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Adding Value to Agro-Industrial Wastes

da Silva LL

Department of Bioprocesss Engineering and Biotechnology - COEBB, Federal University of Technology, Dois Vizinhos, PR, 85660-000, Brazil

Biomass refers to renewable organic materials, including agricultural products and agricultural wastes, wood and its wastes, animal wastes, urban wastes, aquatic plants, and so on [1]. Lignocellulosic materials are the most abundant renewable organic biomass on Earth, being constantly generated through photosynthesis and existing in large numbers and wide variety from the forest to the sea. This biomass is emerging as an energy source among many kinds of new energy including wind energy, hydroenergy, solar energy, nuclear energy, etc.

The use of biomass instead of coal and oil to produce chemical substances that satisfy human requirements has begun to be gradually considered by scientists since the late 1960s when the negative impact of the coal and petroleum chemical industry on the environment was recognized. Besides that, a shortage of fossil energy is considered a serious problem.

Therefore, lignocellulosic biomass not only can ease energy and environmental problems, but also it is renewable. Furthermore all, the proposal of recycling economy and sustainable development strategies, conversion, and research in the application of natural lignocellulosic feedstock are highly valued and widely used. Because of this, lignocelluloses biotechnology has achieved rapid development in recent decades and expanded the research field significantly [2].

Along with the rise of green chemistry, lignocellulosic raw materials can be used for making several products that could replace petroleum derived products, according to the biorefinery concept. The most important applications of lignocellulose biotechnology are in Bioenergy with the bioethanol, biogas, and biohydrogen production and in Chemical Industry with some representative chemicals including acetone-butanol, lactic acid and polylactic acid (all obtained by glucose fermentation); levulinic acid produced from hydroxymethyl furfural (HMF) and used as raw materials in lubricants, softeners, solvents, polymers and other chemical products; xylitol (a sugar substituent), furfural (used as raw material in the synthesis of furan resins, chemicals and nylon) and a gum from where is also possible get thickeners, adhesives, protective colloids, emulsifiers and stabilizers, all obtained from xylose (from hemicellulose hydrolysis) and so on. From the hydrolysis of lignin, a phenolic macromolecule, it is also possible to obtain natural binders and adhesives, coal and free sulfur solid fuel [3].

Besides Bioenergy and Chemical Industry, lignocelluloses are also used in the Pulp and Paper Industry to improve the pulping properties and the quality of the ecological environment by reducing pollutants or by environmental remediation. Lastly, natural cellulosic raw materials can be used in the production of pollution-free biological pesticides, biological nitrogen fixation of organic fertilizer, microbial feed and feed additives, which can advance the level of eco-agriculture [2].

In bioethanol production, agro-industrial waste can be used in two distinct ways: in the second generation (2G) bioethanol production and as natural carbon sources such as those present in coconut milk, pineapple juice and tuna juice which are excellent media for the production of bioethanol by yeasts such as *Saccharomyces cerevisiae*. In the latter case, availability and low cost of the agro-industrial wastes make them highly competitive substrates for 2G ethanol production and reduction of environmental pollution [4]. However, the use of lignocellulosic biomass for 2G ethanol production is more flexible because this kind of biomass is present everywhere on the planet. In this process, biomass is first converted to sugars and then the sugars are fermented to ethanol.

Forest wastes used in paper industry, generate high quantities of solid and liquid residuals which have high content of lignin and sugars representing an important contamination source in rivers and also they are accumulated in landfills. However, they can be chemically or enzymatically hydrolyzed becoming a potentially valuable source of fermentable sugars for 2G bioethanol production [5] as well as other lignocellulosic biomass as sugarcane bagasse [6] and fruit residuals (banana [7,8], pineapple [7], orange [8-10], mandarin [8,11,12], lemon [8,13], apple [8], quince [14] and grape [15]).

Alternative procedures for clean fuel production in the future are the bio hydrogen and biogas production. Biological system for hydrogen (H_2) production (as anaerobic fermentation) offers a great potential of using different agro-industrial wastes as substrates. This strategy opens up infinite possibilities to the development and implementation of sustainable processes for converting renewable materials into different value-added products [16].

Biogas typically refers to a gas produced by the biological breakdown of organic matter in the absence of oxygen. It is primarily CH_4 and CO_2 and may have small amounts of hydrogen sulfide (H_2S), moisture, CO, and so on. In China's rural areas biogas fermented from human and livestock manure has been widely used for household energy. However, with the increasing severity of energy and environmental issues, the requirements for traditional biogas are also increasing [2]. Thus, biogas produced from various biomasses as raw materials would become a new energy source which not only can solve the current fuel shortage but also can be the way to produce alternative energy by large-scale automation of the modern industrial fermentation process in the future [17].

From hydrolysis of lignocellulosic materials is also possible isolate nanocellulose fibers (consisting of alternating crystalline and amorphous strings) and whiskers (elongated crystalline rod-like nanoparticles) which nowadays can be used in various fields, such as the textile, papermaking, and bioenergy industries due to its wide availability and properties [18-20]. Nanocellulose can be obtained by defibrillation of the pulp fibres or partial hydrolysis of cellulose chains [21] by mechanical, chemical, enzymatic and ultrasound sonication methods or a combination of these. Initially the amorphous regions of the cellulose chains are hydrolyzed due to their greater accessibility. When these amorphous regions are completely hydrolyzed, cellulose

***Corresponding author:** da Silva LL, Department of Bioprocesss Engineering and Biotechnology - COEBB, Federal University of Technology, Dois Vizinhos, PR, 85660-000, Brazil, Tel: +55-19-3536-8439; E-mail: lucimarasilva@utfpr.edu.br

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whiskers formed only by the crystalline regions are obtained. The successful nanofibrils extraction from orange peel was performed by its hydrolysis "in natura" using both cost-efficient enzymes from *Xanthomonas axonopodis* pv. citri *(Xac)* and commercial enzymes [10,22]. The nanocellulose isolated from the enzymatically treated solid residues have an average aspect ratio of 47 ± 18 nm, which is considered high and yields of 3% (g g^{-1} of dry orange peels).

Nanocellulose has a high crystal modulus (138 GPa) compared with some materials used in engieneering, as glass and aluminium (both with 69 GPa). Indeed, this natural nanoparticle has been the prime candidate to replace synthetic fibres due to its low cost, low density (1.5 mg m^{-3}), high toughness and biodegradability [21]. So, this natural nanoparticle has great applicability in nanotechnology in order to enhance mechanical and optical properties of materials, enhancing lightweight, biodegradable and transparent nanocomposites. In this context is possible to use biopolymers together with cellulose nanoparticles for the preparation of high performance nanocomposites for use as biomaterials, for example. Some biopolymers as zein and pectin are provenient from corn and orange residuals. Also is possible fermentate sucrosed liquids to obtain dextrana biopolymer (used in food and pharmaceutical industries) for example.

Among fruit agroindustrial residuals, citric ones stand out because they are used in the production of ethanol, cellulose fibers and biopolymer as well as they may also be used to obtain a wide variety of active ingredients as essential oils, carotenoids and bioflavonoids such as hesperidin and hesperetin which have many interesting bioactive properties (antioxidant, anti-inflammatory, hypolipidemic, vasoprotective and anticarcinogenic) that are the objects of intensive research, mainly for use in cosmetic and pharmaceutical industry [23].

Other lignocellulose biotechnology is the enzymes production. Agro-industrial wastes such as brewery waste and apple waste (pomace) are excellent sources for the production of ligninolytic enzymes as manganese peroxidase, lignin peroxidase and laccases [24]. The enzymatic complex that degrades lignin is valuable because it is responsible for the degradation of several organic pollutants, as polymeric dyes.

Summarizing, the use of various agricultural residues for the production of high value-added products represents an emerging topic, with very relevant applications. Various agro-industrial wastes can be converted to sustainable fuels and bio-chemicals as enzymes and other active principles used in the pharmaceutical and cosmetic industry. Also was exemplified the production of advanced nano and biomaterials and the use of organic synthesis in the context of biorefinery. In all these examples of industries the agro-industrial waste can be used to generate high value-added products. In a less significantly, these residues can also be fractionated to enriche animal feed. So, wastes should not be waste…. the future of energy is in the wastes.

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