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Review

Agro-waste valorization for sustainable economy of sugar mills in India

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Indian sugar mills produce a large volume of agro-waste sugar cane bagasse (SCB), which, due to its improper use, causes environmental issues. Contrastingly, the valorization of SCB by integrating advanced technologies for biochemical production can alleviate waste disposal problems, enhance resource utilization, and promote a circular economy. The present review explores recent advances in SCB-derived valuable biochemicals such as bioethanol, biogas, xylitol, carboxylic acids, 2,3-butanediol, and furfural using advanced pretreatment techniques and engineered strains. Furthermore, it discusses the challenges and opportunities in bio-chemical production, the economic and environmental assessment, and the implications of the Government of India's (GOI) valuable schemes for agro-waste valorization.

Keywords: Economic sustainability, Sugarcane bagasse, Sugarcane industries, Value-added products

Agro-based sugar industries have a considerable impact on rural livelihood in India. Approximately 50 million sugarcane farmers and around 0.5 million workers are employed in the sugar industry. In cane cultivation areas, the economic backbone of the farmers is inevitably dependent on sugarcane farming. Around 327 cooperative, 362 private, and 43 public sugar factories have been installed in India, with the efficient crushing capacity to produce about 339 lakh metric tonnes of sugar[1]. At present, around 133 sugar industries in India produce 214 crore liters of ethanol, and 206 cogeneration units generate 3,123 MW of power[2,3,] which highlights more than 70% of mills are still lagging in power and ethanol production.

In sugarcane processing, generated waste includes bagasse, mud, trash, and other materials. The Indian sugar industries produce more than 80 MMT of SCB in crushing season[4]. Generally, every 1 tonne of crushed sugarcane generates 260-280 kg tonnes of wet bagasse[5]. A part of SCB is used for boiler heating and cogeneration, press mud or filter cake is used as fertilizer or sometimes burnt in brick kilns, and molasses is often diverted to distilleries to produce 1G ethanol by fermentation[6]. In the Indian sugar mills, sugar is the main source of revenue, while molasses and press mud are the subsidiary income sources. The bagasse is typically used for heating boilers and electricity production. Except this, SCB is treated as waste material. It has been estimated that near about 50% of the bagasse is often discarded. Incineration of SCB produces excessive fly ash, carbon dioxide, and other gases that can cause severe environmental pollution[7].

In recent times, the transformation of agro-waste into the economy, referred to as a "circular economy," has gained enormous attention due to its resource re-utilization concept[8]. In this context, sugar mill waste valorization provides a platform to create value-added chemicals in the line of a circular economy[6]. Current research has proven that agro-waste SCB is a potential resource and attractive alternative to fossil fuel to create bio-based chemicals such as 2G-ethanol, organic acids, furfural, xylitol, 2,3-Butanediol, and other valuable biochemicals. To explore the implementation of a circular economy in the sugar industry, it is crucial to critically review existing practices and understand the constraints[6].

In the present review article, with our previous work on biowaste[9-12], we have attempted to explore the potential applications of SCB apart from cogeneration and boiler heating. Moreover, we elaborated on recently published synthetic methods for SCB conversion to biochemicals. A circular economy implementation and challenges in biochemical

production on a commercial scale have also been discussed. Besides, we have also discussed various schemes recently announced by the GOI regarding biomass conversion into biochemicals. The manuscript comprises the following sections: an overview of SCB, various valorization methods, the circular economy, challenges, and opportunities in the SCB-based biorefineries setup for biochemical production.

Sugarcane bagasse (SCB): An overview

Sugarcane (*Saccharum officinarum*) is a perennial grass of the family Poaceae, primarily cultivated for sugar production from its sap[13]. It is grown in subtropical and tropical areas. It is the world's largest crop by production quantity, with 1.8 billion tonnes (2017) cultivated in more than 90 countries[14]. About 70% of sugar produced in the world comes from sugarcane[15]. After crushing the cane for the extraction of juice, solid waste is left, referred to as bagasse. While the clarifying extracted juice, soil, and other components are separated called press mud. The clarified juice is then evaporated and crystallized to get the raw sugar. In the crystallization process, a liquid is separated termed molasses.

Excluding sugarcane juice, the rest of the material, such as trash (40-44% cellulose, 30-33% hemicellulose, 17-22% lignin, and 4-5% ash), press mud (10-30% fiber, 5-15% crude protein, 5-10% sugar, 4-10% SiO_2, 1-4% CaO, 0.5-1.5% MgO, 1-3% P_2O_5, and 9-10% ash), and bagasse are rich in organic and inorganic components[16].

SCB is a heterogeneous solid material composed of cellulose, lignin, and hemicellulose as major constituents, which create a more complex and recalcitrant structure (Fig. 1). The cellulose is a polysaccharide composed of 3000 or more glucose units that comprise about 33% of all vegetable matter. Hemicellulose is a complex carbohydrate consisting of hexose, pentose sugars (xylans), uronic acid, and arabinose. Due to the higher concentration of cellulosic material, the bagasse is a valuable source of fermentable sugar[17].

A literature survey revealed that the SCB components such as cellulose, lignin, hemicellulose, fat, waxes, proteins, ash, and other constituents have variable concentrations (Table 1). From the reports, it is clear that cellulosic components have higher concentrations than other constituents.

Bio-based fuels and platform chemicals

Bioethanol

As a green solvent and starting material for many organic compounds, bioethanol has gained enormous importance in synthetic chemistry[30]. Besides, bioethanol plays a pivotal role in the transportation sector as a biofuel. This biofuel obtained from

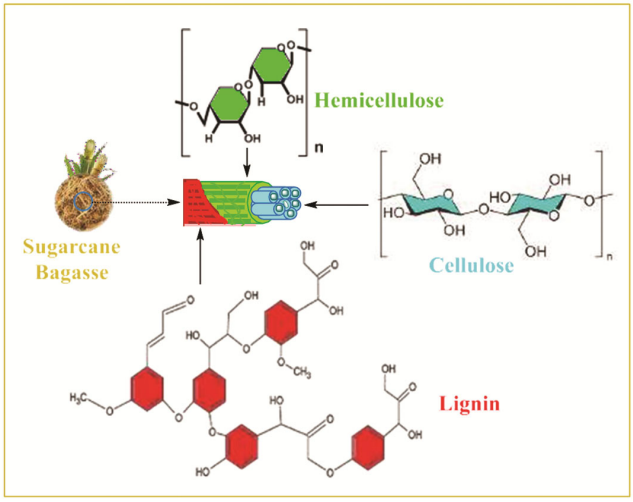

Fig. 1 — Structure of lignocellulosic biomass with cellulose, hemicellulose and lignin

Table 1 — Chemical composition of sugarcane bagasse (%)

Cellulose	Hemicellulose	Lignin	Saccharose	Glucose	Fat andwaxes	Protein	Ash	Ref.
56	6	29	-	-	-	-	7	(18)
40	24.4	15	14	1.4	0.6	1.8	5	(19)
41.8	28	21.8	-	-	-	-		(20)
55.2	16.8	25.3	-	-	-	-	1.1	(21)
40-43	28-30	9-11	-	-	2-2.5	8-9	5-6	(22)
36.32	24.7	18.14	-	-	-	-		(23)
69.4	21.1	4.4	-	-	5.5	-	0.6	(24)
46	24.5	19.5	-	-	3.5	-	2.4	(25)
50	25	25	-	-	-	-	-	(26)
38.59	27.89	17.79	-	-	-	-	8.80	(27)
42.00	28.00	21.00	-	-	-	-	3.00	(28)
35-50	20-25	15-25	-	-	-	-	4-6	(29)

lignocellulosic biomass is a promising alternative to fossil fuels. Good octane number, high oxygen content, clean and green fuels, sustainability, and simple storage are the advantages of bioethanol[31]. Sugarcane bagasse is a rich source of glucose (hexose) and xylose (pentose). The cellulose and hemicellulose fractions of SCB are hydrolyzed to produce hexose and pentose sugars. By using hexose sugars, microorganisms produce bioethanol. Several organisms, such as bacteria, fungi, and yeast are used for the conversion of bagasse to bioethanol. *Saccharomyces cerevisiae* can ferment hexose sugars, and *Pachysolen tannophilus* is a promising pentose-fermenting organism. Therefore, for the efficient conversion of SCB to bioethanol, a mixed culture of microorganisms could be considered[32].

For effective separation of complex fractions and easy accessibility of cellulosic biomass, physical, physiochemical, chemical, or biological pretreatment methods are employed (Fig. 2). After a suitable pretreatment and enzymatic hydrolysis, the obtained hydrolysate is separated from solid residue by filtration, concentrated and detoxified. Then the fermenter is charged with detoxified hydrolysate and suitable microorganisms. After fermentation for a certain period, the prepared raw bioethanol is distilled to get the pure bioethanol[33].

Integrating previously adapted pretreatment techniques with newly emerging technologies like MW, and ultrasonication increases the number of trial possibilities. Several pretreatment trials were proposed and investigated in order to develop sustainable SCB hydrolyzing techniques for fermentable sugar[34].

The effects of fungal (*Ceriporiopsis subvermispora*) pretreatment in combination with MW hydrothermolysis of SCB on enzymatic saccharification and fermentation were evaluated by Sasaki and co-workers.[35] It was observed that MW hydrothermolysis improved enzymatic saccharification and ethanol fermentation of SCB. MW hydrothermolysis with and without fungal treatment gave 35.8% and 27.0% yields of bioethanol, respectively. This process could be beneficial for 2G ethanol production. In another experiment, Yu *et al.*[36] reported bioethanol production from WPS of SCB with molasses. The MW-assisted dilute H_2SO_4 pretreatment method was used, which showed a reduction in the formation of toxic compounds. In this process, a higher concentration of ethanol (41.49 g/L) was obtained by fed-batch SHF. Amoah and colleagues studied the effect of ionic liquid on the co-fermentation of xylose and glucose via SSF of SCB using xylose-assimilating *Saccharomyces cerevisiae* yeast strain. IL 1-butyl-3-methylpyridinium chloride ([Bmpy][Cl]) showed higher saccharification efficiency of SCB resulting in 0.7 g/L xylose and 2.3 g/L glucose and offered 84% ethanol yield[37].

Recently, Da Silva *et al.*[38] implemented an ultrasonic-assisted alkaline pretreatment method for ethanol production from SCB using Cellic® CTec3 (Novozymes) and Thermosac® Dry (Lallemand) strains. Enzyme hydrolysates were simply fermented by the *S. cerevisiae* (industrial strain), resulting in a fermentation efficiency higher than that of steam-exploded and alkali-washed steam-exploded SCB. The ethanol production from sonicated alkali-washed SCB was 40.6%, which was higher than other pretreatment methods. In another work, Neves *et al.*[39] reported steam-exploded and enzymatic hydrolysis (using commercial *cellulase Cellic* CTec2) of SCB (native and ethanol-extracted). It was converted into fermentable sugar and after fermentation (using an industrial strain of *Saccharomyces cerevisiae*), 0.58 g

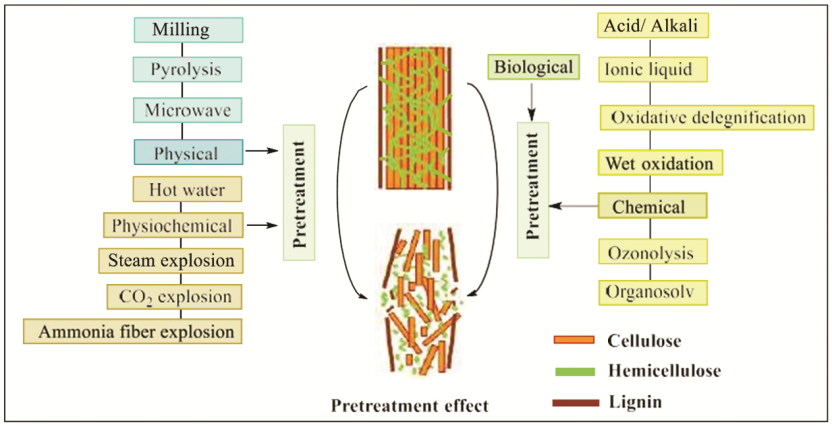

Fig. 2 — Pretreatment methods

L^{-1} h^{-1} of 2G ethanol was obtained. While, Hilares *et al*.[40] evaluated organosolv pretreatment such as Glycerol-H_2SO_4 for SCB in terms of temperature, solid loading, solvent/acid concentrations, and reaction time using factorial design. A 0.38 g/g SCB (0.57 g/L.h of productivity) of bioethanol has been achieved using an industrial strain *Saccharomyces cerevisiae*.

Many advanced processes, such as the biochemical method (pretreatment, hydrolysis, and fermentation of SCB)[41], the thermo-catalytic method (SCB gasification and catalytic conversion of syngas)[42], the hybrid method (SCB gasification and syngas fermentation)[43] or the glycerol method (fermentation or catalytic conversion of glycerol generated during biodiesel production)[44] can be employed for the production of bioethanol.

Biogas

Due to the skyrocketing prices of fossil fuels, their depletion, uncertain supply, and GHG emissions after consumption are leading the world in search of smart fuels. As an alternative to fossil fuels, biogas can circumvent the problems associated with fossil fuels. Anaerobic digestion (in the absence of oxygen) of biomass is rather a complex bio-degradation process in which organic components are decomposed by bacteria to produce CH_4 and CO_2 as the major gaseous by-products. Acidogenesis, acetogenesis, and methanation are the degradation stages. Some common bacteria such as *Bacteriocides*, *Clostridia*, *Bifidobacteria*, *Enterobacteriaceae*, and *Streptococci* are found in the digester[45].

Liu and co- workers[46] reported sequential biogas production from SCB based on a solid fed-batch SSF process. After the evaporation of ethanol, the non-fermented substrates in stillage were used for biogas production. The comparative study revealed that after 6 days, the CH_4 production yield from SCB (306.974 mL/g volatile solid) was higher than molasses (128.958 mL/g volatile solid). In another experiment, Nosratpour and co-workers[47] used Na_2CO_3, Na_2SO_3, and CH_3COONa at variable concentrations for the pretreatment of SCB, as well as hydrothermal pretreatment for SCB. These pretreatments were conducted at different temperature ranges. They found that the highest biogas (239 ± 20 NmL CH_4/g VS) and ethanol (7.27 ± 0.70 g/L) were obtained for 0.5 M Na_2CO_3 pretreated solution at 140 ^{0}C. Armah and co-workers[48] carried out a comparative study of the anaerobic co-digestion of SCB with sugar wastewater (SWW) and SCB with dairy wastewater (DWW). At the optimum temperature of 25 ^{o}C, SCB with SWW produced 4.975 m^3/Kg VS biogas yield, while at the optimum temperature of 55 ^{o}C, SCB with DWW produced 0.160 m^3/Kg VS biogas yield. That means a higher biogas yield resulted from SCB with SWW.

Xylitol

Xylitol is a naturally occurring polyalcohol found in fruits and vegetables. It is widely used in sugar-free chewing gum, candies, and mints. Xylitol, a natural sugar substitute, has prebiotic and anti-cariogenic properties, a low caloric value, sucrose-like sweetness, a low glycemic value, the ability to inhibit microbial growth, and an insulin-independent mechanism[49]. Xylitol is a promising alternative to sugar. The demand for xylitol has recently increased rapidly due to an increase in the number of diabetics. In addition, xylitol finds many commercial applications in various industrial sectors, such as food, pharmaceuticals, and dental-related products[50]. By using direct extraction, chemical hydrogenation, and biotransformation xylitol is prepared. Because of the expensive chemical route, over the past few decades, efforts have been taken to develop cost-effective and environmentally friendly biotechnological processes using organisms[51].

Rao et al.[52] reported the production of xylitol from SCB hydrolysate using a natural isolate, a *Candida tropicalis* strain. They performed three different combinations of mixed sugar control experiments; however, less yield of xylose was obtained. In their experiment to improve yeast growth and xylitol yield from these hydrolysates containing inhibitors, cells were adapted in the hydrolysate medium by subculturing for 25 cycles that offered 0.65 g/g of xylitol. Xylitol production by fermenting xylose hydrolysate from SCB using *C. tropicalis* 31949 strain has been reported by Xu et al.[53] Under the optimal fermentation conditions (10 % inoculum quantity, 20 h, initial xylose concentration 100 g/L) *C. tropicalis* 31949 could ferment SCB hydrolysate, which was pretreated by vacuum concentration and activated carbon detoxification decoloration, to produce 62.9800 g/L of xylitol.

Prakash *et al*.[54] reported the production of xylitol from SCB using a new isolate thermotolerant yeast *Debaryomyces hansenii*. As compared to free cells, the Ca-alginate immobilized *D. hansenii* cells produced 73.8 g of xylitol from 100 g/L of xylose.

Carvalho et al.[55] reported the xylitol production from SCB. They used SCB hydrolysate for batch xylitol production in the stirred tank reactor with *Candida guilliermondii* cells entrapped in Ca-alginate beads. By using a five-fold concentrated hydrolysate, the initial cell concentration (1.4 g/L), air flow rate (1.30 L/min), agitation speed (300 rpm), and the initial pH (6.0) of the fermentation medium resulted in a xylitol production of 47.5 g/L after 120 h of the fermentation.

Thapa and co-workers[56] reported the production of xylitol from SCB by using the response surface methodology. Xylitol was produced through optimization of ultrasound-assisted alkaline pretreatment for the xylan extraction from SCB followed by enzymatic hydrolysis of xylan to xylose and microbial fermentation using yeast (*Candida guilliermondii*), bacteria (*Corynebacterium glutamicum*), and their mixed culture. Several experimental processes were run for xylitol production. At 0.73 M NaOH pretreatment with a 1:38.55 solid-to-liquid ratio, and ultra-sonication (34.77 min.), maximum xylan recovery was 12.059%. The enzyme concentration (400 U/g of xylan) at 48 h of the incubation exhibited 81. 51 mg/g yield of xylose. *Candida guilliermondii* yeast produced 0.43 g/g of xylitol yield after 72 h. This green route could be a suitable alternative to chemical processes for xylitol production.

Due to the rise in health and weight-conscious consumers, xylitol demand is expected to grow in sugar-free and low-calorie food products[57]. The global market for xylitol is estimated at 190.9 thousand metric tons, valued at $725.9 million in 2016. Due to overconsumption, the demand for xylitol will exceed 266.5 thousand metric tons, valued at $1.37 billion by 2025[58].

The implications of lignocellulosic biomass for the production of value-added chemicals like xylitol can help improve the economy of the sugar industry and also mitigate environmental pollution. However, the production of xylitol on a commercial scale using lignocellulosic material is still facing many challenges, such as expensive pretreatment, detoxification, and fermentation processes. In addition, the release of inhibitors, inefficient xylitol recovery, and moderate activity of organisms are affecting the overall cost of xylitol production. Because of these challenges, xylitol production by a chemical process is still dominant. To overcome these hurdles, the design and development of a cost-effective pretreatment process, control of the release of inhibitors, use of effective microorganisms, operational simplicity, and a good yield of xylitol are opportunities for upcoming researchers.

Succinic acid

A naturally appearing succinic acid ($C_6H_6O_4$) (SA) was derived from amber by distillation[59]. Nowadays, it is industrially produced from the hydrogenation of malic acid, the oxidation of 1,4-butanediol, or the carbonylation of ethylene glycol. Global production of SA is estimated at 16000-30000 tons/year, with an annual growth rate of around 27.4% to reach $1.8 billion in 2025[60].

Being a common organic acid, SA is used in several agricultural, pharmaceutical, and food processing industries as a precursor to producing many chemicals such as green solvents, lacquers, perfumes, plasticizers, dyes, and photographic chemicals. It also finds applications as an ion chelator, an additive, an antibiotic, and a curative agent[61]. Chen and co-workers[62] reported the production of SA from SCB using NaOH pre-treatment and multi-enzyme hydrolysis. They have used a microorganism *A. succinogenes* CCTCC M2012036 for converting reducing sugarsinto SA in a bioreactor with a sugar-fed strategy to prevent cell growth limitation. Three cycles of fermentation without activity loss were offered 80.5% and 1.65 g/L SA yield and productivity, respectively.

Borges et al.[63] reported SA production from acid-pretreated SCB hemicellulose hydrolysate using the *Actinobacillus succinogenes* organism. They found that the conversion yield of SA from SCB was relatively high in the batch cultivation of the strain *Actinobacillus succinogenes*. Under the optimized conversion conditions, as per the statistical analysis, a 22.5 g/L yield of the SA was achieved in hemicellulose hydrolysate fermentation. In another experiment, Ong et al.[64] reported the co-fermentation of glucose and xylose from SCB into SA using the *Yarrowia lipolytica* strain. This co-fermentation process offered a 0.58 ±0.01 g/g yield of SA. A pretreated SCB with hot water, ethanol, and NaOH, and obtained hydrolysate used as a carbon resource for SA production was recently been reported by Chen and co-Workers[65]. An in-situ SSSCF procedure for bio-succinic acid production was developed. *A. succinogenes* ATCC55168 organism and NaOH showed good resistance to the phenols generated during alkali pretreatment. It indicates the use of alkali pretreatment liquid to neutralize the fermentation broth is feasible and can reduce the

spent alkali emission and alkali consumption. The yield, productivity, and conversion rates of SA processed by SSSCF were 41 g/L, 300 mg/L/h, and 320 mg/g dry, respectively. In this comprehensive comparison, for every Kg of succinic acid production, the developed coupling method reduced the consumption of NaOH (0.14 kg), water (233.5 L), energy (14000 kJ), and effluent emission (7L), and increased the succinic acid productivity by 1.7 times than non-coupling procedure.

Considering the production route, the market value of chemically produced SA is $2500/ton, while that of biotechnologically produced succinic acid is $2860/ton[66]. Although the chemical route is somewhat cheaper than the bio-based route, GHG emissions and fossil fuel consumption are the major issues of chemical production. In order to overcome these problems, opportunities for bio-based process improvement need to be intensified to reduce processing costs by developing effective SCB pretreatment, suitable organisms, and high-yielding fermentation processes.

Lactic acid

Lactic acid (LA) and its derivatives have numerous applications in the pharmaceutical, cosmetic, and food processing industries. Recently, it has received a lot of attention as a feedstock for the production of polylactic acid, which is useful for environmentally friendly biodegradable plastic. LA is synthesized using chemical synthesis or microbial fermentation. Currently, over 90% of LA is synthesized via fermentation. The fermentation process produces optically pure L- or D-lactic acid, depending on the strains chosen[67].

An eco-friendly integrated system for highly pure LA production from SCB was reported by Oonkhanond and co-workers[68]. Selective SCB fractionation was conducted to produce cellulose-rich material for separate saccharification and fermentation to LA. In this study, SCB was pretreated using two-step methods, such as acid ethanolysis and alkaline peroxide that produced 87.1% of glucose. The SCB hydrolysate was fermented using the *Lactobacillus casei* strain that produced 21.3 g/L of LA after 120 h with a productivity of about 0.63 g/L·h. The low-flux nanofiltration membrane used for LA separation exhibited a higher performance (glucose rejection of about 93.28%) compared to the high-flux membrane.

In another study, dilute acid pretreated SCB was used as a carbon source for LA production. Cellulose hydrolysate obtained from the enzymatic hydrolysis of hemicellulose hydrolysate (HH) was fermented using *Lactobacillus spp*. To investigate HH fermentation to lactic acid, five strains of *Lactobacillus* spp., such as *L. coryniformis torquens* ATCC 8041, *L. coryniformis coryniformis* ATCC 25602, *L. helveticus* ATCC 15009, *L. pentosus* ATCC8041, and *L. delbrueckii lactis* DSM 20076 were screened from which *L. pentosus* ATCC8041 strain revealed the best results. Maximum LA concentration (42.5 g/L) and productivity (1.02 g/L·h) were achieved in the HH batch. In this reported fermentative method, the total consumption of xylose and glucose by the *L. pentosus* strain produced 65.0 g/L of lactic acid with a 0.93 g/g yield and 1.01 g/L·h of productivity[69].

Azaizeh et al.[70] reported LA production from various agricultural residues using the strain *Bacillus coagulans* with yeast extract. SCB fermentation using the strain *Bacillus coagulans* yeast extract resulted in 46.5 g $LA \cdot L^{-1}$, and a yield of 0.88 g $LA \cdot g^{-1}$ sugars. Recently, Nalawade et al.[71] reported LA production from SCB using *Bacillus coagulans* NCIM 5648 strain. Based on bagasse composition, enzymatic hydrolysis, and LA productivity, multiple pretreatment methods such as acid, alkali, hydrodynamic cavitation, and their combinations were evaluated. The L-lactic acid produced from SCB (100.0 g) pretreated with alkali (26.16 g), acid (8.78 g), sequential acid-alkali (14.15 g), sequential alkali-acid (14.33 g), and cavitation with alkali (24.61) showed that alkali pretreatment is quite suitable with L-lactic acid titer (68.7 g/L), productivity (2.86 g/L/h) and yield (0.92 g/g) compared to other methods.

Itaconic acid

Itaconic acid ($C_5H_6O_4$) as an organic acid finds a wide range of applications in the pharmaceutical, agricultural, and medical fields. It is used as a co-monomer for the production of detergent builders, surfactants, polymers, thermoplastics, and polyester resins. It was previously produced from citric acid distillation, now it is commercially produced via submerged fermentation using suitable fungal strain[72,73].

Since 1960, IA has been produced by fermentative methods from carbohydrates (glucose or molasses) using fungal strains such as *Aspergillus itaconicus* or

Aspergillus terras. The smut fungus *Ustilago maydis* is also used as an alternative fungal source[74]. Paranthaman and coworkers[75] reported the preparation of IA using fungal strains such as *Aspergillus oryzae, Aspergillus niger, Aspergillus flavus*, and *Penicillium* spp. via solid-state fermentation of SCB powder. Fungal strain *A. niger* produced the highest IA level (8.241 ± 1.5 mg/kg) when SCB powder was fermented in a solid state at 35 °C with 3.5 pH compared to other species. In another study, the process design and economic analysis of a biorefinery co-producing IA and electricity from SCB have been investigated by Nieder-Heitmann et al.[76]. The three IA biorefinery scenarios were designed and simulated in Aspen Plus® (version 8.8). The economic analyses indicated that cheaper feedstock reduced the IA production cost and resulted in favorable coal-supplemented IA biorefinery. It was also investigated that energy self-sufficient biorefinery was not economically viable. In general, the process improvements made in IA production cause an IA biorefinery, annexed to a CHP and existing sugar mill, to be a realistic endeavor with a great market potential for sugar mills.

The main application of IA is the manufacture of SBR latex. SBR latex is used in the construction industry to bond layers of cement, mortar, and concrete to improve chemical resistance. The IA is also used as a chillant, and dispersant agent in synthetic latex, and in the superabsorbent polymer. Meeting the growing demand for bio-based IA manufactured from sugarcane is the biggest challenge because of insufficient sugarcane availability. The global market size of organic acids such as LA, SA, and IA has been shown in Figure 3 (Ref. 77). SCB is a cheap and abundant resource of carbon for IA production. However, IA production on a commercial scale at an affordable cost must be developed using an improved SCB-based biorefining process with a high titre of IA.

2,3-Butanediol (BDO)

BDO is used in the manufacture of perfumes, printing inks, synthetic rubber, fuel additives, antifreeze agents, food, pharmaceuticals, and intermediate chemicals for plastic and rubber. The BDO demand is increasing regularly due to its widespread applicability. Global demand for BDO was $76 million in 2020, and it is expected to reach $94 million by the year 2027, growing at a CAGR of 2.9 % from 2021 to 2027 (Fig. 4)[78].

Currently, BDO is commercially synthesized by a chemical route using petrochemicals. Although the fermentation procedure is still not economically viable compared to the chemical method, uncertainty in crude oil prices, depletion of fossil fuel reservoirs, and GHG emissions are the facts associated with the chemical route. To overcome these disadvantages, the fermentative route is the economically and environmentally friendly alternative to producing BDO from waste biomaterial. A natural abundance of renewable feedstock as a carbon source, mild reaction conditions, strain and process improvement, and the involvement of stereo-specific enzymes in the microbial system are the key advantages in the biological production of BDO compared to the petrochemical route[79].

Numerous yeasts or algae can produce BDO, but the yield is comparatively low. In contrast, the

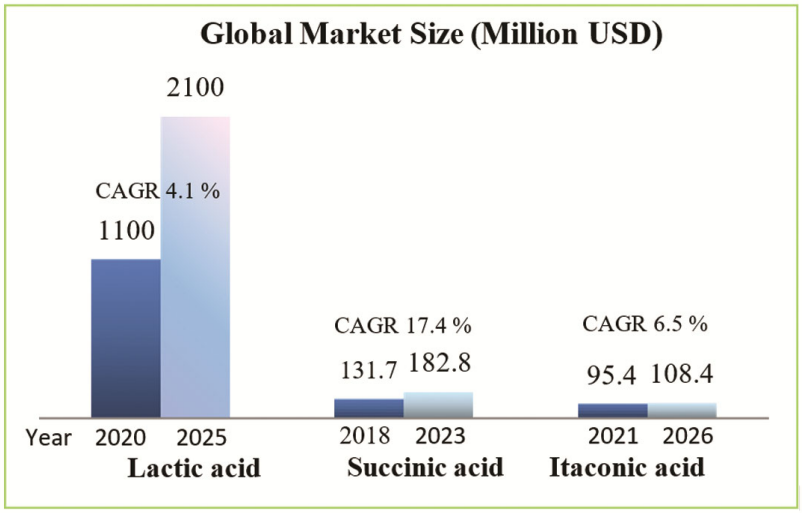

Fig. 3 — Global market sizes of lactic acid, succinic acid and itaconic acid

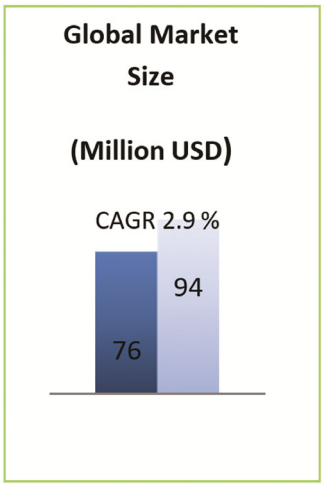

Fig. 4 — Global market size of BDO

bacteria allied to the families of *Enterobacteriaceae* and *Paenibacillaceae* enable the production of BDO in large amounts. Recently, *Pseudomonas chloroaphis* (*Pseudomonadaceae* family) has gained attention due to the formation of an optically active stereoisomer (L-form) in plant rhizospheres[80].

In recent trends, the development of environmentally benign fermentative methods using suitable bacterial strains has significantly increased BDO production from renewable feedstock. As a result, novel fermentation methods for BDO production have recently been reported in the literature that will help BDO production on a commercial level. Um *et al*.[81] reported BDO production from pretreated SCB by a fermentative method using the *Enterobacter aerogenes* strain. This study proved that pathway engineering would be an effective tool for developing industrial strains utilizing SCB.

Narisetty and colleagues[82] reported a high yield recovery of BDO from fermented broth accumulated on xylose-rich SCB hydrolysate by a mutant strain of Enterobacter hudwigii using an aqueous two-phase extraction system. After testing various organic solvents and inorganic salts, as well as optimizing ATPS, it was discovered that adding 30% w/v ammonium sulfate to clarified fermented broth facilitated BDO extraction in isopropanol (0.5 v/v) with maximum recovery (97.9 4.6%) and partition coefficients (45.5 3.5). Under optimized conditions, unfiltered fermented broth exhibited similar BDO recovery and partition coefficients. The present study reveals that a high BDO recovery is possible even without the removal of microbial biomass and unspent proteins.

In the comparative study, the effect of a mutant strain of *Enterobacter hudwigii* on detoxified and non-detoxified xylose-rich hydrolysate obtained from hydrothermally pretreated SCB and pure xylose for BDO production was investigated by Amraoui *et al*.[83]. From pure xylose, BDO production was 71.1 g/L with an overall yield (0.40 g/g), and productivity (0.94 g/L·h). From detoxified hydrolysate, the BDO production was 63.5 g/L with a yield (0.36 g/g), and productivity (0.84 g/L·h), while non-detoxified hydrolysate produced 32.7 g/L of BDO, with a conversion yield (0.33 g/g), and productivity (0.43 g/L·h). Accumulated BDO on pure xylose and detoxified SCB hydrolysate were separated by the aqueous two-phase system using ammonium sulfate as a salting-out agent, and isopropanol as an extractant, resulting in more than 85% BDO recovery. The novel method for BDO production from SCB using the *E. hudwigii* strain reported here is cost-effective, environmentally friendly, and useful for industrial production.

Furfural

Furfural (C_4H_4OCHO) is an organic liquid that is found in various agricultural by-products. The main precursor for furfural production is the acid-catalyzed dehydration of pentoses derived from hemicellulose. It is a non-petroleum-based, renewable, chemical feedstock that can be converted into a variety of solvents, polymers, fuels, and others[84]. On hydrogenation, furfural gives furfuryl alcohol, which is used to produce furan resins. These furan resins are used in thermoset polymer matrix composites, cement, adhesives, coatings, and casting resins[85]. According to recent data, the global furfural market will grow at a CAGR of 4.9% from $551 million in 2019 to $700 million by 2024 (Fig. 5)[86]. Due to a good market value and rising demand for furfural, and its derivatives, improved biotechnological methods for furfural production from SCB have been reported in the literature.

Wang and co-workers[87] reported fast and simultaneous furfural production as well as cellulose-rich residue from SCB using a PPAWS. There is a problem associated with the diversity in the product yield of platform chemicals derived from lignocellulosic biomass via a one-pot acid/organic solvent system. The present PPAWS technology is able to resolve this problem by allowing the selective conversion of hemicellulose to furfural, with high retention of cellulose. By using this novel PPAWS

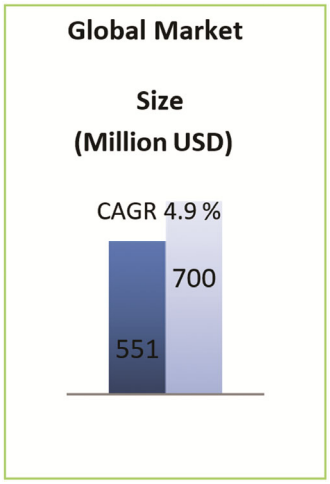

Fig. 5 — Global market size of Furfural

(acetone/water; 7:3 v/v) at 150 °C under 1.5 MPa N_2, furfural production (yield 45.8%), delignification (lignin removal rate 89.8 wt%), and cellulose residue (retention rate 72.9 wt%, purity 92.5 wt%) from SCB were achieved within a short time (5 min.).

A furfural production experiment was performed in a batch reactor. It was also reported that increased pressure inhibits aldol condensation of acetone alone or acetone and furfural.

In another study, Bizzi and co-workers[88] reported the UAAH process for furfural production from lignocellulosic biomass. Several feedstock materials were screened for furfural production under the UAAH process, of which SCB produced 49.9 ± 5.1 mg/g of furfural with a 4.99% yield by employing an ultrasound cup horn system operating at 20 kHz, HNO_3 (20 mL of 4 mol /L) at 30°C, 50% amplitude, and 60 min. of sonication. A cup horn system produced a higher yield compared to mechanical stirring. The UAAH is a promising alternative process to the conventional one with several advantages, such as atmospheric pressure, low-temperature conditions, reagent savings, no lignin removal step, and single-step production of furfural.

In a recent report, Catrinck *et al.*[89] investigated furfural production from SCB via a one-step process using niobium-based solid acid catalysts in an aqueous medium. At 150 °C after 5h, the furfural yield was 52.1 g/kg produced in the presence of NbO, while 59.3 g/kg yield was obtained in the presence of NbP. The yield of xylose and arabinose for NbO was 69.7 g/kg, and 6.4 g/kg, respectively, while, 147.4 g/kg and 11.1 g/kg for NbP, respectively. Hemicellulose, after depolymerization and hydrolysis converted to monomers, which on dehydration, produced furfural, while cellulose and lignin remained and could be used for further processing. It was further reported that while studying the effect of variable SCB genotypes on furfural production, it was found that furfural yield was independent of the genotype used.

The economic and environment assessment

A natural feedstock is a promising resource for biochemical production that helps reduce fossil fuel demand and carbon emissions, alleviate waste disposal problems, and divert waste into the economy. In the context of the circular economy, the agro-waste hierarchy promotes waste prevention as the highest priority, followed by reuse and recycling. Incineration of agro-waste leads to energy recovery; however, the opportunity to gain value-added biochemicals is extensively lost. Moreover, for wet agro-waste incineration, a higher temperature is required, which can increase the carbon footprint. Therefore, agro-waste incineration needs to be prevented, and its management should be shifted towards the recycling and reuse of agro-waste for value-added products[90]. The use of SCB for boiler heating generates fly ash, water vapour, and oxides of C, N, and S that cause severe environmental pollution. The use of ash in landfill can pollute groundwater, soil, and other natural bodies. Therefore, SCB for boiler heating is not the best option. Similarly, dumping of SCB (<50%) in the environment is also causing pollution. A recent study showed that SCB to biochemical production such as ethanol improved air quality by a substantial reduction of oxides of N (97%), S (50%), and particulates (30%). However, SCB is not a suitable candidate for methanol production because this process is expensive and emits methane gas which has a profound environmental impact[91]. Another report showed that SCB-derived lactic acid reduces up to 90% environmental impact than fossil-based lactic acid[92].

The techno-economic assessment (TEA) of biorefinery product succinic acid from SCB was carried out by Shaji et al.[93]. The process includes acid pretreatment, fermentation, separation, and purification. The experimental data showed that processing dry bagasse 4 tonne/h produces 405 kg/h of succinic acid with an equal quantity of acetic acid as a side product. TEA results exhibited that at present the process is not economical, but an increase in fermentation yield will make it cost-effective. The

product cost depends on pretreatment and the strain used in fermentation.

In another study, Mancini *et al*.[94] reported that the use of an ion-exchange column, nanofiltration, and anion-exchange membranes can reduce succinic acid manufacturing costs. They further reported that low-*p*H aerobic fermentation is likely to be a more sustainable strategy compared to neutral-*p*H aerobic fermentation. Economic and environmental analysis of bio-succinic acid production: From established processes to a new continuous fermentation approachwith in-situ electrolytic extraction.

Júnior et al.[95] reported the techno-economic analysis of itaconic acid (IA). IA was produced by fermentation with different recovery methods such as crystallization, adsorption, and electrodialysis. Comparatively, the adsorption method showed the lowest production cost of IA. The IA production on a commercial scale lies in the improvement of three technological bottlenecks such as inexpensive carbon source, fermentation with higher titles of IA, and lower downstream cost.

As an economically and environmentally benign alternative to fossil fuels, bioethanol has gained increasing importance. Nearly, 35% of ethanol is produced worldwide using sugarcane. The two commercial plants producing (40 and 84 Ml/y) sugarcane lignocellulosic ethanol and many other production plants are in progress worldwide[96,97]. Various possibilities for annexing a 2G-ethanol biorefinery to existing sugar mills in South Africa have been studied. The results showed that annexing a biorefinery to an existing sugar mill is more economic than a standalone biorefinery[98].

Indian Government policies on waste valorization

The GOI has set a target to reduce fossil fuel imports by 10% by the year 2022. The National Policy on biofuels announced in 2018 aims to accelerate the promotion of biofuels with indicative targets of achieving 20% blendingin gasoline and 5% in a diesel by the year 2030[99]. To meet the target of a 10% ethanol blend with the projected demand for gasoline in 2021-22, about 450 crore liters of ethanol will be required. Currently, the country produces about 300 crore liters of ethanol[100]. In order to meet the ethanol demand, lignocellulosic SCB could be the best option.

In 2016, a 2G-ethanol project was launched at Kashipur in the Uttarakhand state of India. This is the country's first plant with a capacity to consume 10 tons of biomass per day, and it is based on indigenous technology[101]. Bioethanol production will be the savior of the Indian sugar industry in the downturn in sugar prices. Due to growing ethanol use for fuels and soft drinks, India's bioethanol market is projected to grow from $2.50 billion in 2018 to $7.38 billion by 2024, displaying a CAGR of 14.50% (2019- 2024).[102]

In India, the transport sector is mostly based on diesel (70%), and gasoline (99.6%) as fuels[103]. Around 88.2 billion liters of diesel and 37.2 billion liters of gasoline were consumed by 2020[104]. Considering the huge waste biomass, the Ministry of Petroleum and Natural Gas of India announced the SATAT policy in 2018, which aims to establish an ecosystem for the production of CBG from biowaste. In support of the policy, the RBI included the CBG project under the priority sector, the SBI developed a loan scheme for this project, and the Central Pollution Control Board included the CBG project under the 'White Category'[105]. The SATAT policy is quite economical and environmentally friendly for sugar mills. The use of SCB in biogas production will reduce waste disposal problems, GHG emissions, and fossil fuel demand. In addition, it will facilitate transportation and economic improvement as well.

Challenges and Future perspective

The present review highlights the potential of SCB produced in large volumes by sugar mills in India and its transformation into value-added products for economic sustainability. SCB is composed of holocellulose, and lignin, which creates a complex and recalcitrant structure. Since the structure is complicated, a suitable pretreatment is required to isolate cellulosic material. A good number of pretreatment techniques have been reported in the literature. Recent trends exhibited the combination of ionic liquids pretreatment with MW and ultrasound that improves the enzymatic hydrolysis of cellulose. However, it increases operational costs. Cost-effective IL in combo with MW/ultrasound, in addition, MOF, GO, and other carbon material either isolated or combined with physical, chemical, or biological methods, as well as DES, supercritical CO_2 can be employed for minimization of pretreatment cost with a higher yield of the product. From this perspective, it is important to investigate the right pre-treatment method that is industrially applicable. To get proper fermentation, a well-engineered microbial strain that can enable to metabolizing of C_5 and C_6 sugars is required. Pretreatment methods and microbial strains

are expensive and increase operational costs. However, on-site availability of raw material SCB, electricity (if industry with cogeneration), and an anaerobic digestion unit (if industry with ethanol distillery) will help reduce the cost of conversion of SCB into biochemicals by providing electricity, steam, and water.

Economically, the market value for platform chemicals is good enough and the market forecast indicates rising demand for these biochemicals. In addition, the GOI announced various schemes with financial assistance to uplift the economy of the factories. In order to alleviate the energy crisis and carbon footprint, the conversion of lignocellulosic biomass into high-yielding biochemicals by developing cost-effective pretreatment techniques and microbial strain should be the main thrust areas of future research.

Conclusion

The efficient conversion of agro-waste into useful products has several incredible benefits. It saves resources and energy, reduces or restricts transportation, diminishes fossil fuel imports, mitigates waste disposal problems, creates sustainable bio-based economies, decreases biotic and abiotic stress, reduces greenhouse gas emissions, and makes efficient use of renewable carbon resources. In order to overcome economic crises, the setup of a biorefinery annexed to the existing mill, the manufacture of bagasse-based commercial bioproducts, and the implementation of GOI schemes will help in generating revenue and developing and sustaining the economy of the sugar mills in India.

Declarations

Conflict of interest

The authors declare no conflict of interest.

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Abbriviations

ATPS: Aqueous two phase system; BDO: 2,3-butanediol; CAGR: Compound annual growth rate; CBG: Compressed bio gas; DES: Deep eutectic solvent; DMF: N,N-Dimethylformamide; DMSO: Dimethyl sulfoxide; DWW: Dairy waste water; FRP: Fair and remunerative price; FTIR: Fourier transform infrared spectroscopy; GHG: Greenhouse gas; GOI: Government of India; 1G-ethanol: First Generation ethanol; 2G-ethanol: Second Generation ethanol; GO: Graphitic oxide; HH: Hemicellulose hydrolysate; IA: Itaconic acid; IL: Ionic liquid; INR: Indian rupee; LA: Lactic acid; MMT: million metric ton; MOF: Metal organic framework; NbO: Niobic acid; NbP: Niobium phosphate; PA: Polyamide; PBAT: Polybutylene adipate terephthalate; PBSA: Poly-butylenes succinate adipate; PEF: Polyethylene furanoate; PEG: Polyethylene glycol; PET: Polyethylene terephthalate; PHA: Polyhydroxyalkanoate; PLA: Polylactic acid; PM JIVAN: Pradhan Mantri Jaiv Indhan- Vatavaran Anukool Fasal Awashesh Nivaran; PP: Polypropylene; PPAWS: Pressurized phosphoric acid-acetone-water system; PTT: Polytrimethylene terephthalate; PUF: polyurethane foam; PVA: Polyvinyl alcohol; RBI: Reserve bank of India; SA: Succinic acid; SATAT: Sustainable alternative towards affordable transportation; SBI: State bank of India; SBR: Styrene-butadiene rubber; SCB: Sugarcane bagasse; SEM: Scanning electron microscope; SHF: Separate hydrolysis and fermentation; SSF: Simultaneous saccharification and fermentation; SSSCF: Semi-simultaneous saccharification cofermentation; SWW: Sugar waste water; UAAH: ultrasound-assisted acid hydrolysis; WPS: Whole pretreated slurry.

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