process to generate fuels or chemicals [61]. In the enzymatic hydrolysis procedure, the transformation of cellulose and other carbohydrate polymers into fermentable sugars like glucose, xylose, arabinose, galactose, and mannose is recognized as a critical bottleneck in the biorefinery process. This step constitutes a significant portion of both the cost and time involved in the overall process [26]. Three complicated enzymes, namely cellulases, ligninases, and hemicellulases are used to depolymerize the lignocellulosic biomass. The action of cellulase enzyme in the enzymatic hydrolysis process affects amorphous cellulose for conversion into glucose or soluble monosaccharides through several crucial stages including: 1) enzymes transferred from the aqueous phase to the cellulose surface, 2) enzymes adsorbed and generated to enzyme-substrate complexes, 3) cellulose hydrolysis, 4) hydrolysis products removed from the cellulosic particle surface to aqueous phase, and 5) cellodextrins and cellobiose converted into glucose within the aqueous phase [62]. The hydrolysis process rate is affected by the biomass structure and the cellulase composition and source. Typically, enzymatic hydrolysis is a heterogeneous reaction that requires direct physical interaction to the substrate and the enzyme. In a heterogeneous reaction, an enzyme in the liquid phase diffuses through an aqueous solution, navigating obstacles like lignin, and adheres to the particle surface of cellulose. The ultimate result is the production of its foundational sugar building block.

3.3 *Sugarcane conversion into bioproducts*

The microorganism utilizes the pretreated substrate through several metabolic pathways including the Embden-Meyerhof Parnas pathway (EMP), the hexose monophosphate pathway (HMP), the Entner–Doudoroff pathway (ED), and the phosphoketolase pathway (PK) [61]. The EMP, well-known as the glycolytic pathway, changes the 6-phosphate glucose to pyruvic acid [63], [64]. Under anaerobic conditions, glycolysis transforms pyruvic acid into lactic acid (LA), ethanol, and alcohol [61]. Meanwhile, pyruvic acid is converted to CO_2 through Kreb's cycle or transformed into citric acid, iso-citric acid, and malic acid, respectively. The HMP pathway, also recognized as the pentose phosphate cycle, involves the generation of a variety of precursors including C_3–C_7 for cellular metabolism [65]. These precursors play a crucial role in the synthesis of nucleic acids, coenzymes, histidine, aromatic amino acids, etc. The ED Pathway, alternatively referred to as the 2-keto-3-deoxy-6-phosphate gluconate pathway, represents an anaerobic metabolic route for sugar [61], [66]. It is prevalent in Gram-negative bacteria, e.g. *Zymomonas mobilis*, *Pseudomonas aeruginasa*, and *P. saccharophila*. The PK pathway, also identified as the ketone phosphate enzyme pathway, encompasses both pentose and hexose ketone phosphate enzymes [60]. This pathway leads to the generation of roughly equal quantities of acetic acid, ethanol, and carbon dioxide during its progress.

3.3.1 Chemical process

The chemical conversions involve transesterification and acid hydrolysis, wherein agents like alcohol or acid are used in reactions to yield the desired product [23]. The initial step of chemical conversion, i.e. acid-catalyzed hydrolysis, results in the deconstruction of cellulose or hemicellulose to produce the corresponding monosaccharides. The chemical process is a widely recognized and standardized procedure [67]. Cellulose hydrolysis produces glucose, while hemicellulose primarily produces xylose and glucose. The conversion of these monosaccharides into chemicals typically initiates with dehydration, oxidation, or reduction reactions. In acidic conditions, glucose undergoes dehydration to form 5-hydroxymethylfurfural (HMF), which is hydrolyzed to yield levulinic acid and formic acid in further process [67]. Moreover, in acidic conditions, xylose and other natural pentoses, namely arabinose and ribose, undergo dehydration to produce furfural. Alternatively, glucose and xylose are reduced to produce sorbitol and xylitol, respectively. Conversely, the oxidation results in gluconic acid from glucose and xylonic acid from xylose. Certainly, various products such as HMF, furfural, levulinic acid, xylitol, and sorbitol have been identified as key bio-based platform molecules derived from the chemical conversion of carbohydrates.

While the initial outputs of monosaccharides

through chemical conversion may not possess immediate extensive utility, within the framework of biorefinery operations, they serve as crucial precursors for generating significant chemicals [67]. These include HMF, furfural, levulinic acid, xylitol, and sorbitol, which stand as pivotal bio-based platform molecules. However, chemical conversion technologies necessitate harsh conditions, with the products obtained, apart from power generation, having lower purity [68]. These products are unable to serve as substitutes for fine chemicals derived from oil products, nor can they function as versatile raw materials for various industries to fulfill energy and environmental requirements [68].

3.3.2 Thermochemical process

The conversion of lignocellulosic materials through the conversion of thermochemical methods involves processes, such as pyrolysis, gasification, and combustion. These methods can be tailored to generate heat, electricity, or gaseous and liquid precursors, which can subsequently be upgraded to produce liquid fuels or serve as chemical feedstocks [28], [69]. Thermochemical pathways utilize processes like pyrolysis, gasification, hydrothermal carbonization, and other thermal-based methods. These routes transform biomass resources into energy or other valuable products through the application of heat and chemical reactions [23].

The pyrolysis process converts lignocellulosic biomass into bio-oils, charcoal, and a gaseous phase similar to syngas. Fast pyrolysis is particularly noteworthy as a viable thermal treatment method for transforming biomass into liquid energy carriers or as a compatible compound for integration into existing refineries [27]. Presently, pyrolysis is primarily employed by utilizing the obtained oil and char as fuel in stationary ignition operations. However, the advancement of techniques to utilize pyrolysis oil as a transportation fuel is still in progress [69]. Pyrolysis is the thermal decomposition that occurs in an oxygen-free environment or inert atmosphere, as opposed to gasification, which takes place under a temperature range of 450 °C–600 °C [23]. Bio-oil, which is a dark homogeneous liquid, is generated through cooling and condensing the vapor produced by fast heating of biomass [11]. The products, including char and gas, are utilized to generate the necessary heat for the process, thereby minimizing or eliminating waste streams from the operation [28].

Biomass gasification is conducted at temperatures ranging from 1000–1400 °C with a gasifying agent, like oxygen, or in an oxygen-deficient environment [23]. The primary outcome of this gasification process is syngas, which includes hydrogen, carbon monoxide, carbon dioxide, and methane [28]. The obtained gas, which can be transformed into either fuels or chemical products, is directly used for power generation and heat. The thermochemical reaction involving biomass and oxygen in the presence of air to generate heat and electricity is known as combustion [23]. The integrated biorefinery concept has been devised, incorporating the use of supercritical carbon dioxide (SCO_2) along with a polar co-solvent, followed by thermochemical processes, to retrieve value-added chemicals and fuels.

4 Value-added Products from Sugarcane Biorefinery

4.1 *Ethanol*

Currently, a variety of biofuels, such as bioethanol, biodiesel, biomethanol, and others derived from renewable sources, are widely utilized in various industries (Table 3). Among these products, biofuels, bioethanol has achieved widespread use as the most commonly utilized biofuel on a global scale [3]. It can be mixed with gasoline or employed in the production of ethyl tertiary-butyl ether, serving as an anti-knocking agent in gasoline. In addition to its role as a blending agent for transportation fuels, ethanol is recognized as a versatile platform chemical for synthesizing various value-added chemicals. The catalytic transformation of bioethanol has demonstrated effectiveness in generating significant chemicals, including ethene, n-butyl alcohol, ethoxyethane, and various others [27]. In general, ethanol can be produced through fermentation from both cellulose and hemicellulose fractions using various pathways, allowing the utilization of C_5 and C_6 sugars derived from cellulose and xylan, respectively [1].

Saccharomyces cerevisiae is the yeast that is the most extensively researched for ethanol production. This yeast species is favored due to its tolerance to high concentrations of ethanol and sugar, coupled with its ability to yield significant amounts of ethanol [1], [70]. However, it can only convert glucose derived from

lignocellulose and is unable to convert xylose, which is a component of hemicellulose. Bioethanol production is conducted by the enzymatic hydrolysis or saccharification of cellulose and fermentation of glucose with various fermentation techniques, such as Separate Hydrolysis and Fermentation (SHF), Simultaneous Saccharification and Fermentation (SSF), Simultaneous Saccharification and Co-fermentation (SSCF) and Consolidated BioProcessing (CBP) [71]. The SHF process is separately operating cellulose hydrolysis and fermentation, thereby making it a prolonged and intricate process that involves additional process steps [72]. The SSF process enables the concurrent hydrolysis and fermentation of liberated sugars, resulting in heightened ethanol productivity and substantial time savings [61]. However, its drawback lies in the requirement for optimal temperatures for hydrolytic enzymes (45–50 °C), considerably superior to that for fermentation (30 °C), potentially leading to a reduced enzymatic hydrolysis rate [71]. For optimal conversion of liberated sugars into ethanol with high productivity, it is advisable to use a combination of yeasts or recombinant yeasts during the fermentation stage in an SSCF process, where simultaneous fermentation of C6 and C5 sugars takes place. Despite these efforts, the process generally yields low ethanol productivity, rendering it impractical [23].

SCB was investigated to evaluate its capability of producing ethanol via an innovative and economic pretreatment, namely Densifying Lignocellulosic biomass with Chemicals followed by Autoclave (DLCA). This method used H_2SO_4 as a catalyst under operating conditions of solid loading varying between 20–50%, temperature from 100–140 °C, and time between 15–90 min [73]. SSCF was carried out, yielding substantial ethanol production of 77.51 g/L at a 30% solid loading without the need for water washing, separation of solid-liquid, or the pretreated biomass detoxification. The SCB underwent pretreatment using the *Kluyveromyces marxianus* JKH5C60, known for its tolerance to multiple inhibitors, at a total solid loading of 20% [74]. The fed-batch SSF of SCB was fine-tuned to achieve optimal results, yielding the highest ethanol titer, efficiency, and productivities at 73.4 ± 1.2 g/L, 78%, and 3.0 g/L/h, respectively. This was achieved over 72 h, even in the presence of inhibitors such as acetic acid, furfural, and vanillin.

A novel method involving hydrodynamic cavitation-assisted pretreatment coupled with an advanced oxidative process of SCB was investigated by operating under optimum conditions such as an ozone flow rate and H_2O_2 concentration equal to 10 mg/min and 0.61%, respectively [75]. After enzymatic hydrolysate, hydrolysis yields of glucan and xylan were achieved at 84% and 78%, respectively, and subsequently, these products were fermented into ethanol via *Saccharomyces cerevisiae*. The produced ethanol was later distilled and taken to produce xylitol via fermentation by *Candida tropicalis*. In the production of ethanol and xylitol, the attained yields were 0.41 and 0.55 g/g, respectively, and volumetric productivities were 8.33 and 0.64 g/L·h, respectively. *Candida tropicalis* was also used to produce xylitol and ethanol co-production from SCB and SCS, supplemented with SCM [76]. SCB and sugarcane SCS hemicellulosic hydrolysate were derived from diluted acid hydrolysis using H_2SO_4. Supplementing SCM to achieve a sucrose concentration of 50 g/L in SCB and SCS hemicellulosic hydrolysate resulted in the highest observed concentrations of xylitol (30.61 g/L) and ethanol (47.97 g/L) [76].

4.2 *Xylitol*

Production of xylitol from lignocellulose biomass typically involves the use of a Ni-catalyst [77]. This bioprocess leverages the ability of yeasts that assimilate pentose sugars to transform xylose into xylitol, employing NAD(P)H-dependent xylose reductase as the primary step in xylose metabolism [78]. Xylitol is a polyalcohol with a five-carbon sugar structure [27]. Xylitol holds industrial significance due to its unique properties and significant potential. It has a lower energy content than sucrose and serves as a natural, non-caloric sweetener with additional benefits, including anticariogenic properties [79]. For this reason, it has found extensive application as a versatile substitute in various food products, particularly benefiting diabetic patients. Additionally, it is widely utilized in the pharmaceutical and dental industries, where it has tooth-rehardening properties making it a valuable ingredient in products for human consumption [80]. Examples include chewing gums, toothpaste, and mouthwashes.

Xylitol can be generated using either chemical formation or the process of fermentation, with xylose

serving as its precursor [80]. In chemical synthesis, the industrial manufacturing of xylitol relies on the catalytic reduction of xylose, purified from hemicellulosic hydrolysates (HHs), using a Raney nickel catalyst [81]. The reaction occurs under high pressure and temperature conditions, conversion efficiency is considered inefficient and costly due to several factors [1], [81]. The drawbacks of the process include the intricacy of xylose purification and the elevated cost linked with the Ni-catalyst. Approximately 80% of the overall production cost stems from the substantial energy consumption and the necessity for extensive xylose purification steps [81]. Additional disadvantages include the requirement for expensive and specialized equipment and challenges related to deactivating and recycling catalysts from the final homogeneous solution [1]. The essential factor for utilizing HHs as fermentation media for xylitol biotechnological production is the supplementation requirement [1]. This need is contingent on the characteristics of the raw material, as the composition of HHs varies, providing different amounts of compounds suitable as nutrients for microbial growth and metabolism.

Among sugarcane byproducts, SCB is the most used to produce xylitol products. Xylitol is produced from SCB hydrolysate through various fermentation methods. To improve xylitol production from HHs, obtained by diluted acid hydrolysis with H_2SO_4 of 1.0% w/v in 1:10 solid/liquid ratio at 121 °C for 10 min, these HH samples were fermented by adapted and non-adapted yeast of Candida guilliermondii FTI 20037 [81]. The yeast that underwent adaptation was cultivated in each hydrolysate for a 24 h duration, and then it was sequentially moved to the subsequent more concentrated hydrolysate to attain different levels of adaptation. This operation has enhanced the assimilation of xylose and the production of xylitol, leading to increased hydrolysates in terms of yield and volumetric productivity. For the fivefold concentrated and treated hydrolysate, there was a 62.5% increase in productivity, going from 0.24 g/L·h to 0.39 g/L·h. Additionally, there was a 15.7% boost in yield, rising from 0.51 g/g to 0.59 g/g. Likewise, in the case of twofold concentrated and untreated hydrolysate, these enhancements amounted to 54.5% and 29.6%, respectively. The yeast that underwent adaptation also heightened the consumption of arabinose and decreased the production of glycerol. This implies an enhanced tolerance of the adapted cells to the inhibitors found in the hydrolysates.

The suggestion was to use organic agro-industrial residues (OAIR) as an economically viable approach for the economic production of common products, while also solving environmental contamination. Conversion of OAIR is investigated to produce xylitol by using microbial fermentation with *Pseudomonas gessardii* VXlt-16 [78]. The findings indicated an increase in the product yield to 71.98/100 g. (equivalent to 0.66 g/L·h) Following detoxification with 2% activated carbon, xylitol crystals (48.49 g) with a great purity level of 94.56% were successfully recovered. Several effects, such as inoculation age, inoculum concentration and initial xylose concentration on the fermentation of SCB hydrolysate with Candida tropicalis InaCCY56 [82]. The results indicated that the produced xylitol of 31.7 g/L was achieved under optimal fermentation conditions with a concentration of OD600nm = 5 and an inoculation age of 24 hours, with an initial xylose concentration of 50 g/L.

Various pretreatment methods have different effects on sugarcane fractions, hence the subsequent process also achieves different outcomes. The hemicellulose component of SCB, derived from acid pretreatment by using H_2SO_4 and subjected to fermentation with Candida tropicalis IEC5-ITV, resulted in the production of 5.5 g/L of xylitol [80]. The xylitol yield was 0.39 g/g-xylose, indicating that SCB holds significant potential as a source for xylitol production. For other pretreatment methods, ultrasonic-assisted dual-alkali pretreatment was investigated to produce xylitol by Candida tropicalis fermentation [83]. Among the alkalis investigated, including sodium hydroxide, potassium hydroxide, ammonia, and calcium hydroxide, the combination of sodium hydroxide and liquid ammonia demonstrated the most favorable outcomes. Under optimal conditions with a ratio of sodium hydroxide and ammonia water (2:1), ultrasonic temperature (45 °C), and ultrasonic time (40 min), a maximum xylose yield of 2.431 g/L was achieved [83].

4.3 *Butanol*

Butanol functions as a versatile chemical feedstock, finding extensive applications in the manufacturing of plastics, polymers, lubricants, hydraulic fluids, hormones, drugs, antibiotics, cosmetics, and vitamins

[84]. Moreover, butanol shows potential as a renewable biofuel and as a fitting fuel additive for internal combustion engines [85]. It exhibits superior characteristics in comparison to other fuels like ethanol, featuring a greater boiling point, increased energy capacity, 30% higher energy density, lower viscosity, diminished solubility in water, and lower corrosiveness [86]. Due to its higher energy density and lower hydrophilicity compared to ethanol, butanol emerges as a superior blending agent for gasoline [27]. Notably, the advantage lies in its compatibility without requiring modifications or adaptations to car engines [86]. Therefore, butanol is considered that is one of the most fitting candidate biofuels.

From a chemical perspective, butanol can be produced through two main methods: the Aldol process (which initiates with acetaldehyde) and the Oxo process (which begins with propylene) [1]. In the biotechnological synthesis of butanol, notable challenges include the high cost of the substrate and the inhibitory impact of butanol. The latter can result in low product concentrations in the fermentation broth, given its toxicity to the fermentation of microorganisms [1]. The current emphasis on utilizing lignocellulosic biomass as a feedstock for butanol production has led to a reevaluation of acetone-butanol-ethanol (ABE) fermentation [27]. The objective is to reduce or remove the toxicity of butanol in the culture medium and fine-tune the culture conditions to enhance product specificity and yield [1]. The fermentation process comprises two distinct phases: acidogenesis and solventogenesis [84]. Solventogenic *Clostridia* spp, which encompass strains like *C. saccharoperacetobutylicum*, *C. saccharobutylicum*, *C. Beijerinckii* and *C. Acetobutylicum* (acted as butanol-producing strains), are frequently employed in ABE fermentations. Notably, *C. acetobutylicum* and *C. beijerinckii* are prominent strains utilized in the industry of ABE fermentations for butanol production [84]. Despite considerable commercial interest in bio-based butanol production, the economic viability of this process faces hindrances due to three primary factors: 1) the considerable expense of raw materials, constituting up to 60% of production costs, 2) reduced yields caused by cellular inhibition induced by low concentrations of butanol (1–2%), and 3) expensive downstream processes [86].

The fermentation of sugarcane SCM to produce butanol by *Clostridium beijerinckii* TISTR1461 was explored [84]. Conducted in anaerobic conditions with an initial pH of 6.5, a gas circulation of 0.2 L/min, and a temperature of 37 °C, this fermentation resulted in the highest butanol concentration (8.72 g/L), productivity (0.24 g/L·h), and yield (0.21 g/g). Both the gas-lift column bioreactor and the stirred-tank bioreactors were used to enhance butanol production. The gas-lift column bioreactor produced slightly higher butanol concentration (10.58 g/L), productivities of (0.29 g/L·h), and yield (0.23 g/g). Moreover, the gas-lift column was also used with low-cost fermenters. To improve butanol production, lotus stalk (LS) pieces were employed as support for the immobilization of cells for SCM in *Clostridium beijerinckii* TISTR1461 [85]. Under optimized conditions, fermentation took place in screw-capped bottles at 37 °C with an agitation rate of 150 rpm, using 50 g/L of SCM supplemented with 1 g/L of yeast extract in anaerobic conditions. Using biomass loading of 1:31 (w/v) with size of 4 mm for cell immobilization, the findings revealed a butanol concentration of 12.89 g/L, butanol productivity of 0.36 g/L·h, and butanol yield of 0.36 g/g. These values surpassed those for free cells, which exhibited a butanol concentration of 10.20 g/L, butanol productivity of 0.28 g/L·h, and butanol yield of 0.32 g/g.

The production of ABE from sugarcane bagasse hemicellulosic hydrolysate (SBHH) and SCM was investigated through batch fermentation by using Clostridium saccharoperbutylacetonicum DSM 14923 [72]. After hydrothermal pretreatment, HH was transformed into concentrated hemicellulosic hydrolysate (CHH). After fermentation for 30 h with a fermentation media of CHH25/SCM75 within the pH range of 5.5–6.5, the concentration of butanol was approximately 7.8 g/L and ABE yield was 9.8 g/L. Additionally, ABE and lipids were investigated from SCB through coupled fermentation with Clostridium acetobutylicum and oleaginous yeasts [87]. The peak production of solvents, amounting to 19.640 g/L (comprising 5.580 g/L of C_3H_6O, 13.159 g/L of butanol, and 0.901 g/L of ethanol), along with a corresponding yield of 0.335 g/g, was attained at a sugar concentration of 70 g/L. A three-stage repeated-batch immobilized cell fermentation, consisting of 1) SCM fermentation, 2) SBHH pulse-fed to SCM fermentation, and 3) immobilized cells supplied with undiluted SBHH as well as supplemented with SCM, was investigated to produce butanol by comparing with the efficacy of a

3D-printed nylon carrier for the passive immobilization of *Clostridium saccharoperbutylacetonicum* DSM14923 [88]. Bagasse demonstrated superior performance as a carrier, exhibiting an average xylose utilization of 33%, which significantly exceeded the effectiveness of the 3D-printed carrier treatment, achieving only 16%. Notably, bagasse facilitated the derivation of 43% of the butanol from SBHH.

4.4 *Polyhydroxyalkanoates (PHAs)*

Polyhydroxyalkanoates (PHAs) stand out as promising alternatives to conventional petroleum-based plastics, offering several advantages, such as biodegradability and biocompatibility [89]. Because of these characteristics, PHAs are viewed as promising and superior alternatives to conventionally employed non-biodegradable plastics [89]. Moreover, PHAs can be employed in the manufacturing of a wide range of items, such as packaging materials, films, fibers, and medical devices [3], [90]. Due to their economic viability, multiple companies, including COFCO Corporation (China), Tianjin GreenBio Material Co. (China), and Kaneka Corporation (Japan), have established commercial production processes for various types of PHAs [3]. These include poly(3-hydroxybutyrate) (P(3HB)) homopolyester, polyhydroxybutyrate-co-valerate (PHBV), and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (P(3HB-co-3HHx)) [3].

PHAs are naturally produced polyesters synthesized by bacteria through fermentation [91]. These polyesters are stored intracellularly as energy reserves, forming water-insoluble inclusions within the cytoplasm of the bacteria. Typically, PHAs are generated by polymerizing carbon precursors stored intracellularly, produced through metabolic pathways like 3-hydroxy fatty acids [3]. For 3-hydroxybutyryl-CoA, the biosynthesis leads to the creation of P(3HB), which stands out as the most extensively acknowledged homopolymer within the PHA category. In the presence of 3-hydroxybutyryl-CoA and 3-hydroxyvaleryl-CoA, the biosynthesis results in the production of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [P(3HB-co-3HV)], which is the PHA copolymer that has been most comprehensively characterized [3]. PHA production faces significant limitations, primarily stemming from the need for specific growth conditions and the associated high costs [89]. The high cost primarily stems from acquiring substrates of high purity, like glucose, fructose, and xylose, which account for around 45% of the total production expenses [91].

SCB, pretreated with a combination of steam explosion and sequential steam explosion-dilute H_2SO_4, was studied to produce PHAs. In the optimal conditions, with a steam explosion temperature set at 230 °C, a diluted acid temperature of 137 °C, and an H_2SO_4 concentration of 4.75% w/v for a diluted acid reaction time of 0.7 h, the reducing sugar content reached 12.89 g/L, achieving an 85.93% yield [91]. The pretreatment of SCB, involving a mixture of 10% (w/v) SCB with 1% (v/v) H_2SO_4 and 1.5% (v/v) H3PO4 by a steam explosion at 121 °C for 15 min, yielded reducing sugars in the form of glucose and xylose without the use of toxic chemicals [90]. Using reducing sugars sourced from SBHH as the carbon substrate, *Burkholderia cepacia* ASL22 exhibited a greater PHB yield at 0.22 g-PHB/g-reducing sugar in comparison to *Priestia megaterium* KKR5, which yielded 0.12 g-PHB/g-reducing sugar [90]. SCM as an inexpensive carbon source was used to produce PHAs by a wild strain of *Enterobacter cloacae*, which was isolated with Sudan Black B staining from sugarcane extract [89]. The highest PHA yield, varying between 4.13–4.98 g/L or 48%–56%, was attained following 48–60 h of incubation, with an initial pH of 7, SCM concentration of 4%, and an inoculum concentration of 2%. This indicates that *E. cloacae* has the capability to efficiently utilize SCM for the impressive production of PHA.

The investigation involved recombinant strains of *Ralstonia eutropha* expressing *sacC* gene of *Mannheimia succiniciproducens*, which encodes for *β*-fructofuranosidase. This enzyme facilitated the hydrolysis of sucrose into glucose and fructose of sugarcane. The aim was to produce P(3HB) and poly(3-hydroxybutyrate-co-lactate) [P(3HB-co-LA)] using SCM as a substrate [92]. The inhibitory to cell growth caused by the utilization of raw sugarcane molasses was mitigated by pretreatment with activated charcoal. When treated with activated charcoal, SM exhibited the capacity to support the growth of *Ralstonia eutropha* NCIMB11599 expressing the sacC gene. In batch fermentation, it achieved an OD_{600} of 87.2, along with a P(3HB) content of 82.5 wt%, when introduced into the culture medium containing

20 g/L of sucrose. Moreover, *R. eutropha* 437–540, which carried the *E. coli* ldhA gene encoding lactate dehydrogenase and the sacC gene, produced 29.1 wt% of P(3HB-co-LA) in batch fermentation from sugarcane biomass.

4.5 *Biogas*

With the global population growth and the advancement of the world economy leading to an anticipated increase in energy demand, biogas emerges as an alternative solution during a potential energy crisis. It can serve as a viable option for vehicle fuel and as a source of electric and heat generation [93]. The raw materials for biogas production are typically derived from biomass, such as lignocellulose, and various types of organic waste, including animal dung and industrial wastewater sludge fermented in aerobic conditions [69]. Moreover, the digestion of oily-biological sludge for biogas production offers a method to mitigate its adverse environmental effects [94]. Nevertheless, the carbon/nitrogen (C/N) ratio in oily biological sludge is inadequate, failing to meet the typically required ratio of 20 to 30 for an anaerobic digestion environment [94].

Optimization values of the C/N ratio and the ratio of volatile solids $(VS)_{co\text{-}substrate}/V_{Sinoculum}$ were investigated to improve biogas production from SCB [94]. Under a mechanical and thermo-chemical pretreatment process (sodium hydroxide of 1% (w/v), a solid-liquid ratio of 1:10, and 150 rpm at 100 °C for 1 h) the overall biogas yields from a C/N ratio of 20.0 with a $VS_{co\text{-}substrate}/V_{Sinoculum}$ ratio of 0.06 and a C/N ratio of 30.0 with a $VS_{co\text{-}substrate}/V_{Sinoculum}$ ratio of 0.18 were achieved at 2.777 and 9.268 L, respectively, encompassing methane yields of 0.980 and 3.009 L, respectively, after a 33-day batch anaerobic digestion. The results also showed that biogas and methane yield were increasing when the C/N and $VS_{co\text{-}substrate}/V_{Sinoculum}$ ratios were high. The ratio of C/N was also studied in SCB as raw materials [93]. The effects of the pretreatment method on biogas production were investigated. Physical pretreatment was conducted through grinding, followed by biological pretreatment with a microbial consortium at 5% g/V. The study also explored variations in the C/N ratio, specifically at 25 and 30 [95]. Following a 60-day period with a total solid content of 7%, there was an observed increase in biogas production.

4.6 *Nanocellulose*

Nanocellulose possesses thermal stability and surface morphology, with a specific focus on its shape and size, rendering it exceptionally well-suited as a reinforcing agent in the fabrication of bio-nanocomposites [96]. Nanocellulose is a naturally occurring nanomaterial sourced from readily available materials such as fibers of lignocellulose biomass. Nanocellulose can be utilized in the production of aerogels and foams, either in homogeneous compositions or as part of composite formulations [96]. The application of nanocellulose-based foams is being explored in packaging, serving as a potential substitute for foams based on polystyrene [96]. Nanocellulose particles find diverse applications, serving as reinforcing fillers in polymers, components in composites, materials with biodegradable properties, reinforcements for membranes, thickeners in dispersions, and carriers for drugs in both media and implants [97]. Nanocellulose, typically in the range of 10–350 nanometers in size, is commonly composed of two primary nanostructured forms known as cellulose nanocrystals (CNC) and cellulose nanofibers (CNF) [98]. CNCs exhibit a diameter of 3–5 nm, whereas CNFs have a diameter ranging from 10–30 nm [99]. Cellulose nanocrystals possess an impeccable crystalline structure, while cellulose nanofibers display a rigid, rod-shaped structure akin to spaghetti, featuring a high aspect ratio due to their small diameter and lengths spanning several microns [99]. Nanocellulose is characterized by a notable aspect ratio, robust mechanical stability, minimal thermal expansion, low toxicity, and a substantial number of surface-OH groups, facilitating straightforward chemical functionalization [95]. Due to numerous hydroxyl groups, nanocellulose maintains a stable structure in water [97].

Two particle sizes, small particles (S.P) with a diameter ranging between 0.4–0.5 cm, and large particles (L.P) with a diameter ranging between 4–5 cm, in size from sugarcane bagasse (SCB), were examined to explore their impact on nanocellulose production [96]. Chemical pretreatment was conducted using 2% w/v NaOH at 25 °C for 6 h, followed by acid hydrolysis with a 1% (w/v) ethanedioic acid solution for 48 h. The most effective method for nanocellulose

production was identified as a mild chemical treatment of the L.P of SCB followed by fungal treatment. A pretreatment process involving subsequent pretreatment through mild chemicals and the use of the fungus *P. chrysosporium* was developed, proving to be effective, cost-efficient, and eco-friendly for the production of nanocellulose from SCB. SCB was used to extract nanocellulose by simultaneously ultrasonic and chemical pretreatment [97]. After chemical pretreatment (17.5% w/v NaOH), ultrasonic waves were conducted at 70 °C for 2 h to accelerate the dispersion process of the nanocellulose particles. The results showed that the average size of the nanocellulose particles attained was 132.67 nm. CNCs, which were grafted by glycidyl methacrylate (GMA) to enhance their physicochemical properties and biological activity, were produced from SCB [98]. A high grafting yield, approximately 180%, was achieved through an increase in GMA concentration and a moderate concentration of the cerium ammonium nitrate (CAN) initiator (2 mmol/g). In the initial steps, alkaline pretreatment using a 2 % (w/v) NaOH. Subsequently, SCB was dissolved in an aqueous H_2O_2, serving as a bleaching agent, at a 1:1 ratio, maintained at 75 °C for 15 min [99]. Following this, the fibers underwent gentle acid hydrolysis using 1% (v/v) sulfuric acid solution at 80 °C for 1 h and were subsequently subjected to ultrasonication at 70% amplitude to defibrillate and disperse them. The findings revealed that CNFs exhibited a diameter ranging from 20–30 nm and a length extending up to various micrometers.

Table 3: Value-added products from sugarcane under specific pretreatment and hydrolysis conditions

Feedstock	Pretreatment Method	Pretreatment Condition	Hydrolysis/Fermentation Condition	Product	Product Yield	Ref.
SCB	Dilute acid pretreatment (H_2SO_4)	25% (w/w) H_2SO_4 at 121 °C for 60 min	Cellic CTec 2.0 (1 mg protein/g cellulose) at 42 °C 150 rpm	D-lactic acid	0.58 g/g	[100]
SCB	Syringic acid	9% syringic acid at 180 °C for 20 min	The cellulase dosage was 18 FPU/g cellulose.	Xylo-oligosaccharides	58.7%	[101]
SCB	Alkaline hydrogen peroxide (AHP)	5.5% (v/v) H_2O_2 at 65°C for 5 h	1:10 with cellulase and hemicellulose 10 FPU/g DM and 200 U/g DM at 150 rpm and 50 °C	Succinic acid	41.4 g/L and 63.8 %	[102]
SCB	Acid pretreatment	3.5% HNO_3 and heated at 90 °C for 2 h	Acid hydrolysis (50% of H_2SO_4) at 45°C for 30 min	Nanocrystalline cellulose	5.04 MPa gel strength, elongation value of 51.87%	[103]
SCB	Alkali pretreatment	10% sodium hydroxide w/v at 121°C for 1 h	Cellulase CTec2 at a loading of 5 FPU /g of dry biomass for72 h and 50 °C	Xylo-oligosaccharides	20.4 g/L	[104]
SCB	-	-	SCB mixed potassium carbonate and glycerol 0.02 g Pd/C	Bio-oil	21.3%	[105]
SCB	Dilute acid pretreatment	5% sulfuric acid (w/w) at 170 °C for 15 min	Y. lipolytica PSA02004 at 37°C and 7.5 pH for 72 h	Succinic acid	Productivity of 0.92 g/L·h	[106]
SCB	Alkaline pretreatment	50 g/L NaOH at 90 °C for 90 min under air atmos-phere	S. cerevisiae BCC39850 fermented at 30 °C for 48 h with shaking at 200 rpm	D-Lactic acid	Concentration of 23.41 g/L	[107]
SCB	Acid pretreatment	10% (w/v) of solid loading, and 0.5% (v/v) of H_2SO_4	10% (w/v) of solid loading, and 10 FPU/mL of Ctec2 at 50°C, pH of 4.8 for 72 h	Ethanol	0.49 g of ethanol/g of sugar	[108]
SCS	Acetic acid pretreatment	0.3–0.9 % (w/v) of CH_3COOH at microwave 170–220 °C for 2 min	Cellic CTec2 and *Clostridium beijerinckii* Br21 at 50 °C and 150 rpm for 48 h	Butyric acid	The yield of 0.46 g/g	[109]

Table 3: (*Continued*) Value-added products from sugarcane under specific pretreatment and hydrolysis conditions

Feedstock	Pretreatment Method	Pretreatment Condition	Hydrolysis/Fermentation Condition	Product	Product Yield	Ref.
SCS	Dilute sulfuric acid (H_2SO_4)	0.6% (w/v) H_2SO_4 162°C for 2 min at microwave	CTec2 and *Clostridium beijerinckii* Br21 at 150 rpm 50° C for 48 h pH 4.80	Butyric acid	The yield of 0.49 g /g	[110]
SCS	Dilute ethanol pretreatment	ethanol:distilled water (1:1, v/v) at 190 °C for 90 min	60 % (w/w) sulfuric acid at 45 °C for 45–105 min.	Lignocellulose nanocrystals	40–64 % of the total mass	[111]
SCS	Steam explosion (SE) pretreatment	200 °C and 15 bar for 10 min	Cellic CTec2 at 50 °C 150 rpm	Xylo-oligosaccharides	35 % w/w	[112]
SCB and SCS	Hydrothermal pretreatment	126.4-193.6 °C for 9.6-110.4 with a mass load of 10%	Hydrolyzed in 72% H_2SO_4 (w/w) for 1 h at 30°C	Xylo-oligosaccharides	53.3 mg/g (SCB) and 96 mg/g (SCS)	[113]
SCM	Dilute Sulfuric acid pretreatment	10% w/v of solid loading and 0.5% w/v of H_2SO_4 at 180 oC for 10 min	Cellulase Cellic CTec2	Ethanol	41.49 g/L	[114]
SCM	Sodium hydroxide pretreatment	0.5 M of NaOH at 80 °C for 2 h with shaking at 150 rpm	Autoclaving at 121 °C for 20 min Cellulase (Cellic CTec2)	Ethanol	72.37%.	[115]
SCM	-	-	20 g/L of SCM incubated with Pseudomonas mendocina CH50 for 16 h at 30 °C and at 200 rpm	PHAs	14.2%	[116]
SCM	-	-	R. glutinis R4 cultivated for 120 h in 100 mL of nitrogen-restricted GMY medium, utilizing SCM as the carbon source	Biodiesel	91%	[117]
SCM	-	-	Biomass loading of 5-13% with nitrogen as supplemented at 37°C, 220 rpm for 72 h by using B. licheniformis	Poly-γ-glutamic acid	76.848 g/L	[118]
SCM	N/Aa	N/Aa	Fermentation at 30 ± 2 °C and 150 rpm for 72 h with SCM as media by using B. amyloliquefaciens	Lactic acid	Production of 178 g/L·d	[119]

Note: [a]N/A means not available.

5 Economic and Environmental Impact of Sugarcane Biorefinery

In contrast to contemporary petroleum refineries, lignocellulosic biomass for biorefineries is easily obtainable, cost-effective, and conducive to straightforward scalability [69]. The transformation of biomass into valuable products offers numerous advantages, including the reduction of greenhouse gas emissions and environmental pollution, along with the provision of renewable alternatives to replace fossil-based fuels and products [4]. While striving to produce environmentally sustainable and economically viable products, the biorefinery concept has attained wide attention around the world. The processing of second-generation feedstock in biorefineries is gaining heightened attention as a way to improve the quality of life and foster a circular bioeconomy [24]. Sugarcane sequesters CO_2 during its growth period and later emits it upon combustion During electricity generation, this procedure leads to the release of only 0.624 kilograms of CO_2 per kilowatt-hour [4]. When employed as an activator, CO_2 improves the effectiveness of SCB fly ash in eliminating phenolic compounds from an

inhibitor cocktail. The activation procedure results in a substantial fourfold decrease in the amount of adsorbent required post-application [4].

Life cycle and economic analyses are conducted in tandem to assess the environmental, economic, and indirect impacts across all stages of a product, spanning from its creation to disposal [25]. The circular bioeconomy utilizes biomaterials as input and involves industrial processes and resource efficiency across the entire life cycle chain. A fundamental approach of the circular economy entails defining the end-of-life phase by practices such as reclaiming natural resources, utilizing renewable energy, eliminating hazardous chemicals, and adopting a zero-discharge approach. This necessitates the adaptation of overall operations and business concepts [69]. The life cycle assessment (LCA) methodology is deemed suitable for assessment and has been widely employed by researchers as a tool to ensure that sugarcane-based products truly deliver environmental benefits.

6 Challenges in Industrial Production

In order to optimize economic opportunities, it is advisable to explore further processing of by-products generated from primary biorefinery processes to create higher-value products, instead of immediately converting them into compost or fuel, which is generally regarded as a lower-valued product [19]. However, these process costs must be included in the assessment of the economy for scaling up on an industrial scale. The anticipated expense of producing second-generation biofuels suggests that it is significantly pricier than petroleum fuels when considering energy equivalence [25]. To minimize production expenses, it is crucial to tackle and surmount the diverse challenges related to transforming lignocellulosic biomass into biofuels and chemicals through biochemical methods. Every stage of lignocellulosic bioconversion contributes to the overall costs of the process, starting from pretreatment to disrupt the components in the cell wall, enzymatic hydrolysis, fermentation of monosaccharides, separation of residues, and culminating in the purification of final products [120]. Optimizing water consumption and advancing the pretreatment process through the use of environmentally friendly or green chemicals are imperative considerations.

However, a green method, especially biological approaches utilizing sugarcane wastes exhibits lower productivity and a slower conversion rate compared to the presently predominant fossil-fuel-based chemical production. This may result in reduced economic feasibility. During pretreatment processing, a series of compositional and structural changes take place, giving rise to new substances that have been confirmed to impede the bioconversion process [26]. Additionally, the intricacy and heterogeneity of biomass pose limitations on both conversion efficiency and costs [24].

Conventional biorefinery processes were constrained by limited raw materials and technology, restricting them to a single feedstock and thereby minimizing the production of value-added chemicals [69]. Moreover, the difficulties in biochemical conversion technology involve aspects such as reducing size, crystallinity, deactivating cellulase, and yeast tolerance to ethanol [28]. Achieving optimal cost-effectiveness and environmental sustainability in integrated biorefineries necessitates advancements in the selection of raw materials, conversion steps, and separation techniques. In order to improve the integration of the value chain, including pretreatment, extraction, and byproduct processing, there is a requirement for technological advancements to enhance product valorization. The integrated biorefinery process involves the processing and extraction of products, biomass pretreatment, and potential developmental outcomes, leading to continuous energy generation and the recycling of waste streams through a nearly zero-discharge system. To optimize the utilization of biomass, encompassing generated wastes from diverse conversion pathways, the integrated biorefinery is recognized [19]. Typically, chemical and/or biochemical routes are employed to transform this biomass into bioenergy [19]. The integration of thermochemical and biochemical pathways incorporates either with catalytic or without catalytic processes to transform organic particles derived from biomass into a range of bioproducts [69]. The fusion of thermochemical and biochemical routes involves non-catalytic or catalytic methods to convert organic particles obtained from biomass into various bioproducts. The development of diverse strains is crucial to decrease the requirement for building distinct biorefinery plants and to reduce additional chemical and energy inputs. In addition to progressing cutting-edge pretreatment techniques such as Fenton oxidation, organosolv, subcritical water

hydrolysis, ILs, and DES pretreatments, it is vital to implement these approaches in industrial facilities, along with comprehensive evaluations of profitability. Concerns about the environmental impact of chemical pretreatment of sugarcane residues primarily revolve around the extensive water usage and the application of hazardous chemicals in the procedure.

7 Conclusions

The need to explore new applications and maximize the value of sugarcane has arisen with the shift from manual sugarcane harvesting, resulting in a significant increase in the production of this relatively new residue. The advancement of technology, including improvements in pretreatment methods, fermentation approaches, and strain engineering, has accelerated the evolution of sugarcane waste biorefineries, enabling them to tackle and surmount current challenges. As indicated in this review, beyond the significant role of sugarcane byproducts in enriching soil, it emerges as an appealing feedstock with versatile applications in various fields, including bioenergy, biofuels, and composites. This is due to its makeup, broad accessibility, energy potential, and comparatively affordable expense. To attain process feasibility, there remains a necessity to optimize these processes effectively. This ensures the comprehensive utilization of sugarcane and aligns with the principles of a circular economy.

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Author Contributions

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Conflicts of Interest

The authors declare no conflict of interest.

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