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Chapter

Agro-Industrial Waste Revalorization: The Growing Biorefinery

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Abstract

Agro-industrial residues have been the spotlight of different researches worldwide, due to some of their constituents being raw material to generate a diversified variety of industrial products. Nowadays, this situation keeps prevailing and will increase continuously in the future. In the agroindustry, diverse biomasses are subjected to distinct unit processes for providing value to different waste materials from agriculture, food processing, and alcoholic industries. In this chapter, we reported an updated survey of different renewable organic materials that including agricultural wastes can be converted to bioenergy. Similarly, these wastes encrypt different bioactive compounds with an excellent nutraceutical functions and with high adding value. In addition, biocomposites can be elaborated using fibers from wastes with a wide variety of applications in the automotive and packaging industry. Vinasses derived from tequila industry in Mexico represent a lot of potential to extract biocompounds, and we propose a process to obtain them. A perspective of market trend is mentioned in this chapter for compounds derived from agro-industrial wastes. Adding value to those agro-industrial wastes can provide the reduction of negative impact emission, discharge, or disposal, solves an environmental problem, and generates additional income.

Keywords: bioenergy, biocomposites, bioactive peptides, biocompounds, vinasses

1. Introduction

Agro-industrial residues provide an enormous potential to generate sustainable products and bioenergy. An integrated biorefinery is turning into a promising solution with multiple outputs (biofuels, bioactive biocompounds, and biomaterials). Most of the residues generated are intended for landfill or are disposed in an uncontrolled way, causing environmental damage and economic loss. For that reason, it is necessary to develop a sustainable management of them. An integral waste management is proposed in the concept of circular economy to exploit renewable resources. Circular economy is based on the concept of biorefinery and the approach to

reduce, reuse, and recycle waste with the objective to recover materials derived from waste considering them as renewable resources [1].

A wide range of metabolites, materials, and energy can be obtained through the exploitation of agricultural residues. Being the commercial-scale technologies is the bottleneck to produce marketable bioproducts. In this review, we put aboard the multiple outputs that can have the agro-industrial residues from bioenergy until a wide array of metabolites can be extracted. In addition, we investigate the potential market for some products derived from residues, searching the revalorization of them.

2. Production of bioenergy

Nowadays, due to the increase in population, it is necessary to find a sustainable solution for the enhanced demand of energy in the world. The fossil fuels are limited and nonrenewable resources; the use of biomass for energy production seems to be a solution to provide energy and reduce the dioxide carbon emissions. The term biomass includes energy crops, residues, and other biological materials that can be used to produce renewable energy [2]. The first-generation biofuels are produced from agricultural crops such as corn, sugarcane, soybean oil, and sunflower [3]. However, there is a conflict due to these biomasses being used for food and generating the name "food versus fuel" [4]. Additionally, emissions of greenhouse gases (GHG) are believed to be lesser for second-generation biofuels than the first-generation fuels [3]. For these reasons, agro-industrial residues have gained attention due to their disponibility, and they include residues from crop, food, and oil industries.

2.1 Solid fuels

Pellets are the most common solid biofuels used; they are cylindrical structures made by compression derived commonly from agricultural residues, forest products, and wood industries [5]. Pellets are used mainly for house heating and in industrial sector. Even though the agro-industrial residues have less energy content than fossil fuels, their use presents great advantages such as the reduction of logistic costs, easy storage, and provision of a great opportunity for the revalorization of these unused residues [5]. For the pellet elaboration, the biomass is treated to be compacted and densified; this includes the drying, and after, the biomass is milled to obtain particles with similar size [6]. Afterward, the material is pressed in a pelletizer and pellets are packaged and stored. Some common methods to improve energy density are torrefaction, steam explosion, hydrothermal carbonization, and biological treatment. In torrefaction, reactions of dehydration and decarboxylation occur lowering proportions in O/C and C/H and increasing heating value [7]. Steam explosion is a treatment with hot steam under pressure and followed by decompression which disintegrates the lignocellulosic structure [8]. Steam explosion treatment increased the heating value in pellets from a different biomass [9]. The international market of pellets derived from wood has been increased, the USA, Canada, and Russia being the largest exporters to Europe, which is the main consumer in the world [10]. Several applications and uses have the pellets from residential to largescale power plants. The growing demand of sustainable and renewable fuels places the agro-industrial residue pellets with a great potential to supply renewable energy.

2.2 Liquid fuels

Liquid fuels as diesel and petrol are being replaced by liquid biofuels as biodiesel, bio-oil, bioethanol, and butanol. Biodiesel is obtained from feedstock oil

as waste cooking and frying oil, animal fats, and fish and microalgae oil, leather, winery, and agro-industrial wastes, directly or indirectly. Oleaginous microorganisms are used in the indirect way for biodiesel production; lipids produced are extracted to be transformed to biofuel. For biodiesel production, three main steps are included: pretreatment, transesterification, and separation. Pretreatment allows agro-industrial residues to be assimilable for the microorganisms and is categorized into acidic, basic, thermal, enzymatic, or combination treatments [11]. Other important aspect to consider is that during pretreatments inhibitors for microbial growth as furfural, acetate, and others can be formed and are necessary to find tolerant strains or medium detoxification [12].

Bio-oils are obtained from biomass through two main processes: pyrolysis and liquefaction [13]. Pyrolysis has taken more attention; fast pyrolysis of lignocellulose biomass for bio-oil production is low cost compared to liquefaction that produces low yield at high cost [14]. Due to their physicochemical characteristics, bio-oils cannot be used for fuel applications without previous treatment [13]. Treatments are based in partial or total elimination of oxygen, and two catalytic routes have been proposed: cracking and hydrotreating. Pyrolysis of agro-industrial residues has been reported for sesame, mustard, *Jatropha*, palm kernel, cottonseed, and neem oil cakes showing an additional value for these residues and reducing wastes [15].

Bioethanol is the most common biofuel, and their production involves steps as pretreatment, saccharification, fermentation, and distillation [16]. Pretreatment allows cellulose to unwind from hemicellulose and lignin to be more available for enzymatic hydrolysis, and commonly physical, chemical, and biological treatments are used to achieve this purpose [17]. The enzymatic hydrolysis allows converting cellulose to glucose or galactose monomers and presents a low toxicity as well as low utility cost and corrosion compared to chemical hydrolysis [18]. Biological treatment is an alternative to liberate cellulose with the use of microorganisms mainly as brown-rot, white-rot, or soft-rot fungi [19]. Once the saccharification is obtained, fermentation is carried on with microorganisms able to produce ethanol. For the microorganism selection, some parameters are necessary to have a broad-substrate utilization that is derived in a high ethanol yield and productivity, to be tolerant to high ethanol concentrations, temperature, and inhibitors presented in hydrolysate for which genetically modified or engineered microorganisms are a good option to achieve a complete utilization of sugars and better production [17]. The simultaneous saccharification and fermentation (SSF) and the separate hydrolysis and fermentation (SHF) are the most common processes usually used to ethanol production [16]. SSF using olive pulp from oil extraction and the yeast Kluyveromyces marxianus showed ethanol yields of 76% [20].

Due to its higher heat of combustion and less volatility and it being mixed with gasolines in higher percentage without any modifications in the car engines, butanol is considered a promising renewable biofuel [21]. Butanol is produced through anaerobic biological fermentation process using the *Clostridia* genus [22]. Agricultural residues can be used for economical production of butanol. Simultaneous hydrolysis of wheat straw to sugars and fermentation to butanol resulted in an attractive option for ABE fermentation [23]. Rice bran has resulted to be an effective substrate to butanol production using *C. saccharoperbutylacetonicum* [24]. Agricultural residues can be a promissory source to be efficiently utilized as substrate for butanol production.

2.3 Gas fuels

Biobutanol is a product from anaerobic biological process called ABE fermentation, which converts sugar by using genus *Clostridia* into butanol, acetone, and

ethanol in a ratio of 6:3:1, respectively. In this process, genus *Clostridia* such as *Clostridium acetobutylicum*, *Clostridium beijerinckii*, *Clostridium saccaroperbutylacetonicum*, and *Clostridium saccharoacetobutylicum* showed significant activity for synthesis of butanol with higher yield. Biobutanol is a product from anaerobic biological process called ABE fermentation, which converts sugar by using genus *Clostridia* into butanol, acetone, and ethanol in a ratio of 6:3:1, respectively. In this process, genus *Clostridia* such as *Clostridium acetobutylicum*, *Clostridium beijerinckii*, *Clostridium saccaroperbutylacetonicum*, and *Clostridium saccharoacetobutylicum* showed significant activity for synthesis of butanol with higher yield.

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Lignocellulosic biomass is a potential source of glucose, xylose, mannose, and arabinose and other organic compounds that can be anaerobically degraded to produce biogas [25]. Biogas is produced through an anaerobic digestion with four steps identified as hydrolysis, acidification, and production of acetate and finally methane using a microorganism consortium [26]. The final product is a gas mixture composed mainly of methane and carbon dioxide and traces of hydrogen sulfide, ammonia, hydrogen, and carbon monoxide [27]. For the enhancement of biogas production, it is necessary to apply pretreatments, and the most commonly used are dilute acid hydrolysis, steam explosion, alkaline hydrolysis, and liquid hot water [28], while Song et al. tested nine pretreatments showing that H_2O_2 and $Ca(OH)_2$ enhance methane yields [29].

3. Biocompounds from agro-industrial wastes

3.1 Polyphenols

Phenolic compounds are a group of chemical compounds that are widely distributed in nature, and their basic structure varies from a simple molecule to a complex skeleton and hydroxyl substituents. These compounds are being the most desirable phytochemicals due to their antioxidant activities that can be useful for the control of different human diseases or disorders [30]. Due to their reactivity, these compounds efficiently interact with important biomolecules such as DNA, lipids, proteins, and other cellular molecules to produce desired results, which then are used for designing natural therapeutic agents. Flavonoids, tannins, anthocyanins, and alkaloids are polyphenols with industrial significance and are present in fruits and plants. In addition, most of the phenolic complexes are found in barks, shells, husk, leaves, and roots [30]. Recently, agro-industrial wastes from fruits, vegetables, and crops have been subjected to different metabolite methods of extraction as a potential source of industrial bioactive compound production. For example, tomato processing industry approximately generates 8.5 million of tons of wastes globally [31], wastes such as seeds, pruning, and peels which contain a high concentration of bioactive phytochemicals. In that sense, peels and seeds of tomatoes are a richer

source of bioactive compounds such as carotenes, terpenes, sterols, tocopherols, and polyphenols [32], which exhibited excellent antimicrobial and antioxidant activities and high support of dietary fiber. Other important crop that generates a high amount of waste is the coffee production. Due to the heterogeneous nature of coffee waste, most of the authors are investigating its possible revalorization to determine the content of chemical compounds such as tannins and phenolic compounds. Exhausted and spent coffee ground wastes derived from industries, restaurants, and domestics are a valuable source of phenolic compounds. For example, in coffee waste derived from coffee industries, different ranges of concentrations of polyphenols and tannins around of 6 and 4%, respectively, were found [33]. J. curcas and Ricinus communis are the most important energetic plants for the biofuel industries; these plants generated high amounts of residues such as seed cake, pruning material, and seed shells with high concentrations of bioactive compounds. In fact, shells of this plants contained high contents of phenolic compounds and exhibited strong antioxidant activities [34]. Extracts of residual wastes of seeds, leaves, fruits, stems, and roots derived from *R. communis* exert different nutraceutical effects such as antioxidant, antimutagenic, as well as DNA protection against photooxidative stress [35].

3.2 Pigments

Agro-industrial wastes can be used as a feedstock extraction and for different fermentation processes as a main source of microbial nutrients to produce biopigments useful in food and cosmetic industries. Chemically synthesized food colorants used as the additives in foods cause the risk of toxicity and hazardous effects to the consumers, than the natural pigments, that are quite safer, nontoxic, and nonhazardous for the environment [36]. The production of natural pigments can be derived from direct plant extraction (e.g., anthocyanins, chlorophylls, carotenoids, and melanin) or by fermentative production through the cultivation of bacteria, yeast, fungi, and algae (e.g., phycocyanins, xanthophylls, and melanin) [37]. Cyanobacteria and microalgae produce high amounts of beta-carotene and astaxanthin, which are used in the industries and have a great commercial value in pharmaceutical and food industries [38]. Different microorganisms such as Streptomyces, Serratia, Cordyceps, Monascus, and Paecilomyces, Penicillium atrovenetum, Penicillium herquei, Rhodotorula, Sarcina, Cryptococcus, Phaffia rhodozyma, Pseudomonas, Bacillus sp., Vibrio, Monascus purpureus, Achromobacter, Yarrowia, and *Phaffia* have shown their potential in pigment production as a major source of blue and yellow-red pigments [39]. Other important pigment is the melanin, which is present in animals, plants, and microorganisms to provide stress protection against UV radiation, oxidation, and defense [40]. This pigment is used for the cosmetic and pharmaceutic industries with a photoprotective and antioxidant importance in different products. The use of agro-industrial wastes such as fruits is a potential source for the melanin biosynthesis by microorganisms and is an attractive choice for commercial-scale production. For example, fruit, wheat bran extracts, and cabbage wastes were used as inoculum in Bacillus safensis [41], fungus Auricularia auricula [42], and Pseudomonas sp. [43] for the melanin production. Melanin is specially found in the seed coat of different plants; however, it is also found in other plant structures such as black spots of leaves, flowers, and seeds [44]. There are a few reports related to the melanin extraction from agro-industrial wastes. In that sense, sunflower husk derived from the oil production was subjected to the melanin extraction, and a technological scheme of melanin production from this waste was developed with a potential application as prophylactic mean and medicinal agent for the treatment of human diseases [45]. Similarly, residues as shells and epicarp from walnut contain high amounts of melanin with a high antioxidant capacity [46].

3.3 Peptides

Bioactive peptides are encrypted within the protein sequences with different bioactivity functions and relevant in some important disorders in human health such as cancer, hypertension, antioxidant functions, diabetes mellitus, and other important diseases. These peptides may have different sizes, around 2–20 amino acid residues per molecule with molecular masses between 1 and 6 kDa and based on their physical properties and amino acid composition [47] which make them very attractive for different applications in pharmaceutical and food industries. Waste can contain many valuable substances, and through a suitable process or technology, this material can be converted into value-added products or raw materials that can be used in secondary processes. Residual wastes generated by agro-industries are a protein-rich source and have become an alternative for obtaining compounds with bioactivity, mainly from protein hydrolysates; their extraction processes do not involve negative environmental impacts [48]. The principal residual wastes generated by the agro-industrial activities are soybean meal, residues of oiled plants, and rapeseed meal [48]. Those peptides can generate in the market peptides and protein drugs more than \$40 billion/year, with an accelerated pace in the drug market [48]. The press cake, after oil extraction from *J. curcas* (not toxic genotypes) in biodiesel production, represents a potential of new source of protein for food and feed uses. The seed cake of *Jatropha* contains a high concentration of storage proteins mainly glutelins and globulin fractions [49] that encrypted peptides with antioxidant, chelating, and antihypertensive activities [50]. Some peptides have activities against bacteria that can reduce the human infections. In that sense, a trypsin inhibitor was purified from castor bean waste of seed cakes; the 75-kDa peptide displayed antibacterial activity against Bacillus subtilis, Klebsiella pneumoniae, and Pseudomonas aeruginosa, which are important human pathogenic bacteria. In addition, microscopy studies indicated that this peptide disrupts the bacterial membrane with loss of the cytoplasm content and ultimately bacterial death. The author concludes that this peptide is a powerful candidate for the development of an alternative drug that may help reduce hospital-acquired infections [51]. Other important seed cakes from oiled plants can be used for the peptide characterization. For example, chia (Salvia hispanica) seed cake is novelty for the peptide extraction; the seed cake contains high amounts of proteins that encrypted different peptides with antioxidant, antidiabetic, and antihypertensive activities [46].

4. Biocomposites

Biocomposites are formed by a polymer matrix and natural fibers, which act as reinforcements. There are six types of natural fibers commonly used in biocomposite elaboration: grass and reed fibers (wheat, corn, and rice), core fibers (kenaf, jute, and hemp), bast fibers (jute, flax, hemp, ramie, kenaf, bamboo, and banana), seed fibers (coir, cotton and kapok), leaf fibers (abaca, sisal, and pineapple), and other types (wood and roots) [52].

The composition of natural fibers consists mainly of cellulose, hemicellulose, and lignin. Cellulose in plants is the main component that provides stability and strength to the cell walls, and this component directly influences the biocomposite production for a defined application, whether in the textile, automotive, and others. Lignin is a highly cross-linked structure, and the amount of this directly influences the structure, properties, morphology, hydrolysis rate, as well as the flexibility of the fibers. Besides, fibers with greater amount of lignin have less amount of cellulose, and this will also depend on the application of the fiber.

The fibers can be used in both thermoplastics and thermosets. Thermoplastic matrices include polypropylene (PP), high-density polyethylene (HDPE), polystyrene (PS), and polyvinyl chloride (PVC). Thermosets include epoxy, polyester, and phenolic resins. In recent years, the number of studies focused on these materials has increased, because they are environmentally friendly and have low production costs, easy workability, good properties of lightness, mechanical strength, and thermal insulation [53]. However, due to the hydrophilic nature of natural fibers and hydrophobic nature of polymer matrix, there is no good interfacial interaction between the two materials, and therefore, the mechanical properties are deteriorated. Based on the above, chemical and physical treatments have been developed to modify the surface of natural fibers and promote interfacial adhesion with the polymer matrix [54].

Among the chemical treatments stands out alkali, benzoylation, cyclohexane, silicon, peroxide, acetylation, sulfuric acid, stearic acid treatment, and the modification with maleic anhydride. The chemical modification provides more dimensional stability and reduces water absorption capacity [55]. Alkaline treatment is the most used and consists in eliminating the lignin, wax, and oil of the fibers, since these components act as a barrier between the polymeric matrix and the fibers; and in turn, it is possible to increase the roughness in the surface of the fibers [56]. Another alternative to improve the compatibility between these materials is using compatibilizing agents, such as maleic anhydride grafted with polyolefins, either polypropylene or high-density polyethylene. The main factors that affect the processing and performance of biocomposites are the presence of moisture, type, shape (short or long), concentration, and orientation of the fibers. The processing method for obtaining biocomposites will depend on the type of fiber, for example: twin-screw extruder and hydraulic press, injection molding, melt mixing, and single-screw extruder for short-fiber-reinforced composites [57]. New technologies can improve the processing of these materials to make it easier.

The main applications of the biocomposites are automotive parts, packaging, military industry, aerospace, medical articles, etc. The interest of the automotive sector in developing biocomposites lies mainly in reducing the consumption of fiber glass because it is more expensive than the natural one and, in turn, making the vehicles lighter, and it also contributes to the consumption of less combustible and to the fact of being eco-friendly. In recent years, Toyota, Mercedes-Benz, Ford, Mitsubishi, and Daimler Chrysler AG have incorporated biodegradable materials in the exterior parts of some of their vehicles [58]. Pracella et al. [58] studied the functionalization, compatibilization, and properties of polypropylene (PP) composites with hemp fibers. The fibers were functionalized with glycidyl methacrylate (GMA). PP/hemp composites at various compositions were prepared in a Brabender internal mixer. All modified composites showed improved fiber dispersion in the polyolefin matrix and higher interfacial adhesion with respect to the unmodified PP/hemp. Composites showed an increase in Young modulus as compared to PP due to the addition of PP-g-GMA. Vilaseca et al. [59] studied the effect of alkali treatment on interfacial bonding in abaca fibers. They used an epoxy resin, and the results showed that alkali treatments modify the structure and chemical composition of abaca fibers. Abaca fibers treated in 5 wt. % NaOH showed excellent interfacial adhesion with epoxy resin. Bledzki et al. [60] carried out polypropylene-based biocomposites with different types of natural fibers (jute, kenaf, abaca, and softwood) to compare their performance under the same processing conditions, and they found that the properties of biocomposites depend on geometry of the fibers. Kenaf provides strength to biocomposites, abaca obtains the best results in impact resistance, jute fibers are the most stable thermally, and the wood microfibers have good resistant strength. Currently, several studies have been carried out with other

types of fibers, in which we can mention agave, castor plant, and J. curcas fibers [61]. During the tequila production process, large amounts of waste are produced (mostly fiber), and in the case of castor plant and *J. curcas*, only the seeds are used for the extraction of oils, and the rest of plant is discarded. Therefore, an alternative to take advantage of this waste is to use it to develop biocomposites. Zuccarello et al. [62] demonstrated that the agave variety plays an important role on the mechanical performance of the fibers and they proposed an innovative and eco-friendly method for the fiber extraction based on the simple mechanical pressing of the leaves, alternated to proper water immersions avoiding alkaline treatment. They used an eco-friendly green epoxy and a polylactic acid (PLA) to obtain renewable biocomposites. In another work, Zuccarello et al. [62] studied the effect of agave fiber size on epoxy resin and PLA composites. This study showed that biocomposites with short fibers fail to act as a reinforcement, while the long fibers in the compounds with PLA achieve a high mechanical strength. Vinayaka et al. [63] elaborated composites with polypropylene and fibers extracted from the outer layer of *R. communis* (castor plant), which exhibited an elongation at 5% that was higher than the common bast fibers jute and flax, and the strength at 350 MPa was similar to that of jute but lower than that of cotton. Biocomposites have an enormous potential of applications and a growth market especially in automotive industry.

5. Vinasse and tequila production in Mexico, a case study

The production of alcohol and alcoholic beverages such as wine, beer, and tequila generates two main residues in its process, one of them is the solid part called bagasse and a liquid part obtained from the distiller which is known as vinasse [64]. In Mexico, more than 70% of the establishments that produce vinasse come from the production of tequila and mezcal, 20% from beer, and the rest from the production of wines from grapes and other fruits. Due to the denomination of origin of tequila and mezcal, researchers consider as essential the study of the vinasse process, due to the high environmental and economic impacts in Mexico. In recent years, to decrease the high volume of residual vinasses, it has been decided to generate compost from bagasse and vinasse [65], which is given to farmers to use it in their crops; however, the production of compost uses less than 50% of the vinasses, and the rest is discarded without treatment. The tequila production generates high volumes of vinasses on a ratio of 10–12 L for each liter of tequila produced; they have a high organic content that causes damage to ecosystems by anoxia and acidification of water. Biodigestion systems have been developed for the removal of solids [66]. Nevertheless, the treatments are expensive and with a low efficiency, which has not been achieved an industrial implementation.

Due to the physicochemical characteristics of vinasses, these represent a high source of contamination that must be contained and treated to avoid serious damage to ecosystems [67]. Due to the current production volumes of tequila, it is reported that during 2017 more than 271 million liters were produced (https://www.crt.org.mx/) of which between 2710 and 3252 million liters of vinasse would be obtained [68]. For elaboration of the tequila, two main industrial processes are used to produce the fermentation juice. In the first one, the agave is cooked and squeezed to obtain the juice, and there is a subsequent fermentation process. The most recent and apparently energy efficient is to squeeze the raw agave heart by spraying it with a little hot water for this juice, to be used later in the fermentation process. Vinasse components have been compared between both processes showing significant changes where cooking processes present the highest contents of organic acids compared with spraying with steam [69].

We carry out the characterization of the compounds present in the vinasse that leave the distillation process in order to identify the majority of compounds and to propose an adequate purification process that allows to preserve the properties, as well as to avoid their degradation. The components of the vinasse vary between the different fermentation processes, since they depend on the raw materials; the cooking time will give the characteristics of the juices or liqueurs, the fermentation process, and the variables of distillation, so it will be necessary to carry out a characterization study for the vinasse. Since the vinasse has been treated as a residue, no measures are taken to prevent its degradation or contamination. It is important to obtain reliable results, collect fresh vinasse and free of foreign contaminants, and keep it cool, clean, and not exposed light to prevent its degradation. Vinasse is a complex mixture in which organic compounds with very different chemical characteristics are found. In addition, oils and fats that are contained solubilize another group of compounds, making this mixture difficult to separate.

It is required to carry out an integral development that allows the correct treatment of each component of the vinasse. Three general stages of separation are proposed using as model the composition of the vinasse previously characterized (**Figure 1**). The first stage is the separation of solids and liquids; the second a separation of water-soluble compounds such as alcohol traces and polar compounds of solids belonging to organic matter generated during fermentation and some other solids from the broth culture as carbohydrates, proteins, and mineral salts, among others; and finally the generation of value-added products, organic compounds, and solids of high organic matter content, which can easily be recycled in the form of fertilizer for industrial use.

Each stage requires the implementation of independent processes, but they will guarantee the obtaining of water that is easy to use in compliance with current regulations. The feasibility of obtaining compounds of antioxidant capacity of commercial interest derived from vinasse represents an income that costs the entire process.

As mentioned previously, currently in Mexico the treatment of vinasse has been limited mainly due to the fact that there is no solvency or economic technology that companies can implement. Different types of treatment are being used that depend mainly on the size of the company and the total volume of production; **Table 1** summarizes the strategies used to treat vinasse.

Pretreatments and primary treatments are the most commonly used, as they are economical and simple to implement on any scale. Pretreatments are useful only for acidity reduction but do not eliminate organic load or color. Sedimentation ponds allow the removal of 80% of the sedimentable solids; however, it does not reduce the organic load or fats. The flotation strategy consists of applying air together with

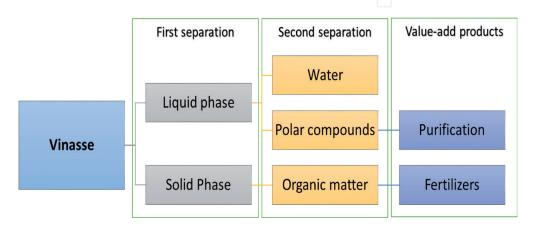


Figure 1.General process to recovery of compounds from vinasse obtained from distillation processes.

Classification	Treatment	Application	Advantage
Pretreatment	Temperature low	Pool circulation	Economic and popular
	pH neutralization	Ca(OH) ₂ addition	Economic and popular
Primary treatment	Sedimentation pools	Storage	Easy for industrial volumes
	Air flash floating	Polymer addition	Easy for industrial volumes
Physicochemical treatment	Coagulation	Al ₂ (SO ₄) ₃ addition	Good remotion of solids
	Flocculation	Cationic polymer addition	Good remotion of solids
Biological	Anaerobic fermentation	Biodigestion	Methane generation
	Acidogenesis	Biodigestion	H ₂ and CO ₂ generation
New treatments	Oxidation	Redox reaction using ozone, H_2O_2 , UV radiation, or Cl	Remotion of color, odor, and organic matter

Table 1.Treatments actually used for the disposal of vinasse.

a polymer that allows accelerating the separation of soluble solids, and it is used as preparation for a biological process. The process is useful for the removal of solids, it is not efficient in the chemical demand of oxygen (CDO), and in addition, it is expensive in industrial scales. On the other hand, these strategies represent a focus of soil and subsoil contamination by filtration. The physicochemical treatments are mostly used on a pilot scale and generally used in two stages; in one, a coagulant is added to agglomerate soluble solids and then a flocculant for remotion. It is efficient in 20–30%, and its ability is being studied to remove the color; at the laboratory level, it has achieved a 70% reduction in color and 30% in CDO. Although there are already reports of a 100% removal efficiency using a cationic polymer [70], to date it has not been implemented on an industrial scale. It is estimated that the cost of these processes is 3.8 USD/Kg of vinasse, but the ecological impact of the emission of heavy metals and the reaction of chlorine salts with organic matter increases rather than decreases the level of toxicity. The main coagulants that are currently used in industries have metallic composition, and some environmentally friendly alternatives are being studied, including sugar polymers from some plant species, such as mesquite gum, shrimp chitosan, and some other vegetable gums [71]. Although removal percentages higher than metallic salts have been achieved by these alternatives, the process of obtaining is still expensive and uncommon.

6. Market of the bioproducts derived from agro-industrial wastes

In the last year, exploitation of agricultural waste for development of new products with a commercial value has been investigated. New related sectors have appeared in the global scene with great growth opportunities in the global market. Therefore, the specialized search engine "Web of Science," using the keyword "waste" in conjunction with the descriptive words of each item shows that the sectors with the greatest number of publications are "biocomposites and the peptides with antioxidant activity." Even though at present research in these fields remains small, it has a great potential for growth in the global market (**Figure 2**).

Globally, sectors related with products from agro-industrial residues are growing, and therefore, there is an increase in the publications showing the enormous potential to enter and take a position in the market. If we look at the size of the market for each compound, we can direct and plan new strategies aimed at the

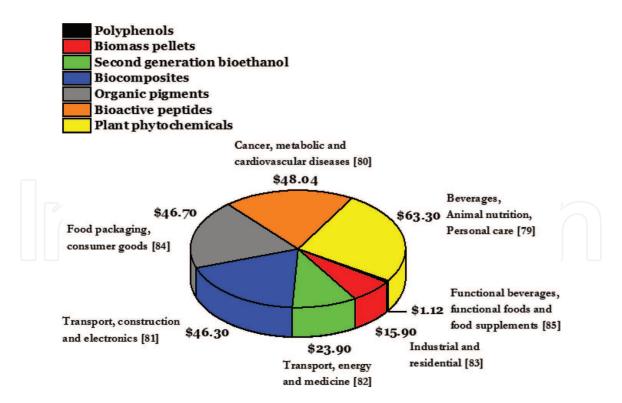


Figure 2.Estimated market of new components obtained from waste (USD, billions) [79-85].

development of products toward the sectors with the highest economic growth and create the interest of companies looking for innovation in each of the product. The main growing market is in the phytochemicals with the extraction of carotenoids, flavonoids, and anthocyanins, among others with potential use in the alimentary industry. Valorization of residues can be achieved such as in soybean residues from pressing oil extraction, which are rich in phytochemical compounds [72]. Thus, there is a growing interest in agro-industrial residues as source of high-benefit products potentially useful as valuable constituents, flavors, and antioxidant in food and cosmetics [73]. The market of phytochemicals is becoming more competitive with the entry of pharmaceutical companies as Cargill, Hormel, and Doehler groups, which ensures a growing market. To pharmaceutical industry, bioactive peptides are considered a growing market and represent a potential solution to more efficacious disease treatment. In addition, peptides promise to combine the lower production costs and high specificity. For 2025, the proposed market growth appears to be near to USD \$48.04 billion (Figure 2). Current trends indicate that a bright future for bioactive peptides and position them as firm candidates to the growth and innovation in pharmaceutical industry with the participation at this moment of companies as Elly Lilly and Pfizer [74], while the biocomposites are being alternatives to conventional petroleum-derived material becoming increasingly utilized in a great variety of applications [75]. An increased research is reflected in the number of publications that indicates a strong trend for applications of eco-friendly materials. Kenaf fiber has been used to reinforce polyurethane composites improving the mechanical and thermal properties [76]. The global biocomposite market is estimated to grow at USD \$46.30 billion for 2025. The trends indicate that the rising awareness among people by the replacement of plastics with biodegradable and environmentally favorable alternatives allows the market growth [77]. Automotive sector is a rising market; the search for new materials that increase the safety of passengers and reduce the vehicle weight spurs market demand [78]. Biomass pellets are an emerging market with a lot of potential. The European Union was the primary market responsible for the global production and

consumption of pellets to residential and district heating East Asia being predicted to become the second largest consumer [6]. Generating an advantage to closing, the circle called "the field to the hand of consumption" creates new opportunities to transform the field of an agricultural activity to agro-industrial activity centered on a circular economy. Circular economy advises the reincorporation of residues into the economy; wastes become a transient phase in an ideally perpetual utilization cycle rather than environmentally sound disposal [1].

7. Conclusions

Utilization of agro-industrial residual wastes can help to reduce them and avoid the environmental contamination, health diseases by the overcrowding, ecological damage, and other pollution-associated problems. Nowadays, there is a growing interest by researchers and industrials by the different substances and properties that exhibit the different agro-industrial residues to obtain a value-added product. Residual wastes have an enormous potential to be revalorized producing solid, liquid, and gas energies, obtaining different bioactive compounds such as polyphenols, peptides, and melanin. In addition, fibers from residues can be used to elaborate biocomposite for automotive industries mainly. New methods are proposed to obtain a value-added product from vinasses in demand not only for the pharmaceutical industries. All of these compounds and mixtures are profitable for a commercial market that grows with a high potential and application for new sectors. In that sense, the future is here.

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Conflicts of interest

The authors indicate no potential conflicts of interest.

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