Agave By-Products

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Throughout this review, we have highlighted the current potential of agave by-products as low-cost and natural materials with several applications as biofuels, materials for nanocomposites, and functional ingredients. Among the methods used for by-products processing, US and microwaves are promising and eco-friendly methods for the efficient saccharification and increased digestibility of agave, that can eventually replace chemical processing, reducing waste generation. In this regard, future studies are required concerning accessible, low-cost, and more efficient technologies as a more attractive way for the industry to make a sustainable utilization of this by-product.

spp. composites emerging technologies biofuels fibers functional foods by-products

1. Introduction

The Agaves are plants commonly known as “magueys”, since ancient times they have had a strong relationship with Mexican culture and history [1]. They were sacred to the Aztec population of prehispanic Mexico and in the Nahuatl language, were named Metl . Agave (Agavaceae) is endemic to the American continent, with a distribution extending from the southern United States (with two disjunct species in Florida) to northern South America, including the Caribbean islands [2]. The genus contains approximately 210 species: 159 are present in Mexico (75% of the total) and 129 are endemic to the Mexican territory, representing 61% of the world’s species [3]. These data are constantly changing as new species are discovered.

Agave is mainly used for the production of distilled (spirits) and non-distilled alcoholic beverages, including Tequila, Mezcal, Bacanora, Raicilla, Sotol and Pulque, all of which have special connections to Mexican history and culture, and contribute to the Mexican economy [4]. Four main species dominate the agave market, namely Agave tequilana , Agave salmiana , Agave angustifolia , and Agave fourcroydes [1]. Their cultivation has been exponentially expanded because of their minimal water and maintenance requirements [5].

Currently, the agave has several alternative uses, including the whole plant and certain by-products. The whole plant is used as a living fence, improving the soil pH, increasing the concentration of phosphorus and potassium, and avoiding erosion, whereas the different by-products have a wide range of applications. In this review, we summarize the main uses for the re-valorization of leaves, bagasse, and fibers that otherwise are considered waste for the agave industry. Particular emphasis is placed on the processing methods for agave by-products and their transformation into high-value products.

2. Chemical Composition of the Main Agave By-Products

The overall composition of agave is cellulose, hemicellulose, lignin, and pectin in fluctuating amounts according to the variety. The plant is a source of other molecules, such as glucose, sucrose, and fructose, fructans, gums, saponins, and phenolic compounds. **Table 1** summarizes the chemical composition of several by-products from agaves. Given the importance of the tequila industry in Mexico, the predominance of A. tequilana by-products and information about their composition is found in the literature. Cellulose, mainly comprising glucans, is the main component of agaves, followed by hemicellulose (mainly xylans), and lignin. Cellulose is a valuable material since it can be hydrolyzed to obtain simple sugars (monosaccharides) that serve as substrates for fermentation and bioethanol production. Nanoparticles and bioplastics made with cellulose have also been obtained from leaves and bagasse [6][7]. Crystallinity is an important feature of cellulose that might be undesirable depending upon the application. A high crystallinity index makes cellulose less digestible and hard to convert into simple sugars by enzymatic or chemical methods [8]. Cellulose from leaves seems to have higher crystallinity than other tissues [6], although nanocrystals with a high crystallinity degree have been obtained from bagasse using an adequate pretreatment [6][7]. Fourier transform infrared spectroscopy (FTIR) experiments have shown that the leaves have a degree of crystallinity of 50.1% [9], proportional to the hydrogen bond formation. Moreover, the leaves have slightly higher concentrations of lignin than other by-products, increasing the recalcitrance of these tissues, which necessitates a pretreatment for delignification before utilization as substrates for biofuel of methane production.

Table 1. Chemical composition of agave by-products.

Component (%)	***Agave tequilana***		***Agave salmiana***		***Agave durangensis***	***Agave americana***		***Agave fourcroydes***	***Agave angustifolia***	***Agave tequilana***
	Bagasse [1]	**Leaves** [2]	**Bagasse** [3]	**Leaves** [4]	**Leaves** [5]	**Leaves** [6]	**Stalk** [7]	**Leaves** [8]	**Spines** [8]	**Bagasse** [9]
Moisture	6.44–8.5	-	-	-	6.9	9.3	-	-	-	7.78
Protein	3.7–3.8	6.6–8.35	2.5–4.4	4.8	-	-	-	-	-	-
Lipids	0.3	-	-	-	-	-	-	-	-	-
Ashes	2.0–7.4	7.5	2.1–6.2	7.6	16.6	3.3	-	-	-	1.3
Holocellulose	-	-	-	-	20.4	-	-	-	-	-
Hemicellulose	4.4–20	15.2 -19.7	4.6	3.7	-	5.6–18.4	-	24	45	34.1
Cellulose	41.8–42.0	38.9–54.5	35.0	20.7	-	65.2–68.5	-	72	52	48.0
Lignin	7.1–20.1	9.8–16.3	13.0–19.1	9.5–26.1	14.5	2.7–9.1	18	14	14	20.7
Xylan	13.0–	9.5–	12.0	9.7	-	-	13.6	-	-	-

Component (%)	Agave tequilana		Agave salmiana		Agave durangensis	Agave americana		Agave fourcroydes	Agave angustifolia	Agave tequilana
	Bagasse 1	Leaves 2	Bagasse 3	Leaves 4	Leaves 5	Leaves 6	Stalk 7	Leaves 8	Spines 8	Bagasse 9
	19.9	18.3								
Glucan	30.9–45.6	35.0–38.8	34.1	35.2	-	-	-	-	-	-
Arabinan	0.5–0.9	1.5–2.1	1.0	2.4	-	-	1.0	-	-	-

1 [10][11][12][13][14][15], 2 [16][11], 3 [11][17], 4 [11][18], 5 [19], 6 [9][20][21], 7 [22], 8 [23], 9 [24].

There are some differences in the composition of leaves and bagasse; it is known that bagasse contains higher amounts of simple sugars and xylan [11], whereas leaves and stalks are richer in lignin. Spines represent an interesting source of hemicellulose, since their content is comparable to that of cellulose [23]; other valuable compounds identified in spines include flavonoids, condensed tannins, and monolignol subunits. Although scarce studies are published on the chemical composition of foliar cuticle, all reported water, cutin and cutan as its main components [25].

3. Main Applications of Agave By-Products

Recently, agave fructans have been employed as functional ingredients for granola bars [26], and encapsulating material for bioactive compounds, given their high degree of polymerization [27].

Regarding agave bagasse, isolated polysaccharides from A. salmiana bagasse were used to elaborate and stabilize indomethacin nanoemulsions, and to improve the cellular uptake in a human dermal fibroblast model [28].

Cellulose crystallinity is another important feature of agave fibers, in this regard, a higher crystallinity index has been related to better mechanical properties for composites, although some studies have not found an improvement of these properties when fibers crystallinity is increased [29].

Lastly, hybrid composites containing pine sawdust, agave bagasse and HDPE were fabricated in a twin-screw extruder [30]. Results showed that the inclusion of agave bagasse increased the flexural and tensile strength, whereas the pine was helpful in reducing water absorption and conferring stability to the composites.

4. Processes and Technologies for the Treatment of Agave By-Products

Alkaline delignification with dilute solutions of NaOH (2%) has been tested on agave bagasse prior to the enzymatic step for saccharification [31]. A higher amount of reducing sugars was obtained with the addition of alkali, specifically, the glucose content was significantly increased compared with an acid pretreatment.

Regarding enzymatic hydrolysis, this method is useful for releasing simple sugars after the chemical pretreatment. The saccharification process is driven by the enzymatic action on the agave fibers to break down complex carbohydrates into simple sugars, which in turn, serve as a substrate for fermentation to produce biofuels such as bioethanol, or anaerobic digestion to produce methane and hydrogen.

Microwave technology has been considered an environmentally friendly method, and suitable for scaling up for industrial applications. With this technique by-products from different agave varieties have been processed to obtain activated carbon, bioactive compounds, and simple sugars. Finally, agave leaves have proven to be good microwave absorbers for anechoic chambers, blocking electromagnetic interferences [32]. Usually, polyurethane is used for this purpose, but it may release toxic gases and represents an environmental problem when discarded. Agave leaves are better absorbers than other wastes tested for this purpose, which makes this by-product a low-cost and eco-friendly material.

The supercritical fluids (SCF) technology has been explored as a pretreatment for the saccharification of agave bagasse and for bioactive molecules extraction, as previously mentioned. Increments up to 40% in the simple sugars content were observed with SCF applied to A. tequilana bagasse [33]. The saccharification yield was highly dependent on the hydration level; at low values of CO_2 the diffusivity was higher, resulting in higher damage to the agave structure. Furthermore, the combined treatment of US and SCF had a good potential for the extraction of saponins from A. salmiana bagasse, preserving the antioxidant capacity of these bioactive molecules [34][35]. Micellar extraction with ionic surfactants has been reported as an alternative method for saponin extraction [36] with high yield (89%), compared with other techniques such as US, but with low recovery for phenolic compounds.

5. Conclusion

Agaves are a rich source of by-products with a wide range of potential applications. Rather than considering these by-products as waste, current reports have shown their value as biofuels, materials for nanocomposites, and functional ingredients. Particularly, the leaves and bagasse from the agave industry, are lignocellulosic materials that can be converted into digestible sugar for bioethanol, methane, and hydrogen production. Most of the by-products have a significant content of saponins, that are valuable biomolecules with application in the food industry (foaming, emulsification, bitterness) and in the pharmaceutical sector (antimicrobial, anti-cancer and anti-obesity activity).

References

1. Bremer, B.; Bremer, K.; Chase, M.W.; Fay, M.F.; Reveal, J.L.; Bailey, L.H.; Angiosperm Phylogeny Group. An update of the Angiosperm Phylogeny Group classification for the orders and families of flowering plants: APG III. Bot. J. Linn. Soc. 2009, 161, 105–121.

2. García Mendoza, A. Distribution of Agave (Agavaceae) in Mexico. Cactus. Succul. J. 2002, 74, 177–187.
3. García Mendoza, A.J.; Franco Martínez, I.S.; Sandoval Gutiérrez, D. Cuatro especies nuevas de Agave (Asparagaceae, Agavoideae) del sur de México. Acta Bot. Mex. 2019.
4. de Lourdes Pérez-Zavala, M.; Hernández-Arzaba, J.C.; Bideshi, D.K.; Barboza-Corona, J.E. Agave: A natural renewable resource with multiple applications. J. Sci. Food Agric. 2020, 100, 5324–5333.
5. López-Romero, J.C.; Ayala-Zavala, J.F.; González-Aguilar, G.A.; Peña-Ramos, E.A.; González-Ríos, H. Biological activities of Agave by-products and their possible applications in food and pharmaceuticals. J. Sci. Food Agric. 2018, 98, 2461–2474.
6. Espino, E.; Cakir, M.; Domenek, S.; Román-Gutiérrez, A.D.; Belgacem, N.; Bras, J. Isolation and Characterization of Cellulose Nanocrystals from Industrial By-Products of Agave tequilana and Barley. Ind. Crop. Prod. 2014, 62, 552–559.
7. Robles, E.; Fernández-Rodríguez, J.; Barbosa, A.M.; Gordobil, O.; Carreño, N.L.V.; Labidi, J. Production of Cellulose Nanoparticles from Blue Agave Waste Treated with Environmentally Friendly Processes. Carbohydr. Polym. 2018, 183, 294–302.
8. Yang, H.; Chen, J.; Chen, Q.; Wang, K.; Sun, R.C. The Synergic Relationship Between Xylan Removal and Enhanced Cellulose Digestibility for Bioethanol Production: Reactive Area, Crystallinity, and Inhibitation. Bioenergy Res. 2015, 8, 1847–1855.
9. El Oudiani, A.; Msahli, S.; Sakli, F. In-Depth Study of Agave Fiber Structure Using Fourier Transform Infrared Spectroscopy. Carbohydr. Polym. 2017, 164, 242–248.
10. Langhorst, A.E.; Burkholder, J.; Long, J.; Thomas, R.; Kiziltas, A.; Mielewski, D. Blue-agave fiber-reinforced polypropylene composites for automotive applications. BioResources 2018, 138, 20–35.
11. Flores-Gómez, C.A.; Escamilla Silva, E.M.; Zhong, C.; Dale, B.E.; Da Costa Sousa, L.; Balan, V. Conversion of Lignocellulosic Agave Residues into Liquid Biofuels Using an AFEXTM-Based Biorefinery. Biotechnol. Biofuels 2018, 11, 7.
12. Perez-Pimienta, J.A.; Lopez-Ortega, M.G.; Varanasi, P.; Stavila, V.; Cheng, G.; Singh, S.; Simmons, B.A. Comparison of the Impact of Ionic Liquid Pretreatment on Recalcitrance of Agave Bagasse and Switchgrass. Bioresour. Technol. 2013, 127, 18–24.
13. Equihua-Sánchez, M.; Barahona-Pérez, L.F. Physical and Chemical Characterization of Agave tequilana Bagasse Pretreated with the Ionic Liquid 1-Ethyl-3-Methylimidazolium Acetate. Waste Biom. Valoriz. 2019, 10, 1285–1294.

14. Wang, J.; Chio, C.; Chen, X.; Su, E.; Cao, F.; Jin, Y.; Qin, W. Efficient Saccharification of Agave Biomass Using Aspergillus niger Produced Low-Cost Enzyme Cocktail with Hyperactive Pectinase Activity. Bioresour. Technol. 2019, 272, 26–33.
15. Delgadillo Ruíz, L.; Bañuelos Valenzuela, R.; Esparza Ibarra, E.L.; Gutiérrez Bañuelos, H.; Cabral Arellano, F.J.; Muro Reyes, A. Evaluación Del Perfil de Nutrientes de Bagazo de Agave Como Alternativa de Alimento Para Rumiantes. Rev. Mex. Ciencias Agrícolas 2018, 11, 2099.
16. Rijal, D.; Vancov, T.; McIntosh, S.; Ashwath, N.; Stanley, G.A. Process Options for Conversion of Agave Tequilana Leaves into Bioethanol. Ind. Crop. Prod. 2016, 84, 263–272.
17. Jones, A.M.; Zhou, Y.; Held, M.A.; Davis, S.C. Tissue Composition of Agave americana L. Yields Greater Carbohydrates from Enzymatic Hydrolysis Than Advanced Bioenergy Crops. Front. Plant Sci. 2020, 11, 654.
18. Perez-Pimienta, J.A.; Flores-Gómez, C.A.; Ruiz, H.A.; Sathitsuksanoh, N.; Balan, V.; da Costa Sousa, L.; Dale, B.E.; Singh, S.; Simmons, B.A. Evaluation of Agave Bagasse Recalcitrance Using AFEXTM, Autohydrolysis, and Ionic Liquid Pretreatments. Bioresour. Technol. 2016, 211, 216–223.
19. Contreras-Hernández, M.G.; Ochoa-Martínez, L.A.; Rutiaga-Quiñones, J.G.; Rocha-Guzmán, N.E.; Lara-Ceniceros, T.E.; Contreras-Esquivel, J.C.; Prado Barragán, L.A.; Rutiaga-Quiñones, O.M. Effect of Ultrasound Pretreatment on the Physicochemical Composition of Agave durangensis Leaves and Potential Enzyme Production. Bioresour. Technol. 2018, 249, 439–446.
20. Hernández-Varela, J.D.; Chanona-Pérez, J.J.; Calderón Benavides, H.A.; Cervantes Sodi, F.; Vicente-Flores, M. Effect of Ball Milling on Cellulose Nanoparticles Structure Obtained from Garlic and Agave Waste. Carbohydr. Polym. 2021, 255, 117347.
21. Hidalgo-Reyes, M.; Caballero-Caballero, M.; HernáNdez-Gómez, L.H.; Urriolagoitia-Calderón, G. Chemical and Morphological Characterization of Agave angustifolia Bagasse Fibers. Bot. Sci. 2015, 93, 807–817.
22. Yang, Q.; Pan, X. Pretreatment of Agave Americana Stalk for Enzymatic Saccharification. Bioresour. Technol. 2012, 126, 336–340.
23. Morán-Velázquez, D.C.; Monribot-Villanueva, J.L.; Bourdon, M.; Tang, J.Z.; López-Rosas, I.; Maceda-López, L.F.; Villalpando-Aguilar, J.L.; Rodríguez-López, L.; Gauthier, A.; Trejo, L.; et al. Unravelling Chemical Composition of Agave Spines: News from Agave Fourcroydes Lem. Plants 2020, 9, 1642.
24. Kestur, G.S.; Flores-Sahagun, T.H.S.; Dos Santos, L.P.; Dos Santos, J.; Mazzaro, I.; Mikowski, A. Characterization of Blue Agave Bagasse Fibers of Mexico. Compos. Part A Appl. Sci. Manuf. 2013, 45, 153–161.

25. Deshmukh, A.P.; Simpson, A.J.; Hadad, C.M.; Hatcher, P.G. Insights into the Structure of Cutin and Cutan from Agave americana Leaf Cuticle Using HRMAS NMR Spectroscopy. Org. Geochem. 2005, 36, 1072–1085.
26. Zamora-Gasga, V.M.; Bello-Pérez, L.A.; Ortíz-Basurto, R.I.; Tovar, J.; Sáyago-Ayerdi, S.G. Granola Bars Prepared with Agave tequilana Ingredients: Chemical Composition and Invitro Starch Hydrolysis. LWT Food Sci. Technol. 2014, 56, 309–314.
27. Cruz-Salas, C.N.; Prieto, C.; Calderón-Santoyo, M.; Lagarón, J.M.; Ragazzo-Sánchez, J.A. Micro- and Nanostructures of Agave Fructans to Stabilize Compounds of High Biological Value via Electrohydrodynamic Processing. Nanomaterials 2019, 9, 1659.
28. Jiménez-Rodríguez, A.; Heredia-Olea, E.; Barba-Dávila, B.A.; Gutiérrez-Uribe, J.A.; Antunes-Ricardo, M. Polysaccharides from Agave salmiana Bagasse Improves the Storage Stability and the Cellular Uptake of Indomethacin Nanoemulsions. Food Bioprod. Process. 2021, 127, 114–127.
29. Langhorst, A.; Paxton, W.; Bollin, S.; Frantz, D.; Burkholder, J.; Kiziltas, A. Heat-treated blue agave fiber composites. Compos. Part B Eng. 2019, 165, 712–724.
30. Pérez-Fonseca, A.A.; Robledo-Ortíz, J.R.; Ramirez-Arreola, D.E.; Ortega-Gudiño, P.; Rodrigue, D.; González-Núñez, R. Effect of Hybridization on the Physical and Mechanical Properties of High Density Polyethylene-(Pine/Agave) Composites. Mater. Des. 2014, 64, 35–43.
31. Hernández-Salas, J.M.; Villa-Ramírez, M.S.; Veloz-Rendón, J.S.; Rivera-Hernández, K.N.; González-César, R.A.; Plascencia-Espinosa, M.A.; Trejo-Estrada, S.R. Comparative Hydrolysis and Fermentation of Sugarcane and Agave Bagasse. Bioresour. Technol. 2009, 100, 1238–1245.
32. Navarro, A.; Montiel, C.; Gracia-Fadrique, J.; Tecante, A.; Bárzana, E. Supercritical Carbon Dioxide “Explosion” on Blue Agave Bagasse to Enhance Enzymatic Digestibility. Biomass Convers. Biorefin. 2021.
33. Liñán-Montes, A.; De La Parra-Arciniega, S.M.; Garza-González, M.T.; García-Reyes, R.B.; Soto-Regalado, E.; Cerino-Córdova, F.J. Characterization and Thermal Analysis of Agave Bagasse and Malt Spent Grain. J. Therm. Anal. Calorim. 2014, 115, 751–758.
34. López-Romero, J.C.; Ayala-Zavala, J.F.; Peña-Ramos, E.A.; Hernández, J.; González-Ríos, H. Antioxidant and Antimicrobial Activity of Agave Angustifolia Extract on Overall Quality and Shelf Life of Pork Patties Stored under Refrigeration. J. Food Sci. Technol. 2018, 55, 4413–4423.
35. Santos-Zea, L.; Gutierrez-Uribe, J.A.; Benedito, J. Effect of Solvent Composition on Ultrasound-Generated Intensity and Its Influence on the Ultrasonically Assisted Extraction of Bioactives from Agave Bagasse (Agave salmiana). Food Eng. Rev. 2020, 144, 98–107.
36. Ribeiro, B.D.; Barreto, D.W.; Coelho, M.A.Z. Use of Micellar Extraction and Cloud Point Preconcentration for Valorization of Saponins from Sisal (Agave sisalana) Waste. Food Bioprod.

Process. 2015, 94, 601–609.