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Valorization of Cereal Based Biorefinery Byproducts: Reality and Expectations

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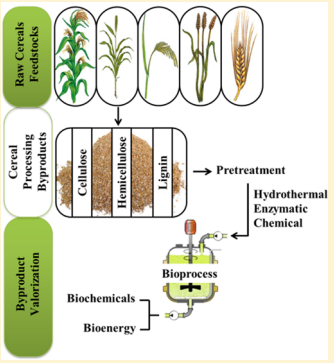
ABSTRACT: The growth of the biobased economy will lead to an increase in new biorefinery activities. All biorefineries face the regular challenges of efficiently and economically treating their effluent to be compatible with local discharge requirements and to minimize net water consumption. The amount of wastes resulting from biorefineries industry is exponentially growing. The valorization of such wastes has drawn considerable attention with respect to resources with an observable economic and environmental concern. This has been a promising field which shows great prospective toward byproduct usage and increasing value obtained from the biorefinery. However, full-scale realization of biorefinery wastes valorization is not straightforward because several microbiological, technological and economic challenges need to be resolved. In this review we considered valorization options for cereals based biorefineries wastes while identifying their challenges and exploring the opportunities for future process.



1. INTRODUCTION

The biorefinery term pertains the production of biofuels, bioenergy, and valuable chemicals from renewable biomass sources[1] and aims to substitute petroleum refineries which produce several fuels and products from petroleum. Biorefinery is the continuous processing of biomass into a range of profitable products (food, feed, materials, and chemicals) and energy (fuels, power, and heat). This conception is similar to that used within the petrochemical industry, but renewable biomass feedstocks are used instead of using oil as the feedstock. "Renewable" is a wide-ranging term, which could include any organic matter that becomes available on a continuous basis. This could include grasses, energy crops, agricultural feeds, or organic waste streams from animals and plants. Grass is one of the promising energy crops for biogas production in some EU countries,[2] where grass is covering a wide areas of agricultural land with high yields compared to other crops in Europe.[3] The biorefinery products (i.e., fuels, therapeutics, food additives, or secondary chemicals) can be obtained using thermal, chemical, mechanical, enzymatic or microbial processes. Biorefinery is targeting the separation of all the added value from the biomass feedstock, with little or no waste. This will lower the total environmental impact, besides improving the economics so that these processes can contend with the petrochemical industry (Figure 1).

Uniformity of feedstock represents one of the common factors between the classic petrochemical refinery process and biorefinery. Biomass feedstocks could have a remarkable geographic and seasonal variations (ranging from simple sugars to complex polysaccharides such as starch, cellulose, and hemicellulose, as well as more complex sources such as lignin, triglycerides, lipids, and proteins). This variation could be viewed as a disadvantage, due to the variation of the consistency and yield of the end products. On the other hand, complexity could be a desirable trait in order to obtain a more expansive range of products, although it needs cautious optimization in relation to the input material. Moreover, one of the major disadvantages of biorefinery, compared to petroleum refinery, is in the miscellany of technologies required to obtain the end products. These include plant breeding and genetics, mechanical processes, sub- or supercritical fluid extractions, thermal treatments, chemical treatments, concurrent thermal and chemical treatment, enzymatic digestion, and biotransformations using microorganisms.[4]

2. BIOREFINERIES

Biorefineries are classified based on their system components,[1] that is, platforms, products, feedstocks, and conversion processes. Platforms determine the complexity of the system in which they represent intermediates that link biorefinery systems and their processes (i.e., C_5/C_6 sugars, syngas, and biogas). Products may be energy, that is, bioethanol and biodiesel, or valuable chemicals (building blocks), that is, organic acids. Feedstocks can come from edible crops, agricultural residues, forestry residues and industrial or domestic wastes (bark, straw, paper mill black liquor, used cooking oils etc.). Currently four major groups of conversion processes are involved in biorefinery systems. These are thermochemical (e.g., pyrolysis), biochemical (e.g., fermentation), mechanical (e.g., size reduction), and (bio)chemical (e.g.,

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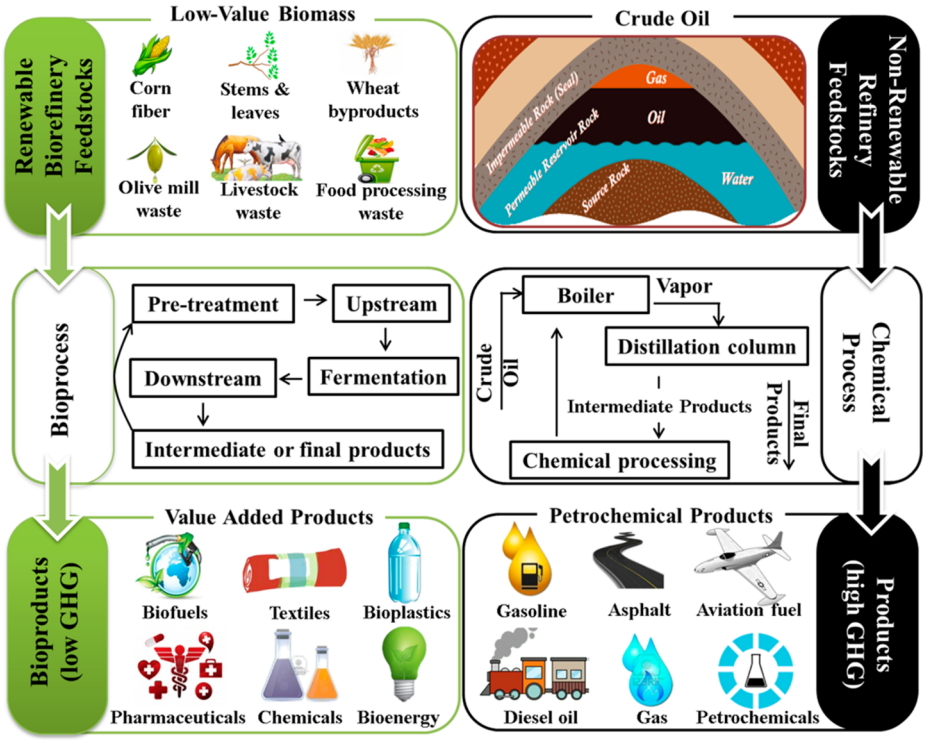

Figure 1. Using biomass in a biorefinery concept instead of oil for producing energy and chemicals.

Table 1. Some Terminologies and Classifications Related to Biorefineries

term	description	reference
conventional biorefineries (CBR)	the separation of biomass into main and byproducts by conversion and upgrading technologies.	131
advanced biorefineries	the combined production of main product with some added-value products.	132
whole crop biorefineries (WCBR)	the application of wet or dry milling of cereal feedstock.	4
marine biorefineries (MBR)	based on integrated cultivation and processing of aquatic biomass.	133
lignocellulosic feedstock biorefineries (LCFBR)	based on the fragmentation of lingocellulosic biomass into cellulose, hemicelluloses and lignin to be processed into biobased end-products and fuels.	25
green biorefineries (GBR)	the treatment of wet green biomass, to produce fiber-rich cake and nutrient-rich juice.	134
1st generation biorefineries	Includes direct utilization of classical forms of agricultural biomass, i.e., wheat, corn and sugar cane.	135
2nd generation biorefineries	Includes direct utilization of lingocellulosic biomass, i.e., straw and wood.	135
3rd generation biorefineries	includes utilization of the high-yield feedstocks of algae.	136
thermochemical biorefineries (TCBR)	applies several technologies such as pyrolysis, torrefaction, hydrothermal and gasification processes	137
two platform concept biorefineries (TPCBR)	based on fractionation of biomass into sugar and lignin fraction, in which sugar fraction is biochemically converted to bioproducts, while the lignin fraction is thermochemically converted into a syngas.	138
energy-driven biorefinery (EdBs)	includes the production of secondary energy carriers, i.e., fuels, power and heat, from biomass and process byproducts are valorized to bioproducts.	139
product-driven biorefinery (PdBs)	includes the production of bioproducts, i.e., chemicals, materials, food and feed, from biomass and process byproducts are used for the production of bioenergy.	140

esterification). The array of the most common terms that describe biorefineries are illustrated in Table 1.

Crop based biorefineries have gained tremendous interest in recent years, several pilot-scale systems have been built and currently a lot of research is going on building full scale systems. As with any other technology, apart from the main products in this case ethanol or lactic acid, several side products and wastes are also generated.[5] The main focus of research so far has been on treatment of these wastes. Also, most of the scientific literature is focused on treatment aspect only, but the focus has moved from treatment to valorization very recently.[6]

Coal displaced the biomass fuels, considering wood, as the main energy source during the industrial revolution. Since then a steady migration toward fossil fuels has continued, moving further away from biomass, not only for energy but also for sources of chemicals used to make everyday items. An outstanding pattern of this is furfural which can be produced from oat hulls. Until 1960s, DuPont produced nylon from biologically derived furfural; however, nowadays it is being produced from fossil resources. The price of such fossil-fuel sources will be affected negatively in the near future due to the depletion of these oil reserves. Industry is therefore now being encouraged to take a more inventive approach, looking ahead of oil and identifying biobased systems as valuable stockroom of crucial chemical building blocks. These chemicals are the basics

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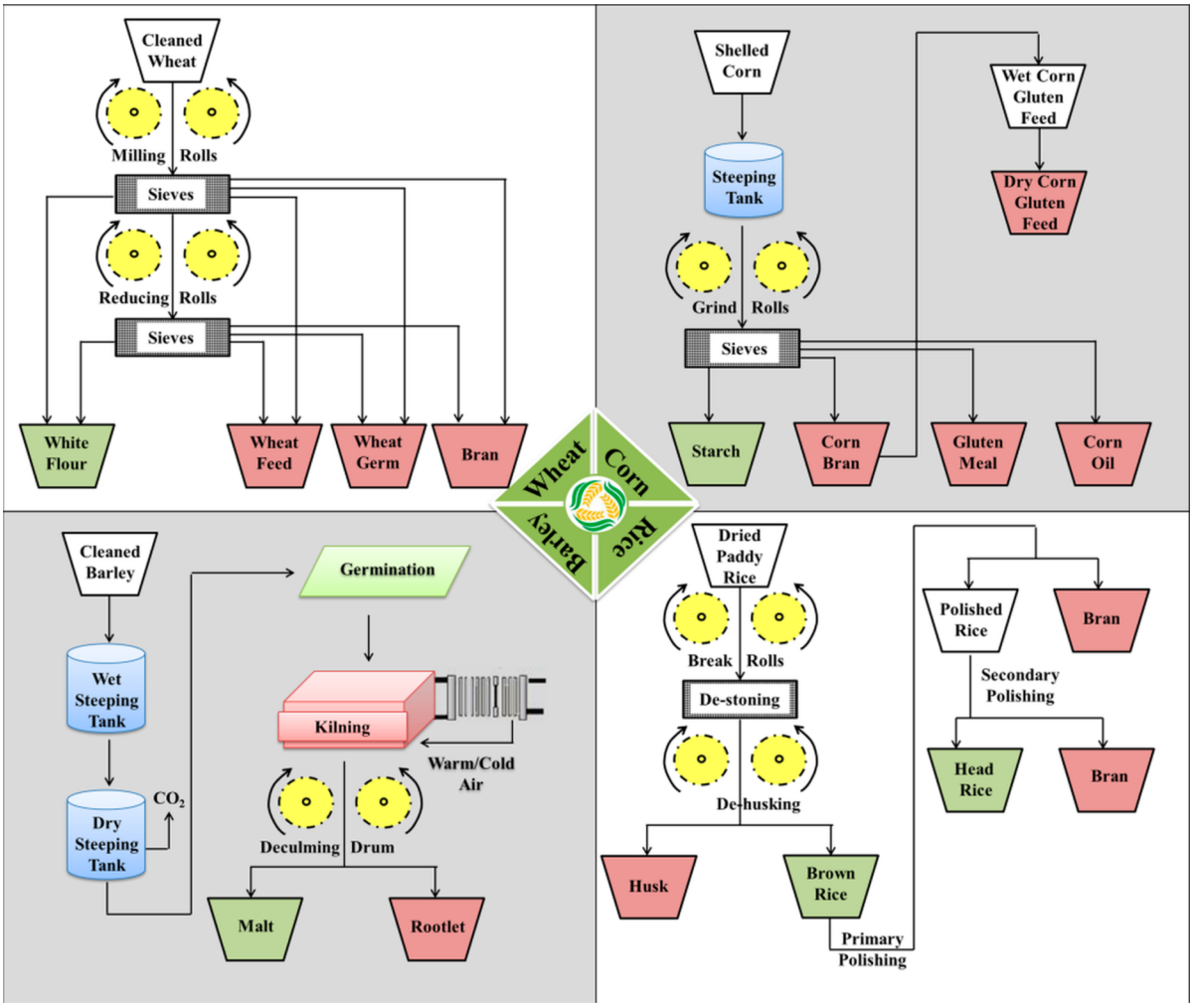

Figure 2. Schematic diagram of the main industrial processing of cereals illustrating products (green shade) and some byproducts (red shade).

of our modern lifestyle and can be found in products as miscellaneous as foods and fabrics.[7]

3. CEREAL BIOREFINERY

Cereal grains have been a primary human food source since thousands of years ago, being one of the most vital source of calories for a large sector of the world population.[8] The nature of grains produced worldwide relies on different factors, mainly being economic, cultural, and environmental. The availability of water and temperature are most likely the important environmental factors that determine the region in which these crops can be grown. World cereal production in 2012 reached 2300 million tons. The estimate for world cereal consumption in 2012/2013 has been increased to reach 2335 million tons (mainly use of maize), 5 million tons higher than reported in the first half of 2012.[9]

The existing cereal biorefinery uses dry cereals such as wheat, rice, and maize as raw materials. Currently, some of these crops, that is, maize and wheat, are used to produce biofuels. Maize starch is the major source for ethanol production in the U.S., where wheat feedstock is used for ethanol production in Canada, Australia, and in some European countries.[10] All of these crops are the conventional ones used for the production of first-generation biofuels. Second-generation biofuels are produced from lignocellulosic crops, such as fast-growing trees and permanent grasses or from straw residues. Great interest has been directed toward producing second-generation ethanol, since the above-mentioned crops can be cultivated in secondary lands without the need to interfere with the fertilized lands generally used for food production. Promising plant species like sweet sorghum have not been taken into account either. These crops can be cultivated in the food-unsuitable poor soils, with relatively low amounts of water, but their productivities are low and a lot of effort is needed to elevate their yields.[11] Wide areas of land are required to cultivate the crops for biofuels production, together with irrigation and use of fertilizers, which may destroy wildlife habitats, as well as affect indigenous and rural poor communities around the world. Instead the byproducts of these crops should be considered as a source of these biofuels.

The cereal grains used for human food are milled to eliminate the bran and germ, in order to meet consumers' sensory expectations. Grains are striped by this process of key nutrients valuable to human health, that is, phenolics, dietary fiber, minerals, and vitamins, which also needs to be studied for their potential as feedstocks.[12] Building economical cereal-based biorefineries as a replacement for petroleum refineries would require considerable improvements in existing cereal processing strategies by applying more proficient processing of cereal grains for the production of a range of value-added products, that is, biochemicals and bioenergy.

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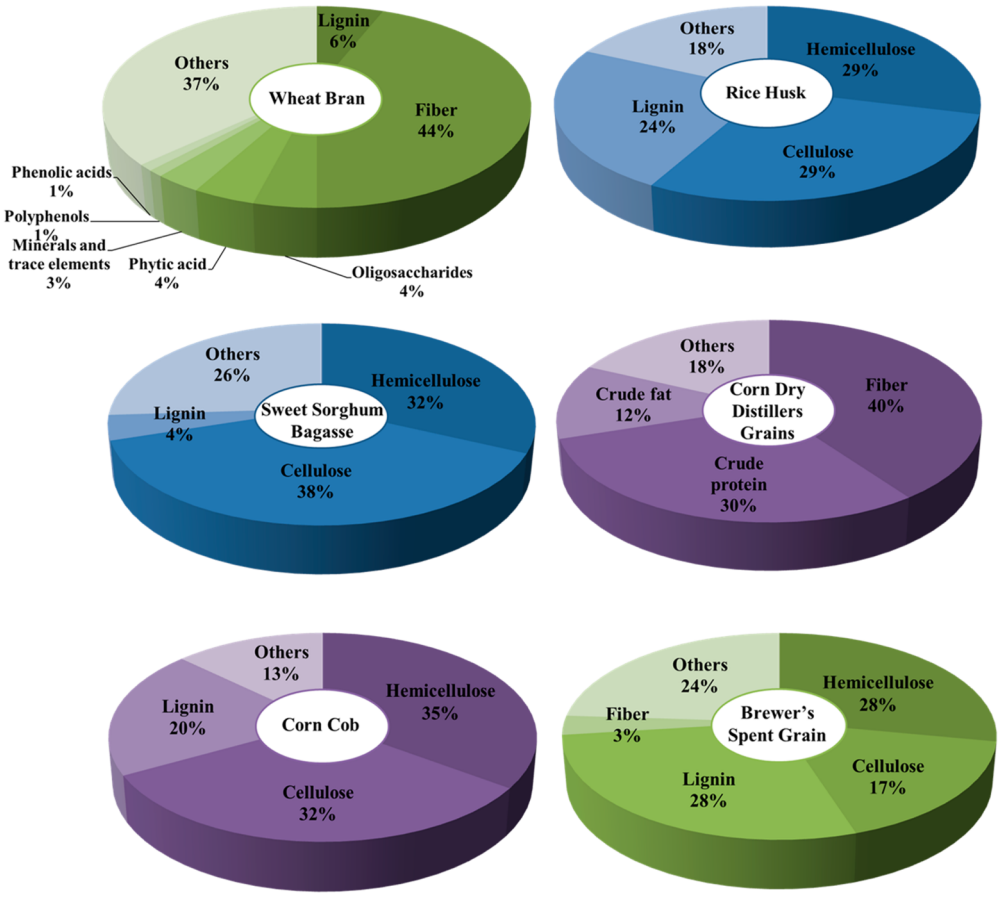

Figure 3. Average percentage content of bioactive compounds of some cereal industrial processing byproducts; wheat bran,[141] rice husk,[142] sweet sorghum bagasse,[143] corn dry distillers grain,[144] corn cob,[145] and brewer's spent grains.[146]

3.1. Industrial Processing. The main schematic industrial processing steps of some cereals are illustrated in Figure 2. Wheat grains are separated into their constituents (bran, germ, and endosperm) by the milling process steps, in which wheat is ground into flour. Before milling, the wheat is passed into conditioning bins to produce uniform moisture content throughout the grain. The bran and germ are separated from the endosperm by a sequence of breaking and grinding processes and subsequently the endosperm is reduced to form a uniform particle size by separating operation.[13]

Competing with wheat, barley is either milled or malted. The cleaned grains for milling are first conditioned, after which barley is washed-out with diluted sulfur dioxide. Barley is then smashed through a pearling process to separate surface layers of the grain. The pearl barley is polished and flakes are made from them by steaming, flaking, and drying. Pearl barley or unpearled barley could be milled to produce barley flour.[14] Furthermore, barley could be processed by malting, in which barley kernels are allowed to grow by first steeping the grains, which are then transferred from the steep tank to the germination vessel. Germination is completed upon the full modification of the endosperm, after which the process is terminated by drying (kilning process). The kilning brittle rootlets byproduct are removed to be used as a high protein feed (75%).[14]

Also, milling is a crucial step in postproduction of rice. This process starts with the removal of the hard protective husk surrounding the grain, which is done by passing the rice through two spinning rubber roles and the resulted rice grain is packaged as brown rice healthy for body functions. The following step includes usage of fine milling to separate germ and bran layers from the grain and expose the white starch pulp, known as white rice.[14]

Corn is processed by a dry milling process (degerming) in which hull, germ, and endosperm are separated prior to milling. This process starts by drying and cleaning the corn, which is then conditioned to 20% moisture. The majority of the outer bran, germ, and tip cap are removed from the moist grains, leaving the endosperm, which is then dried, cooled, and sieved.[14] Corn can also be processed by corn wet-milling, in which the precleaned grains are transferred to large steep tanks where they are soaked in a dilute sulfur dioxide solution. The corn germ is removed from the water soaked kernel, in which the germ is processed to recover the oil, and the remaining corn germ meal portion is collected for feed use. The corn nucleus is sieved to separate the bran leaving the starch and gluten protein. The gluten protein is concentrated and dried to form corn gluten meal with 60% protein feed.[14]

Similar to corn, sorghum grains are processed either by dry or wet milling processes. Additionally, sorghum could be milled for juice extraction by first being conditioned, then squeezed for juice extraction and produce bagasse byproduct which could be used as an excellent supplementation fiber for livestock or converted to a fuel.[15] The filtered juice is precipitated and then the supernatant is evaporated and surface coagulated materials are removed to obtain syrup.[15]

3.2. Byproducts Assortment. Nowadays, there is much attention for universal pollution along with growing production cost, and limited availability of raw materials leading to a special

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highlight on the importance of recovery, recycling, and valorization of food processing byproducts. The amount of biodegradable wastes drained to landfills in EU countries in 2020 is estimated to increase by 35% of its level in 1995. The European manufacturers of processed foods are obliged to meet the terms of EU environmental policy concerned with utilization or disposal of byproducts and the huge amounts of aqueous and solid wastes produced.[16] Although these wastes represent serious economic and environmental challenges, they contain extensive amounts of potentially reusable materials and energy. One of the most contributing wastes to these challenges is cereal byproducts with biochemical oxygen demand (BOD) and chemical oxygen demand (COD) levels that can reach $3.5 \times 10^4 - 5 \times 10^4$ and $10^5 - 1.5 \times 10^5$ mg/L.[5] Generally, as a result of the change in ratio of fibrous and nonfibrous carbohydrates, the energy values for the parent grains are higher than that of mill-feeds. In contrast, the protein contents for the parent grains are commonly lower than that of mill-feeds. The compositional information of some grain milling byproducts is illustrated in Figure 3.

General terms, referring to the cereal milling byproducts, are used to depict related components for several grains, whereas, some of these terms are used exclusively to describe a byproduct of one grain. One of the most important milling byproducts is bran which includes the coarse outer shell of the seed with small amounts of flour and higher content of fiber and protein. The most common types are corn, rice, and wheat bran.[17] The embryo of the cereal seed adds up to form the germ meal which is a byproduct rich in lipids and protein. The most common sources of germ meals are corn and wheat.[18]

After removal of the germ and the starch endosperm during wet milling, the primary substance remaining is the protein rich gluten. It is most commonly the byproduct of the milling of corn and sorghum.[19] Moreover, grain screenings is a byproduct which contains a mixture of chaff, dust, broken grains, weed seeds, and all separated materials during cleaning and processing. The nutritional value of grain screenings varies with the relative proportion of each of the components. Grain screenings are produced from all types of milled cereals with a minimum of 70% grains and maximum of 6.5% ash.

Grain hulls are the outer covering of the grain seed, commonly originating from oat and rice milling. Grain hulls are high in crude fiber and relatively low in energy and protein, whereas rice hulls are high in silica.[20] Also, one of the major byproducts from malting industry is the barley malt sprouts which consist of roots, sprouts, and malt hulls. Malt sprouts are considered as a protein source with minimum crude protein content of 24%. The oat milling byproduct is oat meal, consisting of lower quality oat meal portions with maximum crude fiber content of 4%.[21]

The production of flour is accompanied by some byproducts such as middlings (abbreviated as midds) which contain bran, shorts, germ, flour, and tailings and mostly originate from rye and wheat industrial processing. The maximum levels of fiber for rye and wheat middlings are 8.5% and 9.5%, respectively.[22] The main rice milling byproduct is rice polishing, which is a good source of thiamin and crude fat and relatively a poor source of crude fiber. Also, rice bran is another byproduct which has a high oil content and is a good source of B-complex vitamins, protein, and amino acids.[23]

The frequent corn byproducts of dry milling are corn flour, corn bran, and hominy feed, whereas the common byproducts of corn wet milling are liquefied corn product, starch molasses, germ meal, gluten, hydrolyzed corn protein, and condensed fermented corn extractives. Also, Sorghum milling can produce some byproducts, that is, gluten and grits.[24]

4. CEREAL BIOREFINERY WASTE VALORIZATION

4.1. Bottlenecks. The efficient and economic disposal of cereal processing byproducts is the main concern of industrial society, in order to fulfill the environmental regulations that regard them as wastes destined to be drained off in most cases. This trend may be due to the lack of information for different economic biomolecules availability and technical processes for extracting them, besides the lack of commercial knowledge concerning customer requirements. The value addition and adequate utilization of cereal processing byproducts is very important for the valorization technology of such byproducts. Moreover, if the valorization "know-how" is available for certain industrial byproduct in laboratory or pilot scale, the efficient scaling-up of this technique is limited by the standardization of the production process on the industrial scale.

Current sugar-based platform biorefineries mainly focus on the valorization of cellulose and hemicelluloses,[25] while lignin is generally considered as a low-value residue.[26,27] This may be due to the complexity and polydispersity of lignin compared to sugars normally released as uniform monomeric carbohydrates, which limit lignin wide-scale use in biorefineries. Besides, recovery of lignin from their product streams is difficult, with different composition of lignin contained by the tissues of individual plants and according to its source.[28,29] The efficient utilization of lignocellulosic materials requires its pretreatment prior to the enzymatic hydrolysis and fermentation, which results in opening up the cell wall structure by disturbing the lignin/hemicelluloses complex and exposing the cellulose to enzymatic hydrolysis.[30]

The pretreatment process is considered the most expensive step in the valorization of lignocellulosic byproducts, where it can contribute to about 30% of the total cost.[31] Due to this problem, several methods of pretreatment processes have been investigated which include alkaline or acid hydrolysis, milling and grinding, gas treatment by ozone or sulfur dioxide, steam explosion, organic solvent treatment, liquid hot water, wet oxidation, ammonia fiber explosion, biological treatments, cellulose solvent pretreatment, and ionic liquid.[31−35] On the other hand, some of these methods, that is, acid hydrolysis and steam explosion, produce some byproducts like furfural and hydroxyl methyl furfural (HMF) which negatively affect the fermentation process, and this requires a separate detoxification step, for example, ion exchange, addition of activated charcoal, and over liming, which in turn increase the overall process cost.[31] Also, the expenditures are negatively affected by the power requirements for achieving the optimum reaction conditions for some pretreatments and costly downstream processing to remove extraneous chemicals that are added to the biomass. Moreover, the use of expensive industrial equipments are necessary to avoid corrosion normally associated with acid hydrolysis.[36] All of this reflect the need for integrated technologies for efficient treatment and the maximal recovery of energy from lignocellulosic byproducts. Alternatively, the use of untreated lignocellulosic biomass as substrate cause several problems, that is, substrate agglutination and clogging, in addition to microbial degradation resistance.[37]

The substrate uniformity is one of the most significant factors that influence the energy poise and the total economics in the valorization process of lignocellulosic biomass. With high solid

Table 2. Overview of Valorization Bioprocesses of Wheat, Barley and Sorghum by-Products and Their Main Features.

cereal type	byproduct	valorized product	productivity[a]	hydrolysis pretreatment	microorganism	fermentation type	reference
wheat	gluten	SA[c]	22 g/L	enzymatic	*Actinobacillus succinogenes*	SmF	56
	gruel	amylase	5920 U/g		*Aspergillus oryzae*	SmF	59
	starch	$BioH_2$[d]	65.2 cm^3/g	hydrothermal	*Rhodobacter* sp.	PF/DF	90
	feed		64 cm^3/g		Sewage sludge	SmF	91
	Bran	LA[e]	57.61 g/L	acidic	*L.*[h] *rhamnosus*	SmF	51
		SA	50.6 g/L	enzymatic	*Actinobacillus succinogenes*	SmF	57
		cellulase	1.1 IU/mL		*Aspergillus flavus*	SmF	65
		vanillin	0.09 g/L	hydrothermal and enzymatic	*E.*[i] *coli*	SmF	72
		EtOH[f]	12.1 g/L	acidic and enzymatic	*S.*[j] *cerevisiae*	SmF	97
			13 g/L	acidic and enzymatic	*S. cerevisiae*	SmF	98
			10.7 g/L	acidic and enzymatic	*S. diastaticus*	SmF	99
	stillage		28 g/L	acidic	*Zymomonas mobiliz*	SmF	100
barley	malt	$BioH_2$	1.07 mL/g	hydrothermal	*R.*[k] *sphaeroides*	PF	88
	waste		0.4 L/L	acidic	*R. sphaeroides*	PF	89
		methane	222 mL/g	alkaline	Anaerobic sludge	AnF[m]	119
	BSG[b]	LA	0.59 g/Lh	enzymatic	*L. delbrueckii*	SmF	48
		xylitol	0.78 g/g	acidic	*Candida guilliermondii*	SmF	77
		citric acid	11.8 g/Kg		*Aspergillus niger*	SSF	54
		amylase	21 U/L		*Bacillus* sp.	SmF	60
	bran	laccase	2×10^4 nKat/L		*Trametes versicolor*	SSF	69
sorghum	bagasse	EtOH	4.9 g/g		*S. cerevisiae*	SSF	104
			0.7 g/Lh	alkaline and enzymatic	*Mucor hiemalis*	AnF	105
			21.2 g/L	enzymatic and hydrothermal	*S. cerevisiae*	SmF	103
			53 g/L	hydrothermal	Active dry yeast	SmF	102
			41.43 g/L	hydrothermal and enzymatic	*S. cerevisiae*	AnF	38
			38 g/L	acidic and enzymatic	*S. cerevisiae*	SmF	101
			0.209 g/g	acidic and enzymatic	*Issatchenkia orientalis*	SmF	106
		$BioH_2$	10.6 mmol/Lh	alkaline and enzymatic	*Caldicellulosiruptor saccharolyticus*	AnF	92
		BuOH[g]	12.3 g/L	acidic and pervaporation	*C.*[l] *acetobutylicum*	AnF	118

[a]Productivity is based on volume of product per weight of raw waste or volume per volume of culture. [b]BSG: brewer's spent grain. [c]SA: succinic acid. [d]$BioH_2$: biohydrogen. [e]LA: lactic acid. [f]EtOH: ethanol. [g]BuOH: butanol. [h]*L.*: *Lactobacillus*. [i]*E.*: *Escherichia*. [j]*S.*: *Saccharomyces*. [k]*R.*: *Rhodobacter*. [l]*C.*: *Clostridium*. [m]AnF: anaerobic fermentation.

content, the sugar and resulting product concentrations will increase, which leads to a significant reduction in capital and production costs due to the compact equipment size and low energy consumption during heating, cooling, and distillation. On the other side, these high-solid loadings generate environmental problems due to the absence of free water in the pretreated material and difficulties to handle the slurry.[38] Also, some cereal processing byproducts, that is, liquid stillage, must be dried because of their short shelf life which extends the durability, but increases the overall economics of the valorized product.[39]

4.2. Valorization Approaches. Valorization is the transformation of byproducts to alternative fuels, energy and other useful chemicals, with specific attention for sustainability and environmental objectives. This concept could be applied on cereal based biorefinery. Generally, cereal based biorefinery substrates are chemically (i.e., NaOH) or hydrothermally (i.e., steam explosion) and/or enzymatically (i.e., cellulase) pretreated before fermentation which could be through submerged, solid state, dark or photo fermentation. Submerged fermentation (SmF) is any aqueous fermentation process occurring in the presence of liquid substrate, whereas, solid-state fermentation (SSF) is any fermentation process occurring in the absence or near-absence of free water by employing a natural substrate as a solid support.[40] Dark (DF) and photo (PF) fermentation is the bacterial conversion of organic substrate to biohydrogen through a complex process involving biochemical reactions, with the difference that PF is held by a diverse group of photosynthetic bacteria in the presence of light.[41] The most recent valorization strategies for cereal based biorefinery wastes are illustrated in Tables 2 and 3 and detailed in the following sections.

4.2.1. Biochemicals. 4.2.1.1. Organic Acids. Organic acids and their derivatives are widely used in food, pharmaceutical, leather, and textile industries.[42,43] A lot of these organic acids are produced by bacterial fermentation.[44−46] However, the high production cost becomes a limitation for their applications in more fields. Therefore, much attention has been paid to searching for cheaper sources for the fermentative production of organic acids.[42,43,47] Lactic acid (LA) is one of the most important organic acids extensively used in pharmaceutical, food, chemical, textile, leather, polymer, and cosmetic industries.[48] The replacement of the costly pure raw materials usually used for LA production by agro-industrial residues can provide an attractive substitute because of their low prices.[49,50] These agro-industrial residues include brewer's spent grain (BSG) enzymatic hydrolyzate which was incorporated into culture medium, with glucose as carbon source, for the production of LA by *Lactobacillus delbrueckii*.[48] With this mixture, a yield of 0.99 g/g of BSG was obtained after 60 h of fermentation. This yield dropped to 0.45 g/g when wheat bran acidic hydrolyzate was used as the nitrogen source for LA

Table 3. Overview of Valorization Bioprocesses of Rice and Corn by-Products and Their Main Features.

cereal type	byproduct	valorized product	productivity[a]	hydrolysis pretreatment	microorganism	fermentation type	reference
rice	bran	β-glucosidase	159.1 U/g		*Penicillium citrinum*	SSF	40
		cellulase	196.8 U/mL		*B.*[h] *subtilis*	SmF	64
			5.76 IU/g		*Penicillium decumbens*	SSF	63
		PHA[c]	3.6 g/L	enzymatic	*Sinorhizobium meliloti*	SmF	76
		LA[d]	3.73 Kg/m^{3}h	enzymatic and acidic	*L.*[i] *Rhamnosus*	SmF	53
			280 g/m^3	enzymatic	*L. delbrueckii*	AnF[m]	49
	bran oil	vanillin	2.8 g/L		*Pycnoporus cinnabarinus*	SmF	74
	hull	EtOH[e]	0.11 g/g	acidic and enzymatic	*S.*[j] *cerevisiae*	AnF	107
			0.51 g/g	acidic	*Candida shehatae* and *S. cerevisiae*	SmF	108
	flake	glucoamylase	211.5 U/gds		*Aspergillus* sp.	SSF	61
	mill wastewater	electricity	2.3 W/m^3		Anaerobic sludge	AnF	123
corn	stillage	methane	763 mL/g	alkaline	Biomethanators	AnF	120
	DDGS[b]	protease	0.16 U/mL		*B. licheniformis*	SmF	68
	fiber	SA[f]	35.5 g/L	acidic	*Actinobacillus succinogenes*	AnF	58
		BuOH[g]	9.3 g/L	acidic and adsorption	*C.*[k] *beijerinckii*	AnF	116
			12.9 g/L	acidic	*C. beijerinckii*	AnF	117
		EtOH	44 g/L	acidic	*E.*[l] *coli*	SmF	110
	husk	Rifamycin B	1.95 g/Kg		*Amycolatopsis* sp.	SSF	79
	cob	vanillin	239 mg/L	alkaline	*E. coli*	SmF	73
		cellulase	5.25 IU/mL		*Trichoderma reesei*	SmF	66
		electricity	230 mW/m^3		*Geobacter metallireducens*	AnF	121
		EtOH	56.3 g/L	enzymatic	*Pichia guilliermondii*	AnF	37
	steep liquor		9.6 g/L		*Clostridium* sp.	AnF	112
		LA	110 g/L		*L. rhamnosus*	SmF	52
		biosurfactants	2.2 g/L		*Candida lipolytica*	SmF	82
		pullulan	88.59 g/L		*Aureobasidium pullulans*	SmF	78
	stover	electricity	1180 mW/m^2	acidic and enzymatic	mixed culture	AnF	122

[a]Productivity is based on volume of product per weight of raw waste or volume per volume of culture. [b]DDGS: distiller's dried grains with solubles. [c]PHA: polyhydroxyalkanoate. [d]LA: Lactic acid. [e]EtOH: ethanol. [f]SA: succinic acid. [g]BuOH: butanol. [h]*B: Bacillus*. [i]*L*: *Lactobacillus*. [j]*S*: *Saccharomyces*. [k]*C*: *Clostridium*. [l]*E*: *Escherichia*. [m]AnF: anaerobic fermentation.

production by *Lactobacillus rhamnosus*.[51] Also, corn steep liquor (CSL) was investigated as a sole and low cost nitrogen source in addition to some components to replace yeast extract for the cost-effective production of LA. Production of 115.12 g/L was achieved in shake-flask scale, whereas the concentration of LA in a bioreactor was 110 g/L.[52] Rice bran is one of the most abundant agro-industrial byproducts that was investigated in several studies for the production of LA. In two different trials, *L. delbrueckii*[49] and *L. rhamnosus*[53] were used to produce LA from enzymatically hydrolyzed rice bran which was used as carbon and nutrient source. *L. rhamnosus* (56 Kg/m^3) was superior to *L. delbrueckii* (9 Kg/m^3) and was 1.5 times higher in LA production than the glucose and yeast extract traditional medium due to the high nitrogen content and the presence of rice bran oil rich in fatty acids which is an important factor for LA production.

Citric acid (CA) fermentation by *Aspergillus niger* is one of the world's major industrial microbial processes. The same fungus was used to evaluate the economic CA production from the untreated BSG agro-industrial waste by solid state fermentation (SSF).[54] The resulted CA yield was 11.8 g/Kg after 120 h of fermentation.

Among the vital organic acids is succinic acid (SA), which is conventionally manufactured from petrochemicals through expensive processes. Higher economic benefit could be achieved with the use of agro-industries byproducts as potential resources to produce petrochemically derived products.[55] Two types of wheat milling byproducts were enzymatically pretreated and used to produce SA by *Actinobacillus succinogenes*. The pretreatment process was achieved through integrated biorefinery concept by using some wheat milling byproducts (i.e., bran) as a substrate in SSF for *Aspergillus* strains to produce glucoamylase and protease enzymes, which are used to pretreat wheat gluten[56] or wheat bran.[57] The SA production was doubled from 22 g/L upon using wheat gluten to 50.6 g/L with wheat bran substrate. Also *A. succinogenes* was anaerobically used for SA production from acid pretreated corn fiber byproduct and 35.5 g/L was obtained.[58]

4.2.1.2. Industrial Enzymes. Microorganisms are the most important and convenient sources for the production of commercial enzymes. They can be overexpressed under suitable growth conditions to produce abundant quantities of enzymes. With the initiation of a new era in biotechnology, the amylase enzyme family came forward with lot of industrial applications such as brewing, bread making, pharmacy, starch processing, paper, and textile industries.[59] The untreated BSG was used for the production of α-amylase by *Bacillus* sp. in a submerged fermentation system. The highest tested concentration of BSG (5%, w/v) resulted in a 5-fold enhancement in the enzyme production.[60] Another wheat milling byproduct, called gruel, was used by Kammoun et al.[59] as sole carbon source for the production of α-amylase from *Aspergillus oryzae*. The experimental conditions revealed an enhanced enzyme production of 151.1 U/mL. Also, SSF was applied for the production of this enzyme using paddy rice processing byproduct and the highest enzyme production was 211.5 U/gds (units per gram dried solid).[61]

Cellulases are another example of important industrial enzymes that are capable to degrade the most abundant cellulose biopolymer. Cellulases involve three major enzymes; β-glucosidase, exo-β-glucanase, and endo-β-glucanase. These enzymes act synergistically to convert crystalline cellulose to oligosaccharides and glucose.[62] A high yield (159.1 U/g) of β-glucosidase was achieved from rice bran-based SSF by the *Penicillium citrinum* fungus.[40] Also, Liu et al.[63] optimized the conditions of cellulase production by *Penicillium decumbens* in SSF using rice bran as the substrate and obtained 5.76 IU/g, whereas Lee et al.[64] used rice bran in combination with yeast extract to produce the same enzyme in SmF by *Bacillus subtilis* and 196.8 U/mL was obtained. Different agro-industrial residues were used for the production of this vital enzyme such as enzymatically treated wheat bran which exhibited 1.1 U/mL of the cellulase enzyme under SmF by *Aspergillus flavus*,[65] or untreated corn cob which produced 5.25 IU/mL under SmF by *Trichoderma reesei*.[66]

Proteases are one of the most important categories of industrial enzymes, and the application of alkaline proteases has increased remarkably in a range of industrial processes including food, detergents, silk, and leather.[67] Romero et al.[68] aimed at developing a process for protease production by *Bacillus licheniformis* using corn distiller's dried grains with solubles (CDDGS), a bioethanol industry byproduct, as the sole carbon/nitrogen source. The maximum protease production was 0.16 U/mL after 55 h of fermentation.

Laccases are abundant in white-rot fungi, which are the only living organisms able to degrade whole wood components, particularly, the genus *Trametes* which is the most efficient lignin degraders. The potential of the common brewing industry byproduct, barley bran, as a support-substrate for laccase production by *Trametes versicolor* under SSF conditions was evaluated by Rodríguez Couto.[69] Laccase activity was enhanced by 13-fold in relation to inert support cultures with initial ammonium concentration of 0.2 g/L.

4.2.1.3. Vanillin. Vanillin is used as flavoring agent in food industry, as intermediate in the herbicides industry, drugs or antifoaming agents,[70] as component of household products such as floor polishes and air fresheners. Also it is used as food preservative because of its antimicrobial and antioxidant properties.[71] The precursor of vanillin is ferulic acid which can be released from agricultural residues by physicochemical and/or enzymatic treatments.[72] Di Gioia et al.[72] explored the possibility of obtaining vanillin from the bioconversion of ferulic acid derived from enzymatically hydrolyzed wheat bran by an engineered *E. coli* strain. A vanillin concentration of 0.09 g/L was obtained, due to a high percent of reduction to vanillyl alcohol. Another trial was performed by Torres et al.,[73] in which corn cob was hydrolyzed by alkaline to obtain 1171 mg/L ferulic acid that was used as a medium for vanillin bioproduction by the engineered *E. coli*. A maximum vanillin concentration of 239 mg/L was obtained after 22 h. A different technology of converting ferulic acid, from the rice bran oil byproduct, into vanillin was developed by a combination of the fungal strains *Aspergillus niger* and *Pycnoporus cinnabarinus*, in which the filtrate of *A. niger* culture was concentrated and vanillic acid in the filtrate was fermented into vanillin by *P. cinnabarinus*.[74] The concentration of vanillin reached 2.8 g/L.

4.2.1.4. Biopolymeric Materials. Biopolymers are important materials having applications in several industrial sectors like pharmaceutical, food and cosmetic industries. They can be categorized to polyesters (i.e., polyhydroxyalkanoates), polyalcohols (i.e., xylitol) and polysaccharides (i.e., pullulan). The biotechnological method of producing such polymers has high interest as an alternative to the chemical method because of the little energy required and specificity.[75] However, the cost of these polymers is preventing their usage on a large scale. The carbon cost accounts for more than half of the biopolymer total production cost. Therefore, researchers are trying to use various cheap carbon sources, including agro-industrial byproducts.[76] One of the initial trials was conducted by Mussatto and Roberto[77] to evaluate the applicability of acidic hydrolyzate BSG as culture medium for xylitol production by *Candida guilliermondii*, and obtained a xylitol yield of 0.78 g/g. Recently, the production of pullulan from *Aureobasidium pullulans* was tested using CSL as nutrient along with 15% (w/v) glucose as carbon source.[78] CSL had a positive effect on the pullulan production (88.59 g/L), which accounted for 18% increase compared with glucose. Also, production of polyhydroxyalkanoate (PHA) by *Sinorhizobium meliloti* using enzymatic hydrolyzate of rice bran was tested.[76] The PHA contents increased with the increase in fermentation period from 24 to 96 h, with a maximum production of 3.6 g/L.

4.2.1.5. Other Valorization Products. Valorization options could be extended to the pharmaceutical field for the bioproduction of antibiotics. The rifamycins are a group of antibiotics that are synthesized either artificially or naturally by the bacterium *Amycolatopsis*. Rifamycin B production by *Amycolatopsis* sp. was investigated under SSF using different agro-industrial byproducts (corn husk, corn cobs, and wheat bran).[79] Corn husk was the most suitable substrate (1.95 g/kg) with 4-fold higher production than wheat bran and corn cobs.

As a result of growing environmental attentiveness and the prominence placed on an ecological society in agreement with the global environment, biosurfactants of microbial origin have recently been recommended to substitute chemically synthesized surface active agents.[80,81] Low-cost media based on animal fat and CSL combined with glucose, yeast extract, urea, and other inorganic nitrogen sources were evaluated for the production of biosurfactants by the yeast *Candida lipolytica*.[82] Only 2.5% of the CSL remained after six days and 2.2 g/L of crude biosurfactant was produced, causing a maximum reduction in surface tension from 50 to 28 mN/m.

4.2.2. Bioenergy. 4.2.2.1. Biohydrogen. Hydrogen gas is an eco-friendly fuel with high energy content (122 kJ/g). Unlike fossil fuels emissions, only water vapor is released when hydrogen gas is used which contributes to reducing greenhouse effects significantly.[83] Although H_2 has many obvious advantages, it remains a problem with storage and transportation. Pressurised hydrogen gas takes a great deal of volume compared with other fuels like for example, gasoline that with equal energy content, needs about 30 times less volume at 100 bar gas pressure. Due to the high explositivity there are also obvious safety concerns with the use of pressurized or liquefied hydrogen in vehicles as well as additional energy use for pressurizing or liquefication.

PF by purple nonsulfur (PNS) bacteria, like *Rhodobacter* species, is among biohydrogen production methods that has attracted distinctive consideration. This is due to the fact that these photosynthetic bacteria have a number of advantages such as performing anoxygenic photosynthesis to produce hydrogen without oxygen, absence of hydrogen gas inhibition due to nitrogenase enzyme, utilization of a wide variety of substrates for hydrogen production and conferring different growth modes with respect to energy and carbon requirements.[84,85]

DF is more effective than photo because of the sensitiveness of PF and requirement of low concentration substrates. DF can withstand very high substrate concentrations and even complex substances.[86]

Biomass containing starch and cellulose, that is, agro-industrial byproducts, establish rich and consistent raw materials for biohydrogen production.[83,87] An integrated biohydrogen refinery was suggested by several researchers, in which pretreated barley malt byproduct is utilized to produce biohydrogen by *Rhodobacter sphaeroides*. Redwood et al.[88] used the obtained biohydrogen (1.07 L/Kg) as a fuel for the production of electricity through fuel cell, while Kars and Ceylan[89] coproduced biohydrogen (0.4 L/L) and 5-amino-levulinic acid (67.4 μM) using the same byproduct and microorganism. Moreover, wheat starch was investigated using fed-batch operation for biohydrogen production by combined dark and light fermentation.[90] The optimum dark/light ratio was $^1/_2$ yielding the highest cumulative hydrogen (65.2 cm^3/g). Also, alkaline-treated wheat milling byproduct was fermented with sewage sludge in different fermentation modes (batch, semicontinuous and continuous).[91] The maximum hydrogen yields of 64 cm^3/g of wheat feed dry weight were produced in batch mode. The anaerobic bacteria *Caldicellulosiruptor saccharolyticus* was investigated for the production of biohydrogen from the alkaline pretreated sweet sorghum bagasse (SSB),[92] and a maximal volumetric hydrogen production rate of 10.6 mmol/Lh was obtained.

4.2.2.2. Bioethanol. Bioethanol produced from low-cost biomass is considered as an attractive substitute to fossil fuels to minimize dependence on oil and reduce carbon dioxide emissions.[93−95] Ethanol could be produced from any material containing simple or complex sugars. *Saccharomyces cerevisiae* cells have average theoretical and practical ethanol yields of 0.5 and 0.4 g/g of glucose, respectively.[96] Currently, the main biomass for bioethanol is starch-rich feedstock in which high yields of glucose are rapidly obtained by enzymatic hydrolysis. Substrate is one of the key costs in ethanol production. Putting this aim into focus, many studies tried to investigate the possibility of using agro-industrial byproducts as the main substrate for bioethanol production. Wheat bran is among these byproducts, in which it was used for bioethanol production by *Saccharomyces* species after being hydrolyzed by acid or hydrothermal followed by enzymatic treatment. Under these conditions, different ethanol yields were obtained with average concentration of 13 g/L.[97−99] This amount was doubled (28 g/L) when acidic hydrolyzed wheat stillage (main residue from the starch-to-ethanol fermentation process) was fermented by *Zymomonas mobiliz*.[100]

Also, *S. cerevisiae* was investigated for the production of bioethanol using SSB pretreated with hydrothermal or acid treatment followed by enzymatic hydrolysis in submerged fermentation.[38,101−103] Bioethanol production was almost doubled from 21.2 g/L[103] to 53 g/L[102] due to the usage of sweet sorghum juice mixed with the pretreated and dewatered bagasse. On the other hand, SSB without any pretreatment was used to immobilize *S. cerevisiae* through SSF for the production of bioethanol.[104] The ethanol productivity of the immobilized cells was 2.24 times higher than the free cells, with an ethanol yield that reached 4.9 g/g. The ability to ferment SSB is not restricted only to bacterial cells, but it could be performed with fungal cells as well. Goshadrou et al.[105] studied the production of ethanol from the pretreated SSB by a zygomycetes fungus *Mucor hiemalis*. The bagasse was treated with sodium hydroxide, prior to enzymatic hydrolysis by commercial cellulase and β-glucosidase enzymes. A 24 h fermentation on the pretreated bagasse resulted in about 81% of the corresponding theoretical ethanol yield. The effect of different pretreatments and microbial strains on SSB for bioethanol production was investigated.[106] It was found that maximum production of bioethanol was obtained (209.2 mg/g) after 24 h fermentation by *Issatchenkia orientalis* with dry bagasse previously treated with HCl and enzymes as a substrate.

Moreover, *S. cerevisiae* with acid/enzyme pretreated rice hull as a substrate was used for bioethanol production, and 0.11 g/g of rice hull was obtained with 84% of dissolved sugars converted to bioethanol.[107] This yeast was also combined with *Candida shehatae* to ferment the acidic hydrolyzed rice hull to ethanol.[108] The coculture showed an ethanol yield of 0.51 g/g. The pretreatment of rice hull by the wet air oxidation (WAO) method was inspected by Banerjee et al.[109] The remained cellulose was around 92%, while the recovered lignin was 20%, showing oxidation of the majority of lignin. The high cellulose content and minor residual lignin in the solid fraction would greatly enable subsequent enzymatic hydrolysis, with improved ethanol yields from rice hull.

Different pretreatments with various corn milling byproducts were evaluated for the production of bioethanol. Corn fiber was hydrolyzed by dilute sulfuric acid, and subsequently fermented by *E. coli* to produce 44 g/L of bioethanol.[110] Coupling a pervaporation membrane unit to the hydrolyzate fed-batch fermentation maintained the ethanol production below 25 g/L, with sugar utilized completely, for 5 days, which circumvented the toxicity effect of high ethanol concentration on cells viability.[110] Furthermore, the yeast strain *Pichia guilliermondii* was anaerobically adapted to hydrolyzed corn cob and used for ethanol production without any detoxification or external nutrient supplementation.[111] The maximum ethanol titer reached 56.3 g/L. Maddipati et al.[112] studied the feasibility of substituting yeast extract by the low cost CSL to produce ethanol using *Clostridium* strain. Compared to yeast extract, about 180% more ethanol (9.6 g/L) was produced after 360 h of fermentation in a 7.5 L bioreactor.

4.2.2.3. Biobutanol. Butanol is a carbon branched chain primary alcohol that could be an alternative fuel to ethanol due to its superior properties. Butanol is a metabolite of acetone/butanol/ethanol (ABE) fermentation by *Clostridium* species.[113−115] ABE fermentation has major hindrances, mainly the high cost of substrates and recovery. In order to overcome this shortcoming, the objective of several studies was to evaluate the economical use of pretreated agro-industrial byproducts to produce biobutanol. Qureshi et al.[116] compared acidic to enzymatic pretreatment of corn fiber byproduct subsequently fermented to biobutanol by *Clostridium beijerinckii*. Treatment of acid treated corn fiber with resin removed some of the inhibitors. The maximum production of ABE was 9.3 g/L from acidic corn fiber hydrolyzate. This amount increased to 12.9 g/L, when a mutant of *C. beijerinckii* with considerable inhibitor-tolerance was used for butanol production from nondetoxified acidic corn fiber hydrolyzate.[117] Pervaporation membranes were tested by Cai et al.[118] not only for the detoxification of the treated byproduct, but also for butanol separation from its fermentation broth. *Clostridium acetobutylicum* fermented acidic SSB hydrolyzate to produce 12.3 g/L butanol.

4.2.2.4. Biogas. Anaerobic biomethanation can be used as an alternative potential treatment for valorization of biodegradable

solid waste. Some of these organic solid wastes, that is, lignocellulosic byproducts have a limited biodegradability despite the high COD content.[119] Therefore, several studies were conducted to enhance the biomethanation process of such byproducts. For example, barley waste was pretreated by alkaline before it was anaerobically fermented by activated sludge.[119] This pretreatment reflected positively on the production of methane, which increased to 222 mL/g of volatile solids. Also, corn stillage was evaluated for anaerobic biogas production by biomethanator biomass after pretreatment with alkaline, and 763 mL/g of volatile solids was obtained.[120]

4.2.2.5. Bioelectricity. Regaining biochemical energy available in agricultural biomass is one approach that could be used to counterweight the world's current fossil fuel consumption. Agricultural crop byproducts, that is, cellulose and lignin, contain great amounts of biochemical energy. The potential for direct transformation of lignocellulosic biomass residues to electricity in a microbial fuel cell (MFC) was explored by several authors. Gregoire and Becker[121] developed a new single chamber solid-substrate MFC to hold the cellulose hydrolysis and fermentation processes. Untreated corn cob pellets were used as a fuel for the cell, which continuously produced electricity for more than 60 days. Bioaugmentation with *Geobacter metallireducens* improved MFC performance to generate a maximum power density of 230 mW/m^3. The acidic/enzymatic hydrolyzate of corn stover was used as a substrate for a mixture of electrogenic culture in one chamber MFC to produce bioelectricity, and 1180 mW/m^2 was obtained.[122] Also the performance of MFCs was evaluated while treating rice mill wastewater by anaerobic sludge.[123] Maximum COD removal efficiency of 96.5% and lignin removal of 84% were obtained. Maximum sustainable volumetric power (2.3 W/m^3) was achieved with 100 Ω external resistance.

5. THE LIGNIN ENIGMA

Lignin is one of the key components of lignocellulosic biomass together with cellulose and hemicellulose, representing about 4−35% of most biomass feedstock.[124] Lignins in cereals are guayacyl-syringyl-*p*-hydroxyphenyl with some structural units derived from trans-*p*-coumaryl alcohol.[125] The lignin is separated by either dissolution using solvents, that is, alkali, organosolv and milled wood) or separation of insoluble lignin by acid hydrolysis of cellulose and hemicellulose, that is, Klason and hydrolytic.[126] Generally, all of these methods change the structure of the resulted lignin.[127] This is clear in the Klason procedure that provides quantitative separation of altered lignin.[128] The eco-friendly organosolv technique gives high quality sulfur-free lignins.[129] Kraft lignins (i.e., Lignoboost) are accompanied by structural changes during the pulping process resulting in high content of free phenolic groups and C−C linkages.

6. CONCLUSIONS

This review contributes to knowledge about the future application of carbon rich agro-industrial byproducts for their value addition to biological chemicals and energy. It also offers economic and environmental benefits over traditional ways used to dispose off agro-industrial residues. Massive amounts of agricultural biomass are burnt in an open environment resulting in the release of harmful gases, which is not a sustainable method. It is clear that the utilization of agro-industrial byproducts as fermentation substrates require hydrolysis pretreatment due to the presence of complex polysaccharides in such biomass. Hydrolysis can be accomplished by enzymatic, chemical, and hydrothermal methods. Chemical hydrolysis uses up chemicals and produces chemically destructive effluents, whereas enzymatic hydrolysis requires optimization to achieve the best combination of enzymes for each feedstock and cannot quickly adapt to variable feedstock composition. On the contrary, hydrothermal hydrolysis is an eco-friendly method, even though it consumes energy.[88] Although biomass may be cheap, the costs of processing technologies can be high. These technologies include not only pretreatment of biomass, but enzymatic saccharification of the pretreated biomass, and fermentation of the hexose and pentose sugars released by hydrolysis and saccharification. Each process needs extensive research and improvement to develop productivity and economics. This can be achieved by increasing the efficiency of biorefinery in order to save resources and integrate in the existing industrial facilities, with eye on configurations that are eco-friendly.[130]

Therefore, prior to the successful application of this process on large-scale setups, consideration must be focused on the improvement of techniques for the hydrolysis of lignocellulosic biomass that result in higher sugar yields. Enzymatic hydrolysis requires further improvements especially in the terms of enzyme separation and reutilization after biomass treatment. Also, the complete characterization of the agro-industrial byproducts is required, in which it could be useful for the production of new microbial valorized products. The genetically modified microorganisms could be used to ferment C_5 sugars from hemicellulose, which is not normally assimilated by the natural microbial strains.

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Notes

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