

Overcoming the Structural Adversity of Sugarcane Bagasse with Updated Pretreatment Methods: A Step Towards Ecological Energy Balance

Yashika Karodiwal ^{1*}, Jasneet Grewal ², Ajay Kumar ³ and Surojit Bera ⁴

^{1,3,4} Department of Microbiology, School of Bioengineering and Biosciences,
Lovely Professional University, Punjab-144411, INDIA

¹Email: yashikakarodiwal@gmail.com;

³Email : ajay.24068@lpu.co.in;

⁴Email surojit.25348@lpu.co.in;

²Department of Biochemistry, School of Bioengineering and Biosciences,
Lovely Professional University, Punjab-144411, INDIA

²Email: jasneet.25119@lpu.co.in;

ABSTRACT

Sugarcane bagasse (SCB) is one of the most inexpensive and abundantly produced agro-industrial waste, which provides a natural biodegradable resource for cost-effective bio-energy production. For commercial utilization of SCB, economic and technological factors need a clear identification and discussion. This review revisits the different modes of valorization process which was brought into an application during the due course of time. Pre-treatment is successfully applicable towards improved digestibility of cellulose by enzyme accessibility to the substrate because of the recalcitrant biological structure of SCB. The scope and bottleneck involved in the effectiveness of this procedure have been identified and mentioned here. The relative advantages of pre-treatment processes along with existing challenging methods and various advanced combinatorial methods have been discussed here. The present study will be helpful for designing advanced pretreatment methods to maximize the yield of desired platform chemicals to obtain a sustainable bioenergy market in the future.

Keywords: Sugarcane bagasse, Pretreatments methods, Platform chemicals, Hemicellulose.

Mathematics Subject Classification: 92D40, 92C40

Journal of Economic Literature (JEL) Classification: Q16, Q49, Q56

1. INTRODUCTION

Among the most generated biomass in the world, agro-industrial waste is still the foremost underused till the date. This chemical composition of waste makes them recalcitrant due to the strong bondage between their structural polysaccharide components. Proper disposal of waste produced during product processing is a component of normal guidelines assured by the environmental protection agency. A larger portion of utilizing agro-waste had seen through the process of bioconversion into various value-added chemicals like biofuels, bio-oil, organic acids, C6 sugars, platform chemicals, and cellulose ester, which are sustainable and with low-carbon life. One of the most appreciable approaches of researchers can be seen towards the production of biofuels, in terms of concern regarding the rapid development of

our society and its need to create environmental issues. Lignocelluloses which can be categorized into 4 ways, based on their sources, are: (1) forest residues, (2) agricultural residues, (3) energy crops, and (4) cellulosic waste is an abundant and cost-effective renewable resource (Kumari and Singh, 2018). Sugarcane is one of the leading crops, and India is the 2nd largest producer, covering nearly 15 to 25% of global sugar demand (Solomon et al., 2020). The commercial processing of sugarcane ends up in the generation of residues like press mud, molasses, and SCB. After consuming sugarcane in sugar mills, these factories produce a large number of solid by-products downstream called SCB. About, 100 million heaps of dry SCB are produced on an annual basis all over the globe, and 280 kg is generated per ton of sugarcane (Solomon, 2016). Despite such an enormous amount of bagasse production, half of it remains untreated due to a lack of methods of utilization. On 15th April 2020, a report concluded, India produces 24.8 Mt of sugarcane, and this provides India with the capability to supply within the countries, who are suffering from scarcity, like within the middle east and east regions of Africa, etc (Solomon et al., 2020). Our sugarcane fields cover around 5 million hectares, which is sort of 3% of the total area of our country (Solomon, 2014).

In processing sub-units of industries, SCB has been observed to contain about 41.4% of glucan, 28.2% of xylan, 1.3% of galactan, and 23.6% of lignin in its chemical composition (Thite and Nerurkar, 2019). SCB is a potential resource in the commercial industry with 1.88 Gt annual production and approx. half of its waste remains unutilized (Hans et al., 2020.) These residues are rich in bioactive compounds, which are employed as an alternate source to provide different products which help in various researches and industries.

Most of the prevailing agricultural biorefineries have to purchase expensive enzymes from suppliers (Arevalo et al., 2017) that can be statistically reduced by an integrated enzyme production system within their system itself which also increases the efficiency at the same time (Oliveira Gorgulho Silva, 2017). The methodology can be drafted in several ways with the combinational technique of hydrolysis and fermentation. The process of simultaneous saccharification and fermentation (SSF) was taken into account to provide biofuels/bioethanol from sugarcane waste, which is rich in lignocellulose. The key benefit observed by this processing method is the reduced expenses and product inhibition of the enzymatic hydrolysis. SSF is carried within the continuity of the method of fermentation, just after the completion of the saccharification of SCB (Ibrahim et. al., 2017). Physiochemical conditions, for hydrolysis and fermentation and therefore, majorly challenge the recycling of microbial strains and enzyme consumption. Performing separate hydrolysis and fermentation (SHF) is hydrolysis and fermentation being performed in separate units. The very initial step of processing involves pre-treating SCB to come up with monomeric sugars to ethanol, in a completely isolated section by which hydrolysis and fermentation can be performed over their ideal conditions. However, SHF can operate fermentation in continuous mode with recycling cells. The challenge to be taken care of with this process are the tip products inhibiting the efficiency of cellulase enzymes (Ali et. al., 2020). Another problem to be studied is the risk of contamination, which originates because of a comparatively long-standing period during the method of hydrolysis.

The foremost concern of this review is to study and examine the functioning of the pretreatment methods, which are used to conserve the energy indulged in the processing of agro-industrial waste

and the agro-waste of our interest, that is SCB. Nowadays, agricultural industries are focusing on simpler and cost-effective ways to deal with the waste produced during downstream processing of sugar mills, which will not only help in energy production for their units but also add a source of extra income with the sale of various platform chemicals and biofuels. Various innovative techniques are closely examined to study the effectiveness of each pretreatment method, under controlled physiological conditions.

2. PHYSICO-CHEMICAL CHARACTERISTICS OF LIGNOCELLULOSIC WASTE

2.1. Cellulose

It is the largest carbohydrate that is found in every LCB. Cellulose is homogeneously formed by the association of β -1,4-glycosidic bonds with cellobiose, showing different degrees of polymerization (Liu et al., 2019). These polymers are interlinked together to make microfibrils which are covered by the layer of hemicellulose and lignin. There's potency to circulate through the carbon cycle to return to the soil by biodegradation, making them harmless for the environment. Cellulose is characterized as a biodegradable compound for having an excellent mechanical property and biocompatible with poor soluble in water. (Batista Meneses et al., 2020). The most observed application, they were used as an additive for adhesives, paper-based products, drilling fluids, cement-based materials, food coatings, and catalysis support structures, and proved a large range of applications in biomedicine.

2.2. Hemicellulose

Hemicellulose is the second most abundant polymer after cellulose, consisting of pentoses, hexoses, acetyl groups, and uronic acids (Bhatia et al., 2020). The concept of hemicelluloses includes all or any of those polysaccharides within the plasma membrane that can't be characterized as celluloses or pectins. Hemicelluloses were originally considered as intermediates within the biosynthesis of cellulose. Hemicellulose provides a physical barrier and recalcitrates the availability of cellulase to dissolve cellulose. Industrial applications state it is used in biomedical and pharmaceutical β glucans production and, as an adhesive, and as flocculants (Batista Meneses et al., 2020).

2.3. Lignin

Lignin represents only about 10-25% of the biomass by weight with a long-chain composed of phenyl-propane units linked together (Anwar et al., 2014). Lignin acts as a binding material in LCC which is apparently to blame for gluing the cellulosic and hemicellulosic with the polymers which offer support to plant tissue and supply protection under infection caused by any mechanical injury. Lignin could be a non-sugar-based polymer; thus, it doesn't show any application in ethanol production. This can be explained by the phenolic inhibitors of microbial growth during the pretreatment process and its deposits over cellulose ultimately decreases the performance of 2G ethanol fermentation (Liu et al., 2019). Major applications of lignin can be seen in various forms like a copolymer in plastics, antioxidant coating within

the food industry, and components of batteries for energy storage, adhesives, flocculants, and in various biomedical ranges of approach (Batista Meneses et al., 2020).

3. WHY SUGARCANE BAGASSE IS SO RECALCITRANT?

Sugarcane bagasse constitutes of 32.0–45.0% cellulose, 20.0–32.0% hemicellulose, and 17.0–32.0% lignin which are together with linkage makeup of hydrogen, ether, and ester bonds playing a major role (Ngo and Ho, 2016). There are different intrapolymer and interpolymer cross-linkages which are directly responsible for the recalcitrance of SCB (Roy et al., 2020).

The rich biomass of Cellulose, Hemicelluloses and Lignin, are bonded together by strong interactions in nature, to create lignin-carbohydrate complexes (LCCs). Recalcitrance of LCCs resists their degradation during processing, which explains the requirement of pretreatment. Pretreatment methods come into the picture to separate structural components and enhance enzymatic hydrolysis, for ethanol fermentation by releasing glucose during the method. This process increases the availability of cellulose by making major differences in structural configuration (Steinbach et al., 2017). This process is assisted by providing the availability of some commercial enzymes, which mark the conversion of polymeric structures of carbohydrates into fermentable simple sugars like glucose, xylose, etc. The pretreatment step is a bottleneck for cost-effective bioprocesses comprising 20% of the total production cost making it the most expensive of all the processes (Amin et al., 2017). After studying the following facts, there's a need for research to explore methods for effective reduction in price involved in the conversion process.

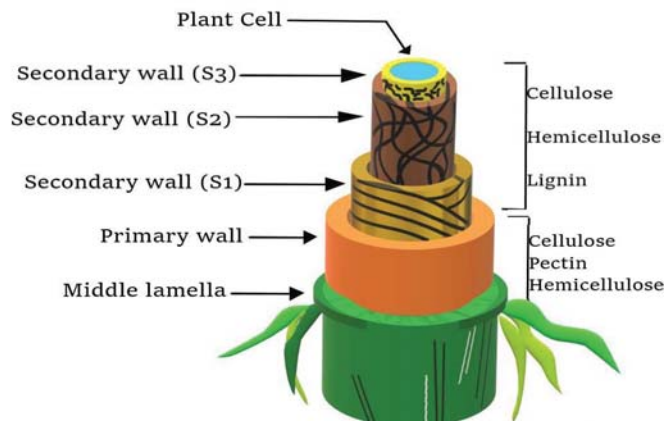


Fig 1. The structural composition of sugarcane stems along with their compositions

The fundamental understanding of every step within the process concerning commercial viability and operation is required for successful transformation and valorization of the waste. By eliminating the flaws an ideal pretreatment method will result in the production of least possible amounts of soluble sugar (SS) and lignin degrading compounds together, with relatively higher recovery of carbohydrates

(Baruah et al., 2018). Production of harmful by-products, which are not conducive to subsequent fermentation and saccharification processes will be strictly avoided making it environmentally friendly. To reduce the capital expense, our ideal process will utilize less energy, operational costs (Chen et al., 2017). Several reports have depicted ways to examine physicochemical changes in the treated biomass using different techniques. Fourier transform infrared spectroscopy analyzes the quantity of released SS, while effects of pretreatments on vascular bundles were observed through scanning electron microscopy. In the case of raw untreated SCB biomass, fibrous structures comprise parallel strips of the fibrous vascular bundle and are surrounded by soft, fragile pith cells showing a flaky appearance, which was observed through the micrographs. A pictorial representation is used to explain the structural and chemical organization of sugarcane stem (Fig 1). Pretreated bagasse shows an observable difference between fibrous vascular bundles from the medullary pith. Light and fluorescence-based microscopy, visualize the effect of enzyme cellulase on the plant cells which is still rare (Thite and Nerurkar, 2019). The procedure for studying this structural deformation in SCB can be designed through following steps: (I) Pretreatment of SCB biomass is conducted, followed by (II) Biochemical analysis of the filtrate for analysing the amount of released SS, (III) Identification of pretreated bagasse for structural and chemical alterations by different techniques, (IV) Assessment of increased exposure of biomass to hydrolytic enzymes.

4. PRETREATMENT

The earliest purpose of pretreatment for lignocellulosic biomass found its origin in wood science for pulp and paper fabrication but, later on, it started finding a wide range of applications in agricultural and crop science for increasing digestibility of forage by ruminants. The supreme purpose of pretreatment is to aim at the disruption of the recalcitrant structure of agro-industrial waste like SCB by removing hemicellulose and lignin in order to enhance the hydrolysis procedure of cellulose by cellulase enzyme. Many publications have made remarkable applications of a diverse range of strategies used for pretreatment on various lignocellulosic waste products. Thus, there is a need to combine and study the most recent studies to evaluate prominent and profound methods. Pretreatment methods have been broadly categorized into 2 major types, biological and non-biological pretreatment methods. Beginning with biological mode from microflora came into the picture, majorly including fungi, bacteria, and archaea which should affect their action through biodegradation. Whereas the Non-Biological mode contradicts the before mentioned category i.e., without having any assistance from microbiota. Non-biological pretreatment methods can be classified into 3 categories; chemical, physical, and physicochemical. Their subcategories can be sectioned on the basis of the type of methodology they are following. If we choose to categorize pretreatment methods based on how conventional and advanced they are because of commercial applications, then we can follow the (Figure 2). Some innovative methods are elaborately explained on the basis of the types, pretreatment conditions, enzyme dosage, and saccharification yield in Table 1 as given below, and discussed in the further sections of the paper.

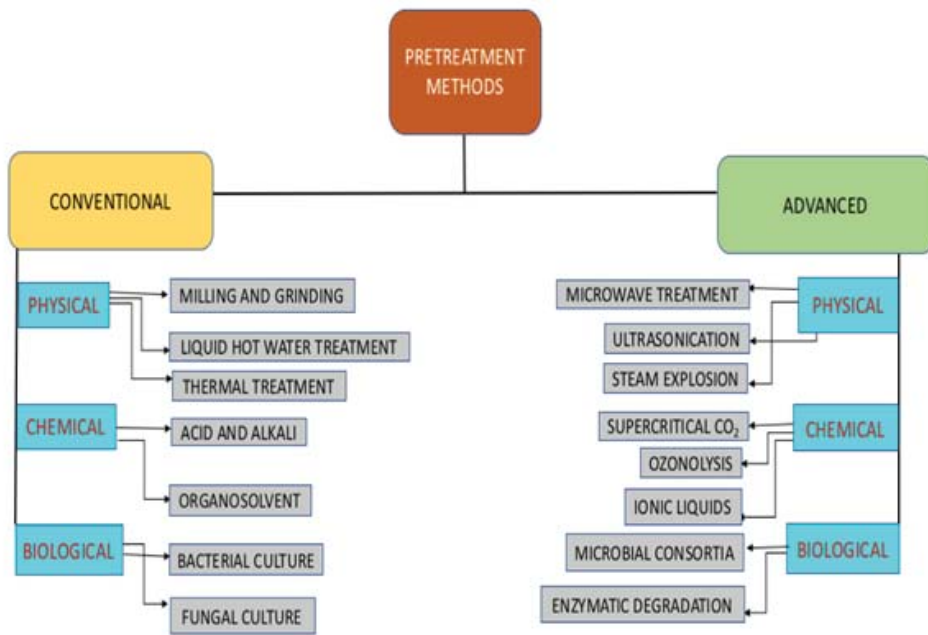


Fig 2. Available pretreatment methods for sugarcane bagasse

Table 1. This tabular data represents the different ways of pre-treating SCB through Physical, Chemical, Biological, and Physio-chemical methods; which include a variation in the chemical composition of the substrate making it more vulnerable to saccharification and fermentation process. By studying the data collected we can conclude that the chemical processes are proven to be the most effective way of pre-treatment. The Physico-chemical method is a new approach to reduce the use of chemicals, and at the same time supporting the processing with the help of temperature and pressure variation.

S No.	Pretreatment Type	Practical Conditions	Enzyme Dosage	Inc. Saccharification Yield	References
1	Biological method	<i>C. subvermispora</i> about 500 mg/kg of SCB with corn steep 5 l/kg at 27 ± 2 °C for 60 days	NA	47% for glucose	(da Silva Machado and Ferraz, et al., 2017).
2	Biological method (Subcritical hydrolysis pretreatment)	<i>S. cerevisiae</i> and <i>S. stipitis</i> at 200 °C, 15 MPa, 20 e 5 mL/min	NA	3.0 ± 0.53 g/L xylose and 6.3 ± 0.5 g/L glucose	(Oliveira et al., 2020).

3	Chemical method (Acid pretreatment)	H ₂ SO ₄ on S/L ratio of 5:2	Primafast 200	25.56% for glucose and xylose	(Thite and Nerurkar, 2019).
4	Chemical method (Acid-catalysed glycerol pretreatment)	Diluted acid 130 °C and glycerol pretreatment at 170 °C at L/S ratio of 5:1 and Rhodosporidium toruloides.	Cellulase of 4.1 FPU/g	91% for glucose and 67% for xylose	(Hassanpour et al., 2020).
5	Chemical method (Alkaline pretreatment)	NaOH (1 N) and Peracetic acid at 100 °C for 45 min with 1:12 S/L ratio.	NA	92.04% for reducing sugars	(Talha et al., 2016).
6	Chemical method (Alkaline pretreatment)	NaOH on S/L ratio of 1:2.	Primafast 200	38.84% for glucose and xylose	(Thite and Nerurkar, 2019).
7	Chemical method (Alkaline pretreatment)	Liq. NH ₄ OH at S/L ratio of 5:2.	Primafast 200	9.61% for glucose and xylose	(Thite and Nerurkar, 2019).
8	Chemical method (Alkaline pretreatment)	Liq. NH ₄ 15.64% (v/v) ammonia; S/L ratio of 10:1 at 84.9°C for 23.95 hr.	Cellic CTec 2(20 FPU/g) 50 °C at 130 rpm for 72 hr.	75.41 ± 1% for Total reducing sugar	(Hans et al., 2020).
9	Chemical method (Combinatorial pretreatment)	1% H ₂ SO ₄ followed by 60% ethanol containing 0.5% NaOH.	Tween 80 of 20 FPU/g at 50 °C and 150 rpm for 72 hr.	84.5% for glucose	(Zhang et al., 2018b).
10	Chemical method (Combined sodium percarbonate and glycerol pretreatment)	12% sodium percarbonate in 80% glycerol 121 °C, 40 min at S/L ratio of 1:5.	Cellulase (Cellic CTec2) of 30 FPU/g at 200 rpm and 50 °C for 96 hr.	16.67 g/L for TRS	(Gong et al., 2020).
11	Chemical method (Ionic liquid)	EmimAc at 140 °C, 120 min reaction time, and 1:20 S/L ratio.	Enzyme loading of 20 FPU/g at 50 °C and 150 rpm for 72 hr.	54.3% for glucose	(Saha et al., 2018).
12	Chemical method (Organosolvents)	Citric acid (6.0 wt.%) and 102.4 min with L/S ratio of 1:25.	NA	28.21% for Total reducing sugar	(Garcia et al., 2020).
13	Chemical method (Sodium hydroxide catalytic ethanol pretreatment)	5% NaOH and 60% ethanol solution at 180 °C for 30 min with S/L ratio of 1/10.	Tween 80+ cellulase 10 FPU/g at 180 °C for 24 hr.	93.0% for glucose and xylose	(Zhang et al., 2020).
14	Physical method (Hydrothermal-carbonization)	170 °C of constant temperature for 3 hr, with 1:5 S/L ratio.	NA	1.23%-glucose, 35.77%-xylose, 30.54%-mannose, 28.52%-	(Chai et al., 2019).

				galactose, and 41.85%-arabinose	
15	Physical method (Mechanical Pulverization)	Mechanical pulverization for 1.4 MPa for 5 min.	NA	10.38% for rhamnose and arabinose	(Chen et al., 2019).
16	Physical method (Mild Hydrothermal Stress)	Hydrothermal stress at 170±2°C for 30 min.	NA	4.8% for glucose	(de Oliveira Gorgulho Silva et al., 2019).
17	Physiochemical method	FeCl ₃ (0.025 mol/L) and Bovine Serum Albumin	Tween 80 of 20 FPU/g at 50 °C and 150 rpm for 72 hr.	97.7% for glucose	(Zhang et al., 2018a).
18	Physiochemical method (Hydrodynamic cavitation)	Hydrodynamic cavitation along with NaOH (0.3 M) and H ₂ O ₂ at 50 °C for 7.5 min	Cellic CTec2 about 20 FPU/g at 50 °C and 200 rpm for 24 hr.	38-48% for glucose and xylose	(Hilares et al., 2019).
19	Physiochemical method (Microwave-assisted acid pretreatment)	SCB with malic acid in a microwave tube with S/L ratio of 1:10 for 5 min with, microwave reactor at 50% magnetic stirring condition at 180 °C for 5 min	1 mL (2%) sodium azide and Cellic CTec2 of 40 FPU/g at 150 rpm, 50 °C for 72 hr.	80.1% for glucose	(Hermiati et al., 2020).
20	Physiochemical method (Sonication boost)	H ₂ SO ₄ (0.25–0.75%) with Sonication (80% amplitude, 0.8 cycle and 10 min) S/L ratio of 1:60 for 18±2 hr	NA	25% for Total reducing sugar	(Bhattacharyya et al., 2012).

4.1. Biological pretreatment

Biological pretreatment employs degrading LCCs by biological live organisms, especially wood-eating and digesting organisms. In our large biological system, this work is carried out by decomposers; microorganisms which feed on complex organic matter and decompose them into simpler forms. Fungi, bacteria, and archaea are composed of this group majorly. Bio-delignification is the term majorly used when this biodegradation is specifically performed with lignin. It is especially used for the purposes to replace or supplement the toxic chemicals used during pretreatments (Anwar et al., 2014). This method operates in a short reaction time and low nutrition requirement, along with its suitability for bioethanol production in such an efficient way.

Major bacterial genera such as *Clostridium* sp., *Bacillus* sp., *Thermomonospora* sp., *Streptomyces* sp. etc., and several fungal species of *Trichoderma* sp., *Aspergillus* sp., etc. are commercially accepted for

their contribution in industrial processing units. There are many benefits of using biological methods for making monomeric sugar molecules out of polymeric molecules and the most important benefit is the elimination of chemical recycling during downstream processing which ultimately reduces the costs, minimized inhibitory compounds, and reduced consumption of energy source. Important factors limiting further advancement of this technology are elevated costs and contamination that results in reduced yield from downstream, and complicated structure of microorganisms making them difficult to handle (Rezania et al., 2020).

Biological pretreatment had shown application in the manufacturing of some platform chemicals in the past. Xylitol contains commercial importance with many applications within the pharmaceutical and food industries and is successfully prepared while undergoing biological methods. Recent study, depicting the possible biotransformation of xylose to xylitol using *Yarrowia lipolytica*, has been done storing a level of 53.2 g/L xylitol using pure glycerol and xylose with a final yield of 0.97 g/g (Prabhu et al., 2020). Lignocellulosic biomass is more preferred over other forms of agro-industrial waste; especially, from the starch or sugar-based crops for the production of biofuels like bioethanol, biobutanol, and biohydrogen. Since it came up with the advantage of not competing with food requirements and taking care of agricultural and plant residues in an environmentally sustainable process (Liu et. al., 2021). Almost all biofuels are produced from grain or sugarcane waste currently. The use of the buffer system and non-ionic surfactants are seeming to be a perfect approach for ethanol production. The ethanol production in the sodium acetate buffer solution system (66.67%) was comparatively higher than that in the deionized water system because the buffer was useful and maintains the activity of enzyme and yeast cells. The introduction of non-ionic surfactants can efficiently increase the rate of fermentation with application of Tween 80, for 82.28% ethanol yield (Zhang et al., 2020). According to a recent study, the best bioethanol production formula made from SCB has a bioethanol content of 2.75% at 45 °C, at centrifugation at 140 rpm from *Trichoderma viride* (Alfian et al., 2020). The previous same approach was made with a Thermophilic bacterium for the production of hydrogen gas from various kinds of sss. This new strain named MJ1 (99% identity to *Thermoanaerobacterium thermosaccharolyticum*) was isolated from paper sludge, which possesses the capability for H₂ production with yields of, 11.18, 4.25, and 2.15 mol-H₂/mol sugar with acid pretreatment. The initial concentration of sugars used was 5 g/L cellobiose, glucose, and xylose, respectively (Hu & Zhu, 2017). One recent example to be studied is from, *Clostridium saccharoperbutylacetonicum* (a robust wild-type strain) produced 5.8 g butanol per liter when fermenting a non-detoxified SCB hemicellulosic hydrolysate enriched with xylose (Zetty-Arenas et al., 2019). This another strain of *Clostridium*, i.e., *C. beijerinckii* was able to produce butanol (1.23 g/L/day) with a yield of 0.18 g/g of sugars like glucose, xylose, etc. from the developed medium of SCB during anaerobic fermentation (Narayanasamy et. al., 2019). In one similar study for extraction of lactic acid from SCB; hydrolysis with Cellic CTec2 at a quantity of 25 mg/g glucan along with a two-step (9% + 9%) substrate feeding strategy. With the direct use of glucose-rich filtrates, it gives 69.2 ± 2.5 g/L of carboxylic acid by assistance from *Bacillus coagulans* NCIM 5648, providing yield obtained for Lactic acid during the process of SHF was 2.88 g/L hr (Baral et al., 2020).

4.2. Non-biological

4.2.1. Physical pretreatment methods

Milling

Milling can open the compact structure of LCBs by the mode of disrupting their outer surface which reduces the size using shear or compression forces created by machines and instruments. They provide a great deal of mechanical comminution to homogenize the biomass, which reduces the particle size and materials crystallinity. This process of grinding leads to a high proportion of the overall operational cost because high power-consuming machinery becomes its limiting factor (Carvalho et al., 2020). This method carries the advantage of a reduced processing time in addition to, decrease in the quantity of water used and increases the porosity over the surface for subsequent hydrolytic processes (Deshwal et al., 2021). According to the observation, this process is not considered enough to provide pretreatment during processing. Thus, milling is operated in combination with either high-temperature heating or hot steam explosion.

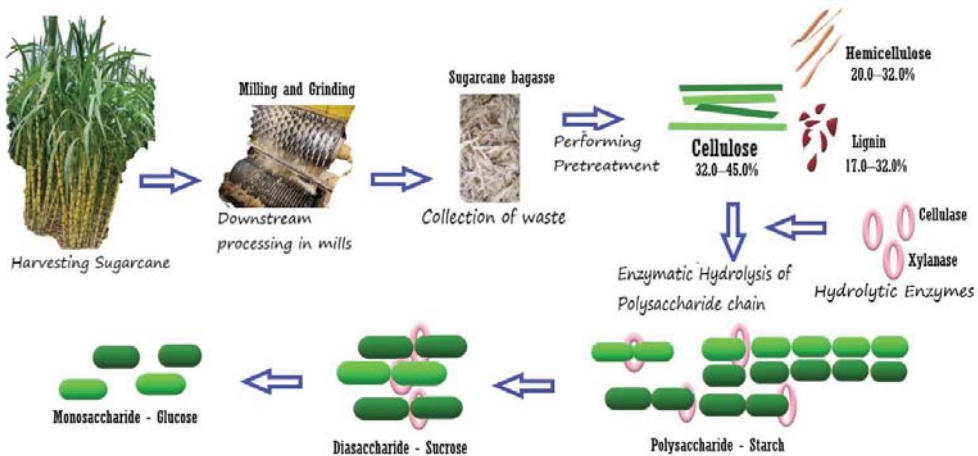


Fig 3. Effect of physical pretreatment (milling) on sugarcane bagasse

Microwave

Microwave-assisted pretreatment is an effective method that works on the mechanism based on irradiation. Researchers have applied this mechanism to obtain bioethanol yield for over 30 years, which has been commercialized constantly from research labs to pilot scale industries (Rezania et al., 2020). General motive of irradiation methods is to boost enzymatic hydrolysis by breaking them down into low molecular weight oligosaccharides by decreasing the crystallinity index of biomass (Pandiyan et al., 2019). One major drawback was seen during the upscaling process, which is found to be very cost-effective and appropriate when used in combination with biological methods of pretreatment. Advantages of this processing include low reaction activation energy and a considerable reduction in reaction time. Many approaches are taken to enhance the application of microwave pretreatments by

designing instruments like microwave vessels for loading biomass and microwave reactors to provide isolated reaction chambers, which are safer and easier to use during heavy operations. The production of 5-Hydroxymethylfurfural using microwave hydrothermal liquefaction was discussed in a study before. SCB in acidic seawater conditions was used during the method to obtain the best yield of 8.1 wt% at temperature of 149 °C for 4 min and an L/S ratio value of 12:1, respectively (Shao et al., 2020).

Ultrasound

The Ultrasound or the technique of sonication explains the use of ultrasonic waves to induce pressure through variations. This technique is limited in liquids where it generates microcavities in which gas bubbles grow and then collapse, this generates shock waves which are responsible for creating a mechanical. Studies showed that the optimum sonication conditions of 80% amplitude, 0.8 cycles for 10 min, showed around 25% improvement of total reducing sugar extraction from SCB (Bhattacharyya et al., 2012). Although sonication is found effective especially in combination methods with chemicals. Another study shows an increase in reducing sugar yield to 0.374 g/g where the conditions of combined pretreatment and hydrolysis with enzyme loading of 20 FPU, surfactant concentration of 0.25% w/w were applied for sonication time of 6 min (Sindhu et al., 2016). SCB hemicellulose hydrolysate has a rich chemical composition for eco-friendly production of succinic acid by ultrasonic combinational pretreatment with acid hydrolysis of SCB with the use of *Actinobacillus succinogenes*. (Xi et al., 2013).

4.2.2 Physicochemical pretreatment methods

Hot water

Pretreatment with hot water of 140-240 °C alters the physicochemical nature of LCB of sugarcane in such a way that, the hemicellulosic component gets depolymerized and the products dissolve in the liquid phase, whereas the cellulose continues to stay in its solid phase only. Lignin suffers from simultaneous depolymerizations and polymerizations, due to its glass transition temperature during which the insoluble lignin possesses as a solid waste (Batista Meneses et al., 2020). The handsheets from the whole SCB pulp at a temperature of 165 °C exhibited higher tensile strength index values than those compared to the sheets of depicted SCB pulp fibers (Pydimalla et al., 2019) proving a great deal of application for SCB. This physicochemical technique does not include any resistance to corrosion in the reactor, and thus the toxicity of compounds reduces giving it an advantage over other chemical pretreatments.

Steam explosion

The steam explosion pretreatment method is effective enough to degrade the hemicellulose fraction of SCB into simple sugar content of the untreated sample was 0.08%, which increased quadratically to 0.53–10.38% (Chen et al., 2019). Major advantages which are provided with this pretreatment are; cost-effectiveness due to moderate energy input, and eco-friendly with minimum environmental issues. No use of any chemical solvents provides a guarantee of much lower detoxification effort with neutralization in biorefinery stages. This not only reduces the cost but ideally makes continuous steam explosion pretreatments dominate and flourish in the market. Pretreatment of bagasse under steam

explosion in addition to NaOH showed destruction of fibers, and removal of lignin at a considerable rate of 65%, and production of reducing sugars at the highest yield up to 9.07 g/L (Silva et al., 2018). The major 2 factors which were considered essentially responsible for the effect of enzymatic digestibility during this pretreatment method is the amount of severity created due to pressure difference during explosion (Pielhop et al., 2016).

Carbon dioxide (CO₂) explosion

CO₂ is the most used supercritical fluid due to its moderate critical temperature of 31.1 °C, critical pressure of 7.38 MPa, nonflammability, and no emission of chemical vapors. Its property of nontoxicity, low cost, easy recovery, and chemical inertness makes it an ideal green solvent and environmentally friendly replacement for organic solvents. It has been confirmed as an effective and eco-friendly approach to conventional pretreatment methods, because of its high total C5 and C6-sugars recovery and influence over the composition and intrinsic features of each biomass. This feature is closely studied in a study of SCB and elephant grass which were used to produce C5-sugars from hemicellulose. Severity factors ranging from -1.17 to -0.04 results in high digestion with glucan to glucose yields of 77.2 mol% for SCB (Toscan et al., 2017). Pretreatment of SCB using a sequential combination of alkaline H₂O₂ along with supercritical CO₂ and at mild conditions was considered effective than the individual pretreatment with supercritical CO₂, ultrasonic waves, or H₂O₂ regarding the yield of cellulose and hemicellulose, which was almost double. Output was observed and analyzed via enzymatic hydrolysis by SEM and HPLC (Phan and Tan, 2014).

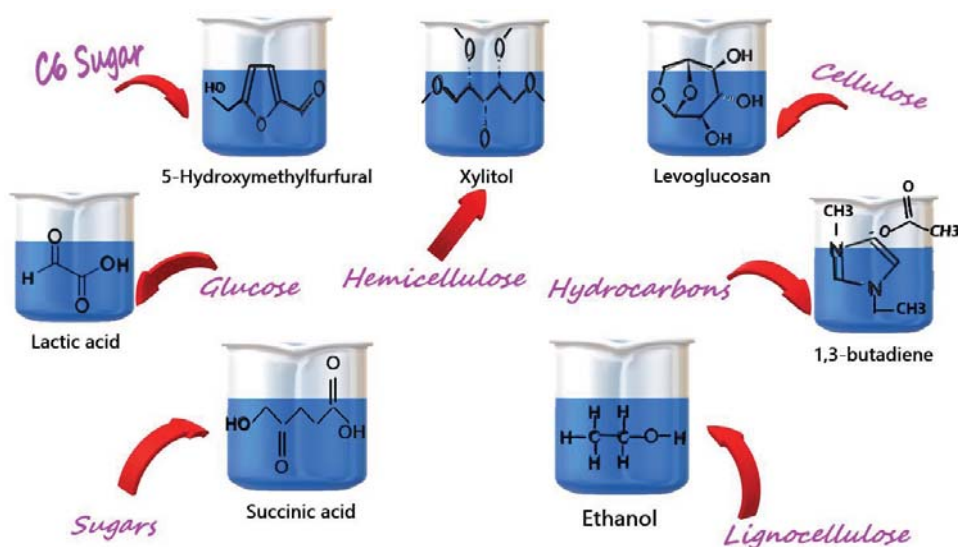


Fig 4. Platform chemicals from sugarcane bagasse hydrolysate

4.2.3 Chemical Pretreatment methods

Acid

One of the most traditional methods of removing lignin and hemicellulose includes treating the biomass with various concentrations of HCl or H₂SO₄. Dilute H₂SO₄ is a frequently used and commercially accepted method for disruption of weedy biomass, herbaceous grass, and agricultural wastes. The procedure uses a temperature range of 130 and 210 °C to facilitate the mixing of dilute acids with sugarcane biomass (Pandiyan et al., 2019). Improved percentage of enzymatic saccharification after acid pretreatments for SCB (~30% glucan conversion) as pretreatment hinders the strength of cellulosic polymers (Thite and Nerurkar, 2019). Acid-catalyzed hydrolysis of SCB for the assembly of levulinic acid had seemed of great commercial importance. An experimental setup was made with temperature ranging from 150 to 200 °C, and the best levulinic acid yield was obtained at 150°C in a combination of H₂SO₄, which is about 194 kg of levulinic acid from every 1 dry tonne of SCB (Girisuta et al., 2013). A generalized method of fast pyrolysis of LCB has been experimented in the pretreatment of SCB for significant structural changes, whose results show a significant increase in levoglucosan yield upto 32%. Acidic pretreatment with H₃PW₁₂O₄₀ on the biomass confirmed by thermal analysis and SEM performed during the treatment. (Teixeira et al., 2020). Although, like every excessive use of a high concentration of acids up to 30-70% shows a high level of corrosion, whereas this toxicity and corrosiveness decreases with increasing dilution. However, the major disadvantage of using acids during the pretreatment method is due to the formation of secondary products which affect the quality of the product by lowering the sugar yield and affecting the process of fermentation (Pandiyan et al., 2019).

Alkali

The most preferred alkali solutions are used for the purpose of maintaining pH level in LCB, which are Ca (OH)₂, NaOH, and NH₄OH, etc. Alkali pretreatment is preferred for various advantages which it brings along with selective removal of lignin, without the actual loss of reducing sugar and carbohydrates. This improves the enzymatic hydrolysis by maintaining pH level for the functioning of important enzymes and delignification of biomass at the same time. During the pretreatment tested for solubility of the SCB, with a observable lignin reduction of 86.27% and progressive yield of biomethane (195.8 mL-gVS⁻¹) after a time interval of 45 min with NaOH at 100°C. The co-digestion ratio was recorded as 25:75 between filter mud and bagasse (Talha et al., 2016). Similarly, like every other process of pretreatment, this alkaline chemical treatment also has drawbacks which include; release of the degradative bi-products, reduced selectivity and process efficiency, along with increased processing costs, and longer reaction time. Recent researches working on the production of concentrated hydrolysate of glucose along with the formation of platform chemicals from SCB involved the use of alkali pretreatment.

Ozonolysis

Ozone is a very potent oxidant that shows high lignin degradation under normal temperature and pressure, which prevents the production of any compounds that can further inhibit or toxicate the

process. Its application is seen on various types of LCB, such as wheat straw, bagasse, pine, cotton straw, bagasse, etc. (Harmsen et al., 2010). The only important drawback is its requirement in a very large amount of expensive ozone which adds up to the overall cost of the product. In a recent study, impregnation of ozone gas in different media in combination with sugarcane straw residue, generation of fermentable sugars is recorded. The best results were obtained for the ozonolysis for ozone concentration of 0.24% for 60 min of time interval under the maintenance of 35% moisture content. This reaction is supported with a basic medium under 80 °C temperature for 8 hr. An observation was made when increasing the ozone concentration from 0.24% to 1.3% is ineffective of the amount of yield for sugars, this indicates that no higher ozone concentrations will create an effect to elevate the yield (Ortega et al., 2020).

Organosolvent

The organosolvation technique is an organic pretreatment method that includes using an organic or aqueous-organic solvent with a combination of varying temperatures (100-250 °C). A major advantage of this procedure is the recovery of relatively pure lignin, with high purity of cellulose with hemicellulose fractionation at high capability. Along with this, organic solvents are reusable after their recovery which is quite simple. Some factors need to be considered while scaling up with organic solvents, which is the cost of an upscaling process that deliberately increases while removing the inhibitors. Ethanol and methanol as commercial alcohols are most acceptable for their low boiling point, low cost, and ease of recovery. Studies show, after one step 60% ethanol in combination with 0.5% NaOH, an observable glucose yield increased by 41% and 205% was recorded after a hydrolysis process on the substrate of SCB (Zhang et al., 2018b). A blender of the pretreated SCB by 25% methanol and 15% ammonia reaches a considerable yield of glucose at 7.84 g/l (Hedayatkhan et al., 2013).

Ionic liquids

Ionic liquids can be defined as molten salts with relatively lower melting points and high thermal stability at 300 °C and above, with low toxicity, and vapor pressure. These green liquids have a unique solvation property selectively removing lignin and hemicellulose part of LCB to provide pure cellulose for further hydrolysis. They possess some tunable properties like polarity, hydrophobicity, and solvent power and can be used several times at 37 °C in the form of liquid salts. Challenges consist of toxicity, pH compatibility, costliness, and process complexity (Batista Meneses et al., 2020). About 90% lignin recovery from SCB in of the previous research during which SCB in treatment with EmimAc at 140 °C of temperature for 120 min reaction time for exhibiting pores and distorting the surface of bagasse. 1:20 ratio was decided to be taken for the processing of substrate for treatment. The impact of this pretreatment from ionic liquid was used for qualitative analysis of pretreated and non-treated SCB, which was further confirmed by SEM analysis (Saha et al., 2018). The application of a protic ionic liquid triethylammonium hydrogen sulfate for pretreatment of agro waste like rice/rice straw, SCB etc., were effective at 170°C for 30–45 min (Chambon et al., 2019). Although these ionic liquids cannot be cost effective enough, recycling and reusing can be proven as a good solution for industries. A study suggests recycling strategy for EmimAc during industrialized technology which includes electro dialysis

ultrafiltration etc., after the pretreatment for SCB. The utmost ionic liquid recovery ratio reached 94.0% showing comparable recyclability for SCB considering the delignin ratio of pretreatment (Liang and Liu, 2020).

Deep eutectic solvent pretreatment

Even though ionic liquids are designer solvents, and are considered ideal pretreatment agents due to their properties, such as non-flammability, low vapor pressure, catalytic activity, and recyclability. However, this cannot deny the fact that ionic liquids are relatively expensive adding to their poor biodegradability. Therefore, deep eutectic solvents recently emerged as a potential alternative green solvent for effective biomass valorization (Roy et al., 2020). Deep eutectic solvent consisting of molecules acting as donors and acceptors in hydrogen bonds, which reduces their freezing point from that of the room temperature (Sharma et al., 2021). Benefits of these solvents include formulation and preparation, lower capital consumption, biodegradability with saccharifying enzymes, recyclability, etc. In a recent study of deep eutectic solvents with sweeping frequency ultrasound in the fractionation of SCB, for enhancing the enzymatic saccharification process was investigated under 40 kHz, at a time interval of 60 min for ultrasound + deep eutectic solvent, 120 °C for the lignin removal rate of 85.62%, and the hemicellulose removal rate of 90.46% (Ji et al., 2021).

5. Conclusion

After going through the variety of bioconversion processes and their support system, we can conclude that there are always open opportunities to develop a novel and green pretreatment method. That ideal method will consider all the aspects for product quality along with cost-efficiency. Energy consumption during downstream processing and purification processes is observed as the major hurdles. Among the pretreatment methods, the utilization of alkali and acid together with ideal temperature and pressure approaches are mature and cost-effective pretreatment technologies for increasing saccharification rate of biomass, production of biofuel, and platform chemical from sugarcane biomass. The biological model of pretreatment, which is operated only with the use of decomposers, is supplemented with physical methods (milling, grinding, microwave, and sonication) to increase its efficiency and advancement of procedures. Rather than making use of direct concentrated acid and alkali, organosolvents (ethanol, methanol, urea) and ionic liquids (liquid triethylammonium hydrogen sulfate, 1-ethyl-3-methylimidazolium acetate) can be used, which reduce the cost involved in detoxification. Deep eutectic solvents have given plenty of advantages that are ideal enough to replace their usage with ionic liquids. Concluding all research till now, it is statistical enough to say that every pretreatment method has its pros and cons, therefore research needs to be done potentially enough. Apart from advancements in detoxification technologies, efficiency can be elevated by directing focus on procedures of carrying out pretreatment and applications of generated by-products from the process. Major steps involved in the conversion of the biomass include conversion in biofuel; which undergoes the following series of action followed by pretreatment, hydrolysis and, then fermentation in bioreactors. It has been proven as a sort of major application prospect for increasing energy production on a regular scale and to boost economic

and social sustainability. 2G Bioethanol, biobutanol, and biohydrogen are the biofuels that are gaining lots of attention for their potential, so carrying lots of energy is efficiently supported with pretreatment procedures. These biofuels have provided us an innovative way to find sustainable energy sources, with a replacement of the hazardous use of non-renewable fossil fuels. The production of these biobased chemicals in a biorefinery can effectively limit the production of chlorofluorocarbons in the atmosphere and expands the bio-based economy for a more environmentally benign chemical manufacturing industrial sector. Food, textile, and paper industries have undertaken a large portion of agricultural products like corn, rice, sugarcane, wheat, maize, cotton, etc; leading to the generation of large amounts of waste during their downstream processing, which is lignocellulosic. The world has always suffered from the issue of waste valorization, which can only be restrained by implementing circular bioeconomic concepts for sustainable management of agro-industrial wastes like SCB from sugarcane for potential opportunities.

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